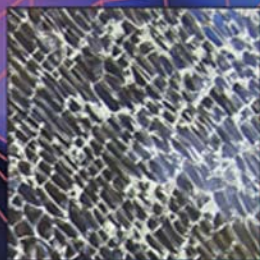


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Computational Methods
and Experiments **IV**



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Computational Methods and Experiments

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Computational Methods and Experiments

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E-Mail: infousa@witpress.com<http://www.witpress.com>

British Library Cataloguing-in-Publication Data

A Catalogue record for this book is available
from the British Library

ISBN: 978-1-84564-189-4

ISSN: 1746-4471 (print)

ISSN: 1743-3533 (on-line)

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Preface

Materials science in recent years has undergone rapid development in part as a consequence of advances in our ability to control and design at very small scales. Nanotechnology is seen as the new frontier in materials, with the promise of performance and functionality far exceeding today's standards. Many "conventional" materials are also benefiting from improvements in our ability to characterize them and better understand their behavior, often leading to incremental performance enhancements.

Characterization has by necessity kept pace with the development of new materials. In many cases, the characterization of complex behavior is made indirectly by the use of a model coupled with experimental data. In other cases, physical testing provides data to tune model parameters. The first part of the book is dedicated to the computational model – experiment interaction. Later sections contain a range of classical testing methods applied to innovative materials and composites, new testing methodologies, and two sections dedicated to cements and construction materials.

We note that many of the challenges that face society as a consequence of diminishing resources, especially energy, will in part be met by better materials, which ultimately should be designed and used with sustainability in mind.

We are confident that the conference will foster fruitful exchanges of ideas, which the book will extend to a wider audience still. The contents of this book reflect the quality of the submissions and the diligence of the reviewers, whom we wish to thank.

The Editors
New Forest, 2009

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Section 1

Computational models and experiments

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Identification of material properties of FRC using coupled modeling

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Abstract

In this paper identification of material properties in the vicinity of reinforcement of FRC is based on coupled modeling. It consists of the mutual comparison of experimental and mathematical models with the aim of obtaining a more accurate estimate of stresses in experiments and more reliable input data in the mathematical treatment. As the measurements on site are very expensive, experiments simulating the system of the concrete-surrounding medium are prepared in scale models in stands (basins with a glazed front side and a length of 2-6 m), where physically equivalent materials substitute the real ones. Based on similarity rules, very good agreement with reality is attained. Typical applications are found in tunnel construction and reinforcement of slopes using recycled reinforced concretes (waste of bricks and used concrete serve as an aggregate in new built concretes). In order to identify the most exacting location in the concrete, coupled mechanical pullout tests are carried out together with chemical analysis conducted by Raman spectroscopy. It appears that the extent of ettringite on the interface fiber-surrounding matrix plays a very important role, and also other minerals occurring there can influence the interface situation, but less than the ettringite. In the numerical treatment a useful trick is applied, which stems from the idea of generalization of temperature effects – eigenparameters. They describe the plastic behavior as well as the damage at the interfaces. Their applications in the paper will be the most important element of the creation of the coupled model.

Keywords: coupled modeling, fiber reinforced concrete, recycled aggregate, chemo-mechanical analysis, eigenparameters; application: slope reinforcement.

1 Introduction

Fibers play a very important role, particularly during the curing process of concrete, as they suppress local cracking and warping in the composite structure



and avoid the possibility of corrosion of reinforcing steel rebars. On the other hand, polypropylene fibers can display other advantages. If aggregate from recycled material (shattered bricks or concretes) are used in the concrete mixture, they essentially increase the toughness of the material and can be applied to the elements that are in tension. It also appears that after mobilization of the fibers, even higher peak stresses can be safely attained. A very important fact follows from numerous experimental studies: since the steel fibers increase the protection of complete concrete against flaws, the fibers in recycled concrete increase the tensile bearing capacity of the material. The pullout problem was carried out for both materials, as a chemo-mechanical analysis explained certain reasons of the behavior in both types of materials: classical concrete reinforced by stiff fibers and concrete recycled with polypropylene fibers. Convergence analysis for determining cohesion and tensile strength is proposed and eventually a nano-mechanical measurement based on Raman microscopy is introduced.

The testing machine MTS Alliance RT/30 was used for carrying out the mechanical tests. From the combination (coupling) of experimental and theoretical methods the possibility of looking into the heart of the problem, the interfacial fiber-concrete mechanical and chemical properties, is enabled. The interfacial mechanical characteristics are involved in the angle of internal friction and cohesion. With these mechanical characterizations the chemical spectra and, consequently, the description of chemical elements and minerals, express the connection of nano- chemo- and mechanical properties.

2 Experiments with classical concrete

The testing machine MTS Alliance RT/30, see Fig. 1, is used for the pullout tests that are carried out for the purpose of this study. It is an electromechanical tool for compressive, tensile, and bending tests of materials. The maximum compressive and tensile force is 30kN. The size of the possible samples is 150 x 150 x 250 mm (width x length x height). The velocity of loading was in our case 0.04 mm/minute.

The scheme of the container in which the fiber-concrete aggregate samples have been tested is depicted in Fig. 2. In the container the cement paste with one fiber symmetrically positioned in the aggregate is cured. Six samples have been tested. The results in time of curing are given in Fig. 3. The experiment was prepared with a high quality of preparation of cement paste and the positioning of the fiber was also extraordinarily accurate. The results of this study testify to this, as the variance is very small. Fig. 4 shows the appropriate graph obtained from statistical averaging of the previous results.

We would probably be interested in the reason why the steel reinforced concrete loses its bearing capacity during the curing process. The answer may follow from the chemical test descriptions that are presented in the next section. In the case the steel fibers, or other polymerized fibers used in a humid milieu, similar results can be expected. The peak stresses are attained not at the end of the curing and hardening process of concrete, but early in the beginning. Our interest is concentrated exactly on the time interval when the mixture loses its water contents and this is the moment of the highest admissible stress.





Figure 1: Testing machine.

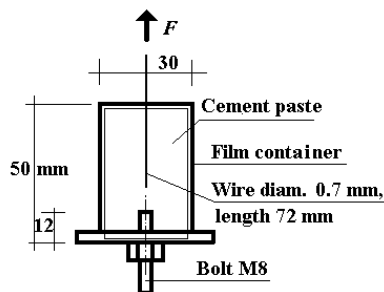


Figure 2: Scheme of the tested samples.

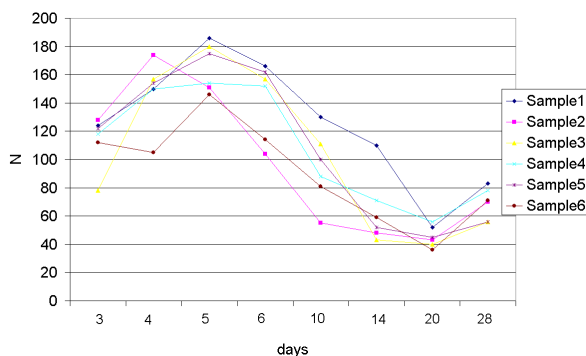


Figure 3: Admissible forces for six samples at the time of concrete curing.

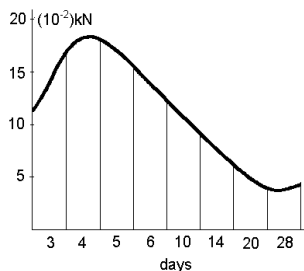


Figure 4: Resulting average admissible forces at the time of concrete curing.



3 Raman spectroscopy of cement–steel interfaces

As mentioned above, it is widely accepted that the mechanical behavior of composites is highly dependent on the interface between the fiber and the matrix. The interface exists at some area around the fiber surface, where the local properties, including the morphological features, chemical compositions and thermo-mechanical properties, begin to change. The range of the microstructure and mechanical property gradients within the interface is from nanometers to micrometers. Several different test methods, such as the Raman spectroscopy stress field analysis, were used to investigate the interface properties. The microstructure of the paste matrix in the vicinity of the transition zone of the fibers is considerably different from that of the bulk paste away from the interface. It was observed that the transition zone in the mature paste composite is rich in Ca(OH)_2 , usually in direct contact with fiber surface, and is also quite porous, making it different from the microstructure of the bulk paste. The Ca(OH)_2 layer is about 1 μm thick and resembles the duplex films. Pullout tests were carried out for chemical and mechanical characterization of the bonding. It was found that frictional as well as anchoring effects controlled the pullout resistance of the straight fibers.

The application of Raman and infrared spectroscopy in the field of cement and concrete chemistry are quite significant. Measuring the relative intensity of Raman peaks associated with C_3S and calcium hydroxide followed the progress of the reaction. These data sets show that a change in the hydration mechanism occurs at about 13 hours.

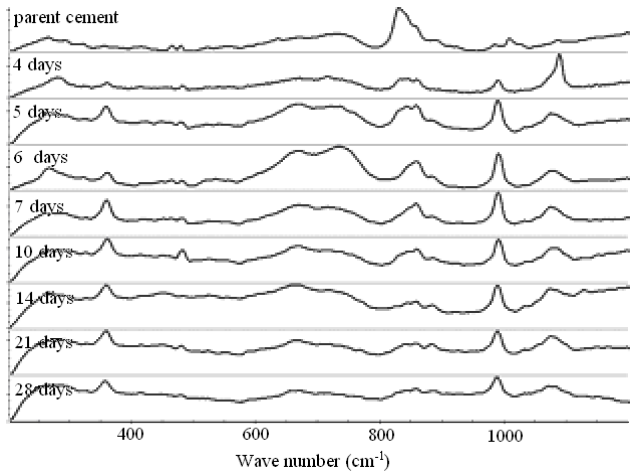


Figure 5: Raman spectra of the hydrated Portland cement during 0 to 28 days.



Raman microspectroscopy chemical mapping has been used in this work, both for the monitoring of Portland cement hydration during 28 days and for spectroscopic analyses of differences in chemical composition of the interface area around the steel fiber surface in comparison with the surrounding bulk cement matrix composition (Fig. 5).

The five micrometer steps were selected for microspectroscopic mapping and the whole mapping area was 450×450 micrometers. The average spectrum has been computed from the set of measured mapped spectra. The hydration process is represented by a set of chemical equations describing the hydration of the main cement phases C_3S , C_2S , C_3A and C_4AF (the nomenclature used here for cement is $C=CaO$, $S=SiO_2$, $H=OH$, $A=Al_2O_3$, $F=Fe_2O_3$, $\hat{S}=SO_4$). Raman microspectroscopy has been used as a powerful technique for the analysis of the hydration cement products, e.g. $Ca(OH)_2$ and ettringite ($C_6A \hat{S}_3H_{32}$). Fig. 6 shows the Raman spectra of the hydrated Portland cement at 0 to 28 days period. The increasing intensity of $Ca(OH)_2$ and ettringite and decreasing of the C_3S and C_2S , respectively, is distinct. These chemical properties are probably the prevailing reason for the decrease of the bearing capacity of the fibers imbedded in the concrete.

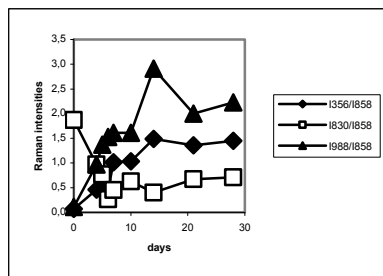


Figure 6: Changes in the relative abundance of $Ca(OH)_2$ (I_{1356}/I_{1858}), C_3S (I_{1830}/I_{1858}) and ettringite (I_{1988}/I_{1858}) versus days of the cement hydration.

4 Recycled concrete and polypropylene fibers

Among promising structural concretes one also can include ones that are created from recycling materials. They can substitute and spare the natural resources of gravel aggregates. Using additional scattered synthetic fibers, the structure of concrete is stiffened and former brittle material becomes ductile, which shows both high tensile strength and ductility. For concrete mixer creation, clean and unclean brick rubbish (waste) was used, i.e. structural rubbish in the second case contained imparted pieces of bricks, pore-concrete blocks, face bricks, floor tiles, ground concrete, backfill, and so on.

The strength of the materials strongly depends on the amount of cement. The following are certain material properties for various mixtures measured against the standard concrete M20:



a) brick-concretes with lower amount of cement (denoted as C1T)

- tensile strength at bending 5.24%
- compressive strength 10.24%
- strength in transversal tension 13.50%

b) brick-concretes with higher amount of cement (denoted as C2H)

- tensile strength at bending 7.98%
- compressive strength 16.27%
- strength in transversal tension 19.47%

Denotation C3T and C4H refers to the same material properties after 90 days of use. Absolute values of the observed concretes with brick waste aggregates are illustrated in Fig. 7.

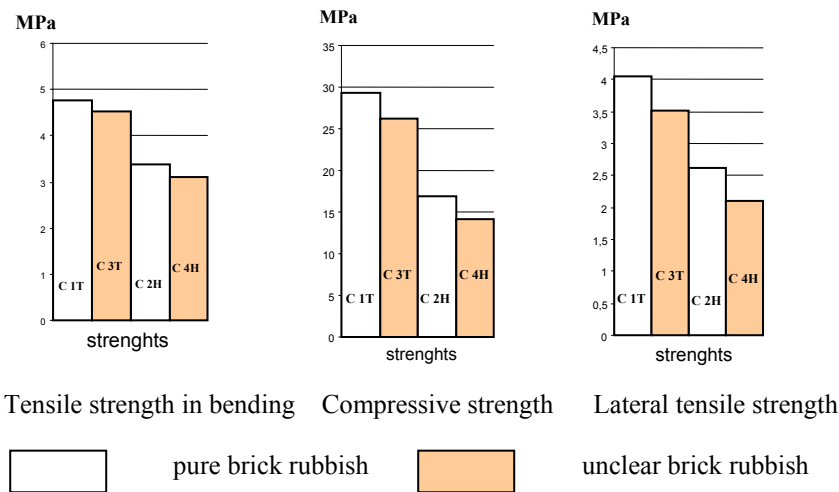


Figure 7: Comparison of basic characteristics of brick concretes with fibers.

The strength of brick concrete was lower than that of fine grain concrete, which is an impact of the inactive component, i.e. brick rubbish. Fibers scattered in the structure of brick concrete change the character of classical damage of trial bodies. Fibers also change the values of tensile strengths in bending under reloading by one or two concentrated loads. Last but not least, it is possible to produce the brick concrete without expensive admixtures. For tests on watertight concrete following the standard “Determination of water-tightness of concrete”, samples from brick concrete with fibers C3T and C4H from unclean brick rubbish aged 3 months were selected. Three cubes with sides of 150mm were loaded in a watertight box for 24 hours by water pressure 0.1 MPa and then another 24 hours by pressure 0.2 MPa. Leakage through the parallelepipeds attained nearly the upper surface of the cubes and the area of each shattered by

lateral tension was more than 90% wet. With respect to the results of the tests, the water-tightness of the brick concrete with fibers is negligible.

For the typical structure of three types of concrete with waste brick aggregate, the pullout test results are seen in Fig. 8. Here the increase of admissible stress is obvious after the polypropylene fibers have been mobilized. A small deviation of force–displacement curves also indicates relatively reliable samples prepared for these tests.

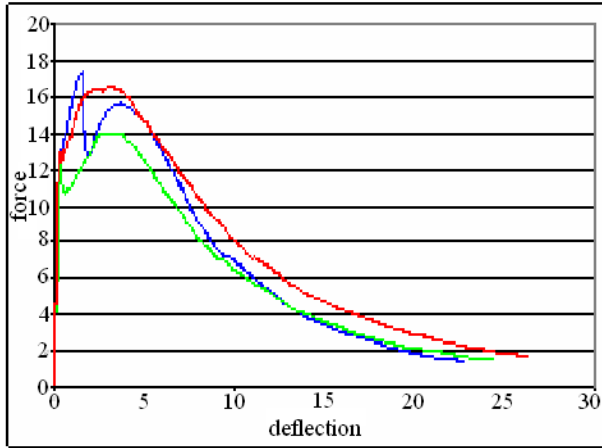


Figure 8: Diagram force (kN) deflection (mm) for recycled concrete.

5 Mathematical formulation for the coupled modeling

Because of the shape of the samples, the axisymmetric problem is solved. The displacements are described by a vector function $\mathbf{u} \equiv \{u_r, u_\theta\}$ of the variable $\mathbf{x} \equiv \{r, \theta\}$. The traction field on the interfaces or boundaries is denoted as $\mathbf{p} \equiv \{p_r, p_\theta\}$. Assuming the “small deformation” theory, it may be satisfactory to formulate the essential contact conditions on the interface as follows (no penetration conditions):

$$[u]_r = u_r^c - u_r^a \leq 0 \quad \text{on } \Gamma_C \quad (1)$$

where Γ_C is the interfacial boundary between the fiber and the matrix, u_r^c is the outward normal (radial) displacement of the fiber at a current point and u_r^a is the same displacement at an adjacent point inside the concrete matrix on the interfacial boundary Γ_C . Similarly we define

$$[u]_t = u_t^c - u_t^a \leq 0 \quad \text{on } \Gamma_C \quad (2)$$

At each adjacent point on the interface $\bar{p}_r \leq p_+$ has to be valid, where p_+ is the tensile strength and $\bar{p}_r = p_r + \delta_r$, where δ_r is an internal parameter. Similarly introduce $\bar{p}_t = p_t + \delta_t$, where δ_t is another internal parameter. In this way, in the radial direction Fischera's conditions should be fulfilled:

$$[u]_r \leq 0, \quad p_+ \kappa(p_+ - p_r) - p_r \geq 0, \quad \{p_+ \kappa(p_+ - p_r) - p_r\} [u]_r = 0 \quad (3)$$

where κ is the Heaviside function. In the tangential direction it should be valid that:

$$c \kappa(p_+ - \bar{p}_r) - \bar{p}_r \tan \varphi - |\bar{p}_t| \geq 0, \quad |[u]_t| \geq 0, \quad (4)$$

$$\{c \kappa(p_+ - \bar{p}_r) - \bar{p}_r \tan \varphi - |\bar{p}_t|\} |[u]_t| = 0$$

where $\tan \varphi$ is the tangent of the internal friction of both materials (Coulomb friction), τ_b is the shear strength or cohesion, both being given material coefficients that are different for different coupled materials on contact. These conditions describe the generalized Mohr-Coulomb law involving the exclusion of tension.

We concatenate the above conditions and generalize them to obtain a realistic model of the interfacial behavior. Then, the problem can be formulated in terms of penalties as coefficients of constraint (side conditions). Setting

$$\bar{p}_r = k_r [u]_r, \quad p_r = k_r [u]_r - \delta_r, \quad \text{and} \quad \bar{p}_t = k_\theta [u]_\theta, \quad p_t = k_t [u]_t - \delta_\theta, \quad (5)$$

where k_r, k_θ are normal spring and tangential spring stiffnesses. The extended Lagrange principle provides (Γ is the external boundary and $a_s(\mathbf{u}, \mathbf{u})$ is the bilinear form of the system fiber concrete matrix):

$$\begin{aligned} \Pi = & \frac{1}{2} \sum_{s=1}^2 a_s(\mathbf{u}, \mathbf{u}) - \int_{\Gamma} \bar{\mathbf{p}}^T \mathbf{u} \, dx + \\ & + \int_{\Gamma_C} \{k_r ([u]_r)^2 + k_r [u]_r |[u]_t| + k_t ([u]_t)^2\} \, dx - \\ & - \int_{\Gamma_C} \{(p_+ \kappa(p_+ - \bar{p}_r) [u]_r + c \kappa(p_+ - \bar{p}_r) |[u]_t|\} \, dx \end{aligned} \quad (6)$$

Note that the spring stiffnesses k_r, k_t play the role of penalty. The problem can also be formulated in terms of Lagrangian multipliers, which then leads to mixed formulation. The latter case is more suitable for a small number of boundary variables; the problem looked at here decreases the number of unknowns introducing the penalty parameters.

6 Coupled modeling

Considering the external boundary conditions and the material constants are given, the main objective here is to adopt the numerical results and the experimental conclusions. One possible approximation is the assumption that formulates the transformation formulas for interfacial forces. In the example



presented hereinafter, the normal internal parameters δ_r are assumed too small in comparison to the real tractions and the tangential internal parameters are selected in such a way that $\delta_t = ap_t$, where the coefficient is to be determined from the condition: calculated external energy is equal to measured external energy.

As the assumption applied here is in fact very simple, the algorithm is easy. Calculate the response of the force applied in real situation and compare the results expressed in terms of external energy. Since most probably they will not be equal, calculate the internal parameter. This is not easy in this case as the relations between internal parameters and the energy are not linear. On the other hand, a smart algorithm can be used, such as the steepest descent or Raphson iteration. The material properties are selected as: $E_f = 170$ GPa, $E_m = 17$ GPa, $\nu_f = 0.3$, $\nu_m = 0.16$. The radius of the fiber is 0.6 mm, the coefficient of Coulomb friction is 0.23 and the shear bond strength is 43.5 kPa.

Sample results are depicted in Fig. 9. It is seen that the normal tractions do not principally change, but the shear tractions are basically improved by the optimization. The optimal appears to be $a = 1.76$.

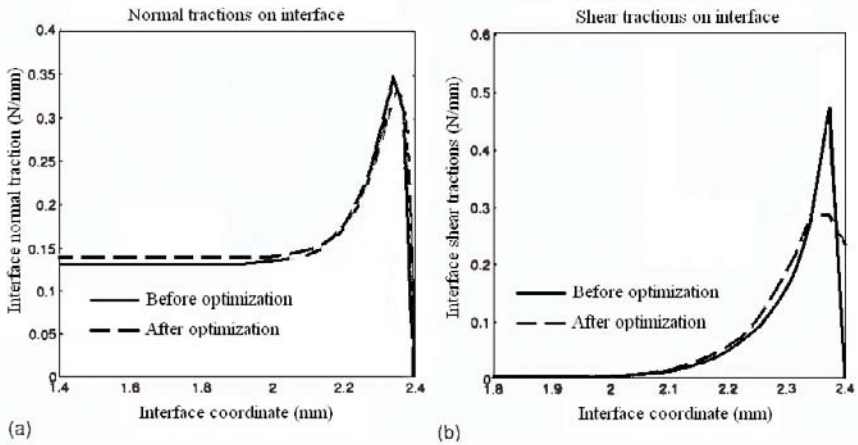


Figure 9: Interface tractions

7 Possible application in increasing slope stability

In this section the aim is focused on possible application of the recycled composite material in geomechanics. The reinforcement of slopes is very important in certain cases of extensive objects, deposits from open pit mines, tailing dams and such. If not stiffened, they occupy large areas of agricultural lots, or lots for dwelling buildings. In Fig. 10 the influence of nails from the material under consideration principally improves the slope stability. The distribution of vertical displacements for unreinforced (left picture) and reinforced (right picture) are depicted. Principal shear stresses with marked

possible slip curves also illustrate the improvement of the stability situation using reinforcement by the recycled material (FRP). The final pictures are drawn in hypsography, which enables one to realize the stability situation before and after reinforcement. An unstable slope obviously turns to be stable when reinforcement is applied.

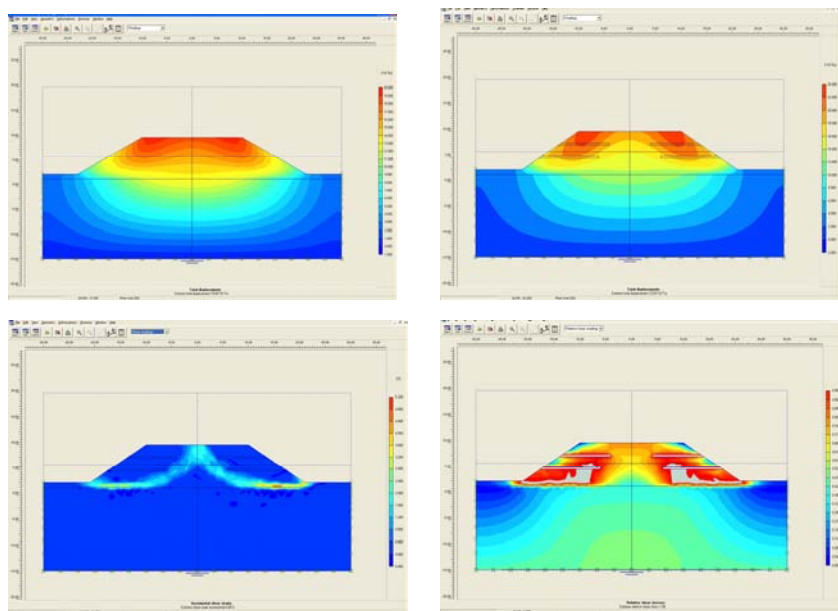


Figure 10: Displacements and principal shear stresses in unreinforced (left) and reinforced (right) slope.

8 Conclusions

In this paper chemical and mechanical properties are applied for investigation of contact zones in fiber reinforced concrete. The chemical treatment has been carried out by Raman microspectroscope, while the mechanical properties have been derived from results conducted in cylindrical samples (pullout test). It was shown that the results from both approaches should be observed simultaneously. Coupled modeling proved to be a powerful means for understanding the material behavior of the composite systems. Examples of practical applications of stiff and weak fibers have been presented.

Acknowledgements

The financial support of GAČR, project number 103/08/1197 is appreciated. The research has also been supported by a grant from the Ministry of Education of the Czech Republic number MSM6840770001,5.



A micromechanical model and numerical simulation of framework interstice concrete

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Abstract

Being a kind of framework material, framework interstice concrete is composed of single-grade or gap-grade aggregate which are bonded by cement or bitumen, whose structural characteristic is “bonding crunode + aggregate + space”. This paper develops a kind of micromechanical model, carrying out numerical simulation of flexural performance of the framework interstice concrete. The calculating results basically conform to the experimental result gained in the laboratory. The method discussed in the paper can be developed to apply in calculating analysis on all kinds of framework interstice concrete materials.

Keywords: framework interstice, framework interstice concrete materials, micromechanical model, numerical simulation.

1 Introduction

To accomplish a pavement’s service functions, such as water permeability and noise reduction, framework interstice concrete material has been recently used more and more in pavements. In the perspective of its internal structure, cement or asphalt cementitious matter is used to bond single-grade or gap-graded aggregate to form a “bonding crunode + aggregate + space” internal framework structure. The framework formed by aggregates and elastic nodes endows materials with strength and deformation properties, and the connective space allows for its water permeability and noise reduction functions; therefore, framework interstice concrete material is a new kind of pavement material with good performance.



Because of the existence and processing of inner structural space, it is difficult with this kind of material to build finite-element models and to simulate its mechanical performance.

Currently a variety of concrete micromechanical models have been established to research the relationship of concrete's micro-formation and its macro properties. In article by Tang [1], a plane model is used to analyze the concrete's properties. In the micro-models, the author considers the concrete as consisting of three sorts of materials – cement materials, aggregate and interface materials. When setting up models, the aggregates in fixed size are stochastically scattered in a certain plane area; the gaps among the aggregate are filled with cement material and the surface material with a certain depth is added as the third type of material outside the aggregate. The models were efficient to simulate the fracture process, especially when cracks emerge from the interface. For the properly-designed framework interstice concrete materials, cracks usually emerge in the bonding material, so there is no need for the third-phase material. In addition, it is hard to deal with the spaces in these models.

Adler *et al.* [2] proposes a method to deal with concrete internal voids from the viewpoint of geometry, but still much work needs to be done to build mechanical models. Articles [3–5] present a method of simulating the mechanical properties of asphalt bituminous concrete with the lattice model. In the micro lattice model, the aggregates are simplified as rigid joints, and the interaction of asphalt membrane among aggregates is replaced by a bar, whose mechanical parameter is gained by analyzing the asphalt membrane, and then a lattice structure can be established to simulate the performance of asphalt concrete. The advantage of the lattice model is that there is no need to consider the concrete's internal space and it's feasible to simulate the mechanical properties of concrete. But apparently, this kind lattice model cannot get the aggregate's influence on the property of the concrete, meanwhile, it cannot efficiently check the stress state of the bonding material. To some extent the performance of framework interstice concrete is decided by the bonding material, so both to investigate the stress state of the bonding material and to investigate the relationship between the bonding material and the whole concrete are important.

In order to research the performance of framework interstice concrete, this paper develops a micromechanical model, which can easily consider the spaces in framework interstice concrete and the effect of the aggregates. Based on the micromechanical model, the simulation results conform to that gained in the laboratory. The advantage of the method mentioned in the paper is that the study result of the stress state of bonding materials can guide the design of framework interstice concrete.

2 The calculating principle

Static finite element numerical calculation is to disperse the structure space and make displacement interpolation at the discrete nodes.



$$u_i(x, y, z) = \sum_{I=1}^n N_I(x, y, z) u_{iI} \quad (1)$$

$i=1,2,3$ are indicators of spatial coordinates. $I=1,2,...n$ are finite element node; U_{iI} is the first element node in i direction displacement, $N_{1(x,y,z)}$ is the first element of Lagrange interpolation function. We use elastic-plastic constitutive equation to calculate. The unit of the constitutive equation is written in form of matrix, geometric equation,

$$\varepsilon = Lu \quad (2)$$

physics equation,

$$\sigma = D\varepsilon \quad (3)$$

balance equation,

$$L^T \sigma + q = 0 \quad (4)$$

stress boundary condition,

$$L_n^T \sigma = p \quad (5)$$

displacement boundary condition,

$$u = \bar{u} \quad (6)$$

elastic strain,

$$\{\varepsilon^{el}\} = \frac{\sigma^e}{E\varepsilon^e} \{\varepsilon^{nl}\} \quad (7)$$

plastic strain,

$$\{\varepsilon^{pl}\} = \{\varepsilon^{nl}\} - \{\varepsilon^{el}\} \quad (8)$$

elastic-plastic matrix,

$$[D_{cp}] = \frac{\sigma^e}{E\varepsilon^e} [D_c] \quad (9)$$

The elastic matrix of aggregate is gained by inserting anisotropic stress-strain relationship into isotropic materials. It can be expressed as:

$$[D_c] = \frac{E}{(1+\nu)(1-2\nu)} \begin{bmatrix} (1-\nu) & \nu & \nu & 0 & 0 & 0 \\ \nu & (1-\nu) & \nu & 0 & 0 & 0 \\ \nu & \nu & (1-\nu) & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{(1-2\nu)}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{(1-2\nu)}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{(1-2\nu)}{2} \end{bmatrix} \quad (10)$$

$\{\varepsilon^{nl}\}$ is the general strain vector, $\{\varepsilon^{el}\}$ is strain vector. $\{\varepsilon^{pl}\}$ is plastic strain vector, $[D_c]$ is elastic matrix, $[D_{cp}]$ is plastic matrix, L is differential operator, D is rigid matrix, q is volume force vector, p is surface force vector.



3 The micromechanical model of framework interstice concrete

3.1 Geometric model

This article adopts a plane model to simulate the mechanical properties of the framework interstice concrete.

Because the framework interstice concrete's features and force carrying characteristic are dependent on its inner structural constitution "aggregate + elastic nodes + void", in general, the aggregate size of the framework interstice concrete only influences the space size, but little to the main performance of the framework interstice concrete.

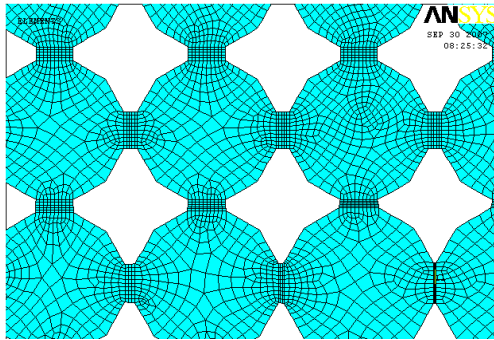


Figure 1: The shape and arrangement of aggregate and bonding material.

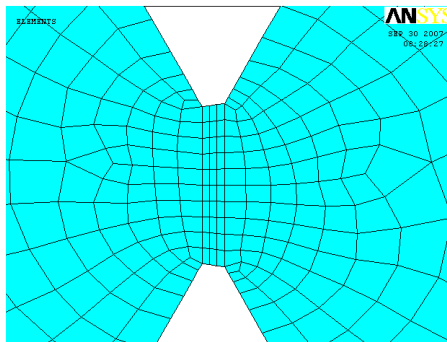


Figure 2: The mesh of aggregate and bonding material.

During calculations, when the bonding material is more cured, the aggregate can be simplified to a single size. In the model, the aggregate shape is treated as a twelve-edged polygon with same long sides for the convenience of modeling (Figure 1). Accordingly, the gaps between two aggregates are filled with bonding material evenly.



The advantages of this kind of modeling are: when the aggregate is simplified, the aggregate's adjacent edges are straight, and it is easy to get bonding material mesh without an abnormal unit (Figure 2); moreover, the other gaps which are not filled with bonding material left on the geometry can be regarded as the natural spaces of the framework interstice concrete to achieve the physical similarity (Figure 1). In this way, one can focus more on the bonding material in the calculation, at the same time, pay attention to the relationship between the bonding mechanical parameter and the overall performance of framework interstice concrete.

3.1.1 Aggregate

Aggregate size: diameter unified as 5mm. In practice, framework interstice concrete usually adopts gap-graded or single-graded aggregate; considering the focus of the calculation is to find the bonding's effect on the overall performance of the framework interstice concrete and to simplify the model, the aggregate size is unified as 5mm which is near to the actual size. Meanwhile the smaller the aggregate size is, the more convenient to get befitting mesh of the two different materials—aggregate and bonding material.

Aggregate shape: when the aggregate is simplified as circular, the circle of two aggregates will lead abnormal mesh and stress singularity (Figure 1, 2). Therefore, it is simplified into a twelve-edged polygon with the same surface.

3.1.2 Bonding material

The bonding thickness between aggregate is 0.1-0.5mm according micro-measure. In usual, the bonding thickness is 0.5mm, so in the model the bonding material thickness is chosen as 0.5mm (Figure 2).

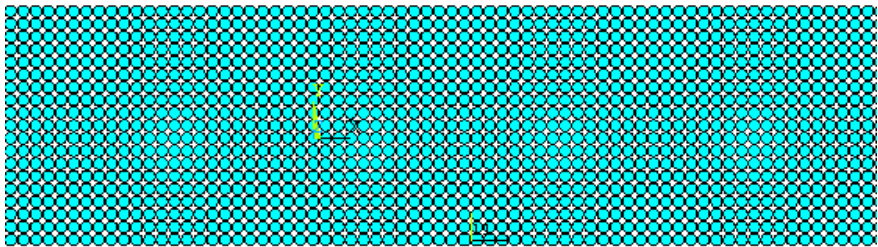


Figure 3: The overall model of framework interstice concrete.

3.1.3 The overall model

Aggregate is in a parallel arrangement and only the gaps between two adjacent parallel edges are filled with bonding material (Figure 1, 2), while the other parts aren't filled, the rest of the parts simulating the natural spaces.

These two kinds of materials in accordance with the planar combination eventually form 10×40 (cm) planar pieces (Figure 3) so that we can compare the results with the 10×10×40 (cm) bending experimental test.

3.2 Unit analysis

Unit type: because of the difficulties and the feasibilities of the three-dimensional model, we choose the plane model which can consider thickness for analysis. ANSYS' PLANE42 is able to establish two dimensional entity structural models. The unit can be used as both a plane unit and axisymmetric unit. At the same time the unit can deal with plasticity, creep, large deformation and large strain problems. The overall model of framework interstice concrete has 1,109,723 units and 1,182,901 nodes.

3.3 The model mesh

Bonding material: it can be divided into three units in thickness, ten units in length, and the unit's ratio between width and length is 1/5, that accord with the basic requirement of units (Figure 2).

The aggregate: the adjacent part of aggregate and bonding coordinates with the bonding material's unit, while other parts divide by themselves according to the principle of adapting. Aggregate and its units dividing is illustrated in Figure 1.

3.4 Material mechanical parameter

3.4.1 Aggregate's mechanical parameter

The aggregate material used in the test is granite, whose elastic modulus is 50-85GPa. According to the test and related test data, the elastic modulus in the calculation is 60GPa. Granite Poisson's ratio is between 0.20 and 0.30 in test, and it is 0.27 in the calculation. Granite Stress-strain relationship is linear.

3.4.2 Bonding material mechanical parameter

In this paper, the bonding material used in the test is polymer cement material, whose parameters are from the actual test data in the laboratory. The following figures are two representative curves of the polymer cement material measured in the test.

Through experiments, it is found that the bonding material elastic modulus is between 7000~8000Mpa (Figure 4). So it is 7500Mpa in the calculation

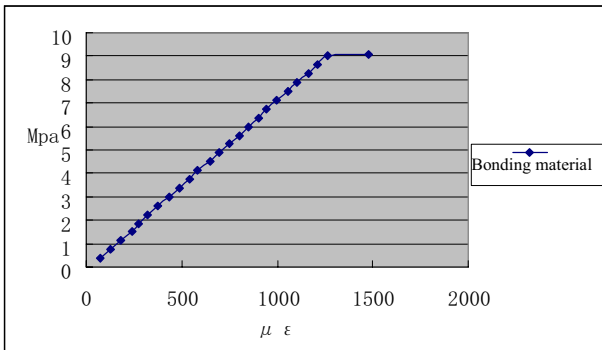


Figure 4: Bonding material stress-strain curves from experiments.

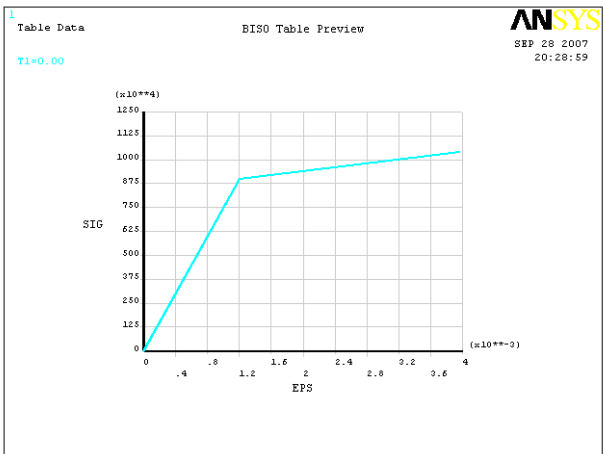


Figure 5: Bonding material stress-strain curves in the calculation.

(basically one degree lower than that of aggregate) and the Poisson’s ratio is 0.23. According to experiments its stress-relationship is chosen as typical dual line (Figure 5).

The first segment of the straight line, as in the test: the yield stress can be looked on as 9Mpa, and we choose the straight line before the stress reaches 9Mpa; the second segment: it is a little slope so as to avoid the dis-convergence.

3.5 Boundary condition and loading

Linear loading is adopted in the calculation. Loading location and the supporting condition is in accordance with that in the experiment (Figure 6).

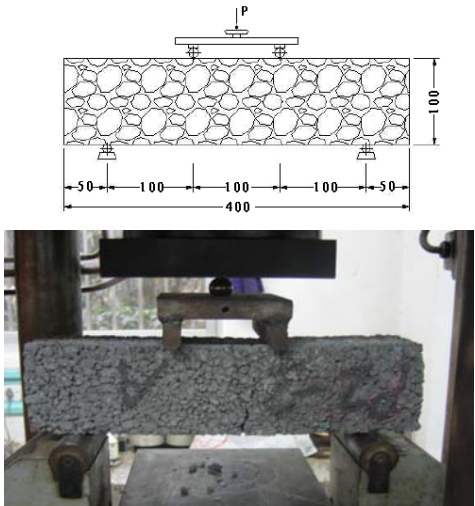


Figure 6: Schematic diagrams of loading (unite: mm) and loading photo.

3.6 Solution method

The paper adopts Newton-Raphson method to solve the equations. The finite element formulation of Newton-Raphson divides the entire load-displacement process into a series of incremental segments; and in each increment, the structure’s loading response is nearly as linear. Besides, after each increment’s load is increased, structural tangent stiffness matrix would be modified many times according to the required status variable to eliminate the unbalanced force and make sure that the calculation results satisfy the given precise requirement. And then considering the status as the equilibrium state, we continue to act on the loading increment to get incremental displacement by solving linear algebraic equations.

4 Calculation results analysis of framework interstice concrete

4.1 The simulated results of flexural test

After the simulated flexural specimen, which is loaded according to Figure 6, the framework interstice concrete’s mid-span load-displacement curve is gained. (Figure 7.)

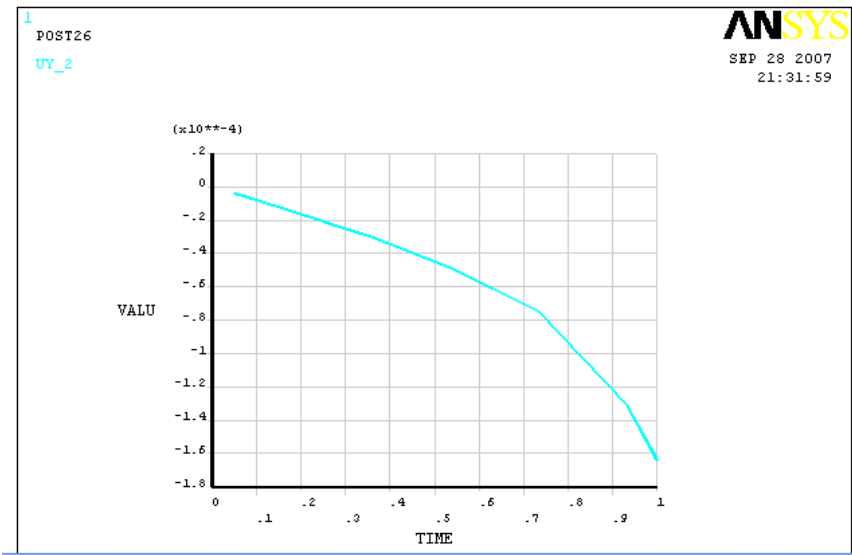


Figure 7: Framework interstice concrete’s mid-span load-displacement curve.

The calculated curve shows when the load is added to 14.6KN (the load is two times of TIME STEP in ANSYS), the framework interstice concrete appears yielding, at this time, the corresponding displacement is 0.075mm.



4.2 Experimental results

Figure 8 is an actual measuring stress-strain curve, and in test the measuring point is at mid-span bottom of the concrete beam. From the chart: when the load is increased to 12.3~15.2KN (in the loading as Figure), the concrete stress at mid-span bottom has a specifically relation with loading, $\sigma = PL/(bh^2)$, the framework interstice concrete appears yielding.

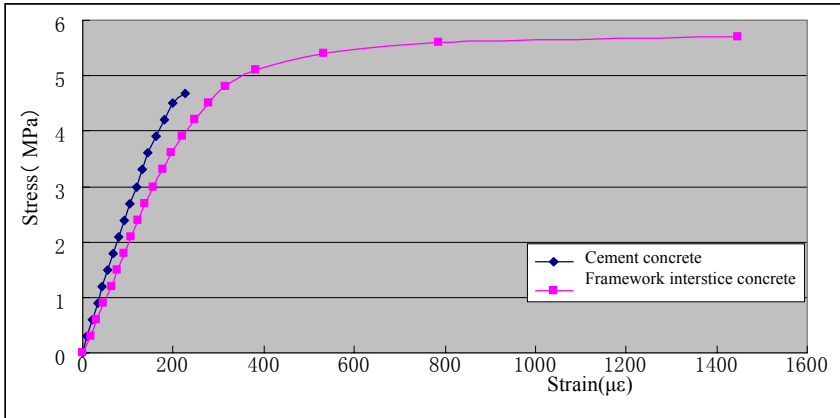


Figure 8: The representative stress-strain curve of framework interstice concrete (the measuring point is at mid-span, bottom of the concrete beam)

4.3 The comparison of the calculation result and experimental test

Comparing the result of test with that of calculation, the calculation yielded load has 5%~18.7% difference with the actual yielded load in experimental test, but the mid-span displacement has about 30% difference with the actual (it is maybe because the support has local deformation). From the comparison, conclusions can be drawn: the calculation model in the paper can better simulate the framework interstice concrete's mechanical properties.

5 Conclusions

The micromechanical calculation model developed in the paper, with a clear concept and convenient modeling, can better forecast and analyze the mechanical properties of framework interstice concrete, whose calculation results are consistent with that in the laboratory. The method in the paper can further simulate and study the mechanical actions of framework interstice concrete under other loading conditions, and popularize to study the creep of bituminous concrete materials. Henceforth, the model can be further developed into a three



dimensional model in order to better simulate framework interstice concrete materials' mechanical features.

Acknowledgements

The study has been supported both by Ministry of Transport of the People's Republic of China through project (2008 318 814 62) and by Chongqing Science & Technology Commission projects, whose support is gratefully acknowledged.

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Optimization of a numerical model of three-dimensional heat transfer during friction stir welding of 304L stainless steel

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Abstract

A numerical model of friction stir welding has been optimized to fit experimental data of three welds of 304L stainless steel at various weld velocities and spindle speeds. Optimization was used to determine the values of six model parameters that describe phenomena during the welding process. The parameter values were then compared to each other and to the default values. Predicted tool slip was determined to vary significantly with differing weld conditions. The coefficient of friction was also shown to vary. The mechanical efficiency of the three welds was predicted to range between 0.80 – 0.90. Optimization of additional welds is suggested so that correlations of the model parameters to weld velocity and spindle speed can be determined.

Keywords: friction stir welding, FSW, optimization, 304L stainless steel.

1 Introduction

Friction stir welding (FSW) is a solid state welding process in which a rotating tool generates heat along the joint interface, resulting in the flow of plasticized material around the tool. Since 1991, when FSW was developed at TWI [1], many models (both analytical and numerical) have been documented. An effective model of FSW can be a valuable predictive tool, allowing researchers to develop the process much more rapidly than could be accomplished through experiments only. Also, a good model of FSW can help researchers come to a better understanding of *how* the process works.

In this paper, a model of friction stir welding developed by Nandan *et al.* [2,3] is explored. The use of the model, which will be referred to as the Penn State model, requires the user to input six parameters that describe various



aspects of the process—a slip constant, a friction constant, a viscous dissipation constant, a mechanical efficiency factor, a “fraction of heat entering the workpiece” factor, and a constant for the heat transfer at the bottom face. These parameters can be difficult or near impossible to measure, so an optimization approach is used to determine the parameter values that will “best fit” the model to experimental data. If the Penn State model is to be used to predict weld behavior, these parameters must be 1) bounded with some confidence and 2) known to what extent they vary with weld velocity and spindle speed. This paper will explore both issues.

2 Description of optimization approach

2.1 Experimental data

The data used to optimize the Penn State model comes from an unpublished work of 11 welds of varying rotational speeds and feed rates performed by Owen [4]. Each weld was performed on a 304L stainless steel workpiece with dimensions 60.96 cm x 20.32 cm x 0.635 cm. The tool used for the welds was a MegaStir Technologies™ E44016 Polycrystalline Cubic Boron Nitride (PCBN) tool. For reference, the welds are given corresponding numbers in Table 1.

The majority of welds will be used in determining the correlation, if one exists, of the model parameters to the weld conditions given. The remaining welds will be used to test the accuracy of the correlation.

Table 1: Welds performed by Owen [4] and their intended use.

<i>Weld No.</i>	<i>Spindle Speed (rpm)</i>	<i>Feed Rate (mm/s)</i>	<i>Used to determine correlation</i>	<i>Used to validate correlation</i>
1	300	0.423	X	
2	300	0.847	X	
3	300	1.693		X
4	300	2.54	X	
5	400	0.847		X
6	400	1.693	X	
7	400	2.54		X
8	500	0.423	X	
9	500	0.847	X	
10	500	1.693		X
11	500	2.54	X	

Model accuracy is assessed by comparing the predicted temperatures at specific locations in the workpiece with those obtained experimentally. Each workpiece was instrumented with 16 thermocouples distributed as shown in Figure 1, where the y position indicated is the distance from the weld centerline (positive y is the retreating side). All thermocouples were placed at a depth of $z = 3.4$ mm. Spindle torque and forces in all three directions were simultaneously recorded. The most interior thermocouples were placed very close to the stir zone of the tool, but were not displaced during the weld.



By using two thermocouples at identical y locations (but different x locations), Owen was able to show a repeatability error of only $\sim 25^\circ\text{C}$ [4]. This indicated that the steady-state assumption used in numerical models of friction stir welding was suitable for the welds he performed. The repeatability error is also useful for establishing an acceptable level of model accuracy. The model error is given by

$$E = \sum_{i=1}^n (T_{i,\text{measured}} - T_{i,\text{predicted}})^2 \quad (1)$$

where $T_{i,\text{measured}}$ is the peak temperature measured at location i and $T_{i,\text{predicted}}$ is the peak temperature predicted by the model at the same location. Thus, using eqn (1) for n monitoring locations, the model error is not expected to be less than $E = 25^2n$ or $E = 625n$.

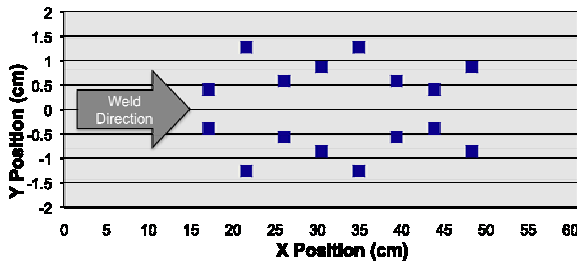


Figure 1: Locations of thermocouples in workpiece (not to scale) as given in [4].

2.2 Optimization routine

Optimization of the Penn State model is accomplished through the software package OptdesX. The objective of the optimization was to minimize the error function given in eqn (1) by changing the six model parameters previously mentioned. Six monitoring locations are used, with y values corresponding to the thermocouples at -1.27, -0.86, -0.40, 0.40, 0.86, and 1.27 cm. The optimization does not require any constraining functions. Since it is possible that more than one combination of model parameters may yield similar results – in other words, the solution may not be unique – the default values for 304L stainless steel (Table 2) are used as the initial starting points for each optimization routine. This helps to ensure that each search begins by looking for a minimum in the same area. The GRG algorithm within OptdesX was the search algorithm used.

A shell file written for OptdesX controls the flow of information in the process by calculating the model error and updating the values of the analysis variables as directed by OptdesX. The shell file serves as a link between the analysis engine (the Penn State model) and the optimization engine (OptdesX). In this approach, there is not one optimization problem, but rather seven optimization problems, where the welds used for correlation (see Table 1) are



optimized. The remaining welds will be used to validate the correlation obtained.

3 Preliminary results

The optimal values for the six model parameters have been determined for Welds No. 1, 4, and 9. They are shown below in Table 2. For Weld No. 1, the default parameters led to a model error of $E = 116,260$, which by eqn (1) and for six monitoring locations corresponds to an average location error of 139°C. Optimization reduced the error to 3,040 (22.5°C) – slightly less than the minimum expected value of 3,750 (25°C). Similarly, Welds No. 4 and No. 9 began with high model errors at the default position (154°C and 113°C, respectively), and ended with lower errors at the optimum position (44°C and 30°C). In each case, the model initially under-predicted the temperatures at all locations, but especially those closest to the weld.

Table 2: Optimal coefficient values for the welds tested.

Parameter	Default Values	Optimal Values for Welds		
		No. 1	No. 4	No. 9
Slip constant, δ_0	2.0	1.97	3.18	0.77
Friction constant, μ_0	0.45	0.50	0.58	0.46
Viscous dissipation constant, β	0.005	0.005	0.005	0.005
Mechanical efficiency, η	0.8	0.92	0.98	0.8
Fraction of heat entering workpiece, f	0.41	0.584	0.568	0.45
Heat transfer constant at bottom face, h_b	0.004	0.0037	0.0041	0.002

Plotting the predicted peak temperatures at the specified monitoring locations against the data obtained experimentally shows that the model is fairly accurate (see Figure 2). Welds No. 1 and 9 were much hotter than Weld No. 4. This is due to the feed rate in Weld No. 4 being six times higher than in Weld No. 1 and three times higher than in Weld No. 9.

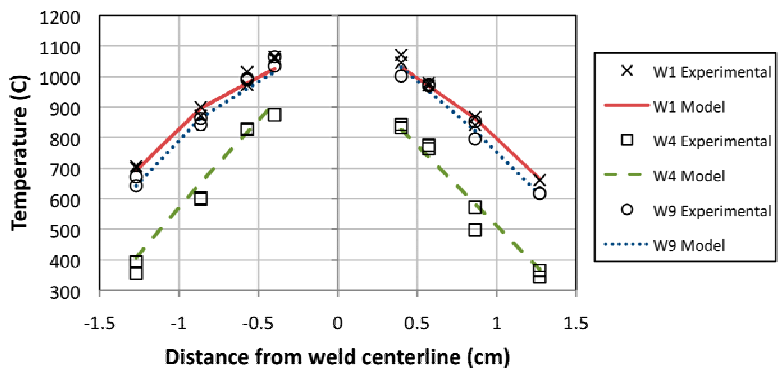


Figure 2: Peak temperatures in Weld Nos. 1, 4, and 9.



3.1 Slip constant

Slip at the tool-workpiece interface is modelled according to

$$\delta(r) = 1 - \exp\left(-\delta_0 \frac{\omega}{\omega_0} \frac{r}{R_s}\right) \quad (2)$$

where δ is the fraction of slip, ω is the rotational speed of the tool, ω_0 is a reference value of rotational speed, r is the distance from the tool axis, and R_s is the radius of the tool shoulder. The constant δ_0 is the user-adjustable parameter of interest. Thus, the fraction of slip throughout the tool for the welds studied is distributed according to Figure 3. The default value ($\delta_0 = 2.0$) seemed to match closely with the optimal value of 1.97 for Weld No. 1, whereas Weld No. 9 had a significantly lower fraction of slip. This indicates that more sticking occurs at higher spindle speeds, which is a result that was not expected. Further work will demonstrate whether this is a consistent result. Also, the optimal value of slip for Weld No. 4 indicates that higher feed rates may also increase the amount of sticking.

3.2 Friction constant

The optimal friction constant for Weld No. 1, $\mu_0 = 0.5$, was higher than the value chosen by Nandan *et al* [3] for mild steel. They chose $\mu_0 = 0.4$, and showed that in their case, adjusting the friction constant between 0.3 to 0.5 affected the peak temperature in the plate by about 100 K. Since Owen showed, as mentioned in Section 2.1, that the average error in thermocouple measurement was 25 K, a difference of 100 K is fairly significant.

The friction constant is used to scale the coefficient of friction according to

$$\mu_f(r) = \mu_0 \exp(-\lambda \delta \omega r) \quad (3)$$

where λ is a constant equal to 1 s/m. Since the coefficient of friction is function of two user-adjustable parameters (δ and μ_0), each weld studied had a slightly different shape and scale for the distribution for friction. The friction coefficient for the welds studied is shown in Figure 3. From the distributions of slip and friction shown, it appears that there is a correlation between the two parameters: the higher the friction coefficient, the more slip is present. It is unknown if this relationship only applies to the model, or if it represents real phenomena during FSW of 304L stainless steel.

3.3 Viscous dissipation constant

The viscous dissipation constant β is used in determining the heat generated from plastic deformation, S_b , by the equation $S_b = \beta \mu \Phi$. The function Φ is defined as

$$\begin{aligned} \Phi = & 2 \left(\left(\frac{\partial u_1}{\partial x_1} \right)^2 + \left(\frac{\partial u_2}{\partial x_2} \right)^2 + \left(\frac{\partial u_3}{\partial x_3} \right)^2 \right) \\ & + \left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1} \right)^2 + \left(\frac{\partial u_1}{\partial x_3} + \frac{\partial u_3}{\partial x_1} \right)^2 + \left(\frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2} \right)^2 \end{aligned} \quad (4)$$



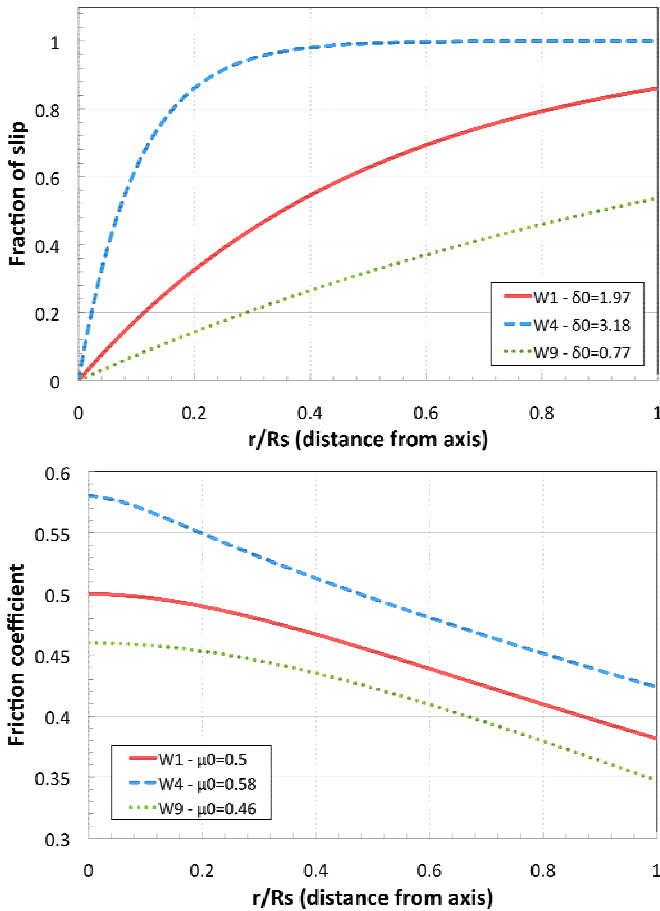


Figure 3: Fraction of slip and coefficient of friction used in the optimization of Welds No. 1, 4, and 9.

Optimization showed that the temperature profile of the workpiece was not sensitive to changes in β . This was anticipated since the heat generated due to viscous dissipation is fairly small. Yet, as Nandan *et al* conclude, without this term, the temperature profile does not vary with respect to changes in viscosity [3].

3.4 Mechanical efficiency

The mechanical efficiency η is used in determining how much heat is generated at the tool-workpiece interface (S_i) according to

$$S_i = \left[(1 - \delta) \eta \tau + \delta \mu_r P_n \right] (\omega r - U_i \sin \theta) \frac{A_r}{V} \quad (5)$$



where τ is the shear stress at yielding, P_N is the normal pressure, θ is the tilt angle of the tool, U_f is the weld velocity or feed rate, A_r is any small area on the interface, and V is the control volume enclosing the area A_r .

The model is predicting that mechanical efficiency diminishes as the rotational velocity increases. The change in η from Weld No. 4 to No. 9 was quite significant – a decrease of about 18 percent. Optimizing the other welds will clarify whether this change is solely due to changing the rotational speed or if other factors are contributing.

3.5 Fraction of heat entering workpiece

The fraction of heat entering the workpiece, f , is a parameter that when combined with the mechanical efficiency describes the percentage of power from the FSW machine that is converted into heat in the workpiece. Although the user is free to choose any value for f , Nandan *et al* [3] suggest using the following equation, which comes from steady-state one dimensional heat transfer from a point source located in the interface of two dissimilar materials at the same temperature [5].

$$f = \frac{J_w}{J_w + J_T} = \frac{1}{1 + \frac{(k\rho c)_T}{(k\rho c)_w}} \quad (6)$$

Using eqn (6) for a PCBN tool and 304L stainless workpiece, f is calculated to be ~ 40 percent, which is the value chosen by Nandan *et al* [2] in their study of stainless steel. This is comparable to the optimal values for the welds optimized so far, especially Weld No. 9 ($f = 45$). The welds with slower rotational velocities predicted more heat entering the workpiece.

The fraction of heat entering the workpiece seems to be calibrated low in the model. Eqn (6) assumes that both the tool and the workpiece are at the same temperature, a condition perhaps true towards the end of the plunge phase, but not during the weld, when the tool is moving into much cooler workpiece material. Shercliff and Colegrove state that heat lost into the tool is typically on the order of 10% or less [6]. When combined with the mechanical efficiency, the total predicted amount of power from the machinery entering the workpiece is ηf , which in the welds studied is only 0.35 – 0.55. Chao *et al* showed that this “heat efficiency” during FSW of aluminum was about 95 percent, which is much higher than the heat efficiency of traditional fusion welding (60-80%) [7]. However, they noted that the energy in FSW is converted from mechanical energy to heat and deformation, so that the term “heat efficiency” is not quite the same. It is unknown why the Penn State model predicts such a low fraction of heat entering the workpiece.

3.6 Heat transfer constant at bottom face

The heat transfer at the bottom surface ($z = 0$) is modeled as Newtonian cooling under natural convection:

$$k \left. \frac{\partial T}{\partial z} \right|_{\text{bottom}} = h(T - T_a) \quad (7)$$



where T_a is the ambient temperature. The contact resistance “convection” coefficient h is given by $h = h_b(T - T_a)^{0.25}$ where h_b is our unknown parameter with units equal to $\text{cal/cm}^2\text{-s-K}^{1.25}$ [8]. Thus, the heat transfer coefficient at the bottom face is a function of the temperature at the face and the constant h_b given by the user. The optimal h_b for Welds No. 1 and 4 stayed close to the default value ($h_b = 0.004$), corresponding to an h value of about $900 \text{ W/m}^2\text{-K}$ under the tool. Weld No. 9 however, had an $h_b = 0.002$.

Shercliff and Colegrove have suggested using a spatially variable (rather than temperature variable) heat transfer coefficient due to the different conditions of contact resistance between the workpiece and the backing plate [6]. Below and behind the tool, the contact resistance is low, due to the downward force. Away from the tool, however, the contact resistance is high; the clamping points can be neglected. Thus, the heat transfer constant h_b should not be a function of weld velocity or spindle speed.

4 Conclusion

A method for determining previously unknown parameters in the Penn State model through optimization techniques has been discussed. Results were shown to lead to accurate predictions of workpiece thermal profiles. Because the model is still under development, this method will be helpful in identifying discrepancies between the model and experimental data. It is probably too early to make any definitive statements on how the model parameters should be adjusted with regards to weld velocity and spindle speed. Likewise, although the optimized parameters correspond to material behavior during friction stir welding, statements on the characteristics of 304L stainless steel during FSW would be premature.

Although the use of optimization techniques is a roundabout way of determining the values of model parameters, it has been shown to yield reliable thermal profiles of the workpiece. Optimizing the other welds will allow more concrete statements to be made about model performance and predictions. In addition, correlations of the model parameters will allow the model to be used in a more predictive way, and it will yield further insight into the behavior of 304L stainless steel during friction stir welding.

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ANN Model to predict the bake hardenability of Transformation-Induced Plasticity steels

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Abstract

Neural networks are useful tools for optimizing material properties, considering the material's microstructure and therefore the thermal treatments it has undergone. In this research an artificial neural network (ANN) with a Bayesian framework able to predict the bake hardening and the mechanical properties of the Transformation-Induced-Plasticity (TRIP) steels was designed. The forecast ability of the ANN model is achieved taking into account the operating parameters involved in the Intercritical Annealing (IA), in the Isothermal Bainite Treatment (IBT) and also considering the different prestrain values and the volume fraction of the retained austenite before the Bake Hardening (BH) treatment. This approach allowed one to overcome the need to know the metallurgical rules that describe all the active phenomena in multiphase steels. The neural network approach allowed one to overcome the lack of prediction capability in the existing numerical models.

Keywords: bake hardening, Transformation-Induced Plasticity, neural network, Bayesian framework.

1 Introduction

The increasing demand for the reduction of automobile CO₂ emissions for environmental preservation has lead the automotive industries towards the weight reduction of mechanical components. The main focuses of the automotive market are, indeed, to guarantee safety and comfort while maintaining the light weight of the cars. The Transformation-Induced Plasticity (TRIP) steels allowed one to achieve these goals.

TRIP steels have a multiphase microstructure composed of a ductile ferrite matrix, hard bainite, hard martensite, and retained austenite in metastable



conditions. The volume fraction of the retained austenite is the origin of the so called TRIP effect that consists of the increasing elongation and strength capability of material produced from the transformation of the retained austenite to martensite under mechanical loading conditions. In order to obtain a large amount of retained austenite, the material is subjected to two thermal treatments, called respectively Intercritical Annealing (IA) and Isothermal Bainite Treatment (IBT).

Another important objective in the development of automotive steel is to reach a good combination of strength and formability. Formability is required when the sheet is shaped into an automobile body panel, whereas high strength is required after assembly. Bake-hardenable steel sheet was developed by exploiting the occurrence that these two properties are not simultaneously needed. After the manufacturing and assembly processes of a car body component, painting and baking are carried out. These processes involve heating the steel body panels to about 443°K and maintaining it at this temperature for 30 minutes. At this temperature, the carbon atoms dissolved in the steel diffuse, segregating in the regions around dislocations where the stresses are compressive. This results in a locking of the dislocations, which is called strain aging. This mechanism makes the steel panels harder after baking than after press forming. The utilization of this bake hardening phenomenon has made it possible to use steel sheet that has good formability during press forming and that can withstand severe working, whereas it is hard and less prone to denting when assembled in the car body.

The experimental characterization of the material response, at different values of the main variables that influence the Bake Hardening (BH) and the mechanical properties of TRIP steels, may be both expensive and time consuming, but the evaluation of these factors is necessary to produce components with the desired properties.

Many constitutive numerical models have been developed to evaluate the mechanical properties or the BH properties of TRIP steels. As described in the following section, for each proposed constitutive model, it is possible to identify a range of thermo-mechanical parameters in which a lack of fit between the experimental and modelled data appears. Furthermore, the metallurgical complexity of these steel requires one to consider the behaviours of each existing phase and also to translate into mathematical expression the phase interactions developed under thermomechanical cycles.

The artificial neural network (ANN) tool offers a forecasting method that may overcome the lack of fit to numerical models and moreover, is able to model the phase transformations phenomena influenced by strong non linear factors. This approach in addition offers the forecasting capability of a model for two aspects, as the ultimate tensile strength (UTS) and the BH, which are produced from different and complex metallurgical modifications. The literature researches offer some neural models able to predict the BH of TRIP steels that start from the chemical composition of material. In this research the capability to take in to account the material variability at the volume fraction retained austenite parameter is assigned (Barcellona et al. [1], Wasilkowska et al. [2], Girault et al. [3].)



The aim of the conducted study is to develop a model that is able to predict the mechanical strength and the BH effect of TRIP steels as a function of the main parameters that are influent in the three treatments, IA, IBT and BH, by means of a neural network approach with a Bayesian framework. Several published data on the microstructural composition, BH and mechanical properties of TRIP steels related to the times and temperatures for performing the above mentioned thermal treatments, have been joined with the authors' experimental data in order to define a significant training and validation data set.

2 TRIP and BH effects

The designing activity for a forecast tool for the mechanical and functional properties of multiphase materials, such as TRIP steel, needs to start from a deep knowledge of the main metallurgical aspects that affect the BH and the mechanical properties of TRIP steels both in the case in which the phenomenological approach is considered and in the case of a neural model. The following summarizes the main metallurgical aspects characterizing the TRIP and BH effects.

2.1 TRIP effect

TRIP steels are characterized by a very low content of alloying elements, such as in the tested material the total content of alloying elements is about 3.3 wt. pct; in particular C, Mn, Si, Al are present and other residual elements (0.8 wt. pct).

For a given chemical composition, the presence of the trip effect is produced from the two-stage heat treatment after cold rolling: the IA and IBT treatments. Considering that carbon is one of the stronger austenite stabilizer elements, the amount of the austenite phase at room temperature in a metastable condition is connected to the austenitic carbon content reached during the Isothermal Bainite Treatment (IBT). In fact, the IBT is the most critical stage of the production process for any TRIP steel. During the IBT, the carbon, which cannot produce the carbides typical of the bainite phase because of the silicon presence, diffuses into the austenitic regions and leads to the stability of the retained austenite at room temperature. The final amount of retained austenite depends therefore on the holding time during the IBT step without the carbide precipitation phenomena and also on the Si content. The silicon alloying also determines the ferrite matrix strengthening by means of solid solution.

During the martensitic transformation of the retained austenite upon mechanical loading, the regions surrounding the transformed phase, in order to accommodate the deformation produced by the phase transformation, undergo a plastic deformation that is added to the deformation produced from the mechanical load. The understanding of relationships between microstructure and mechanical properties requires the analysis of different phase roles.

The TRIP effect arises from the strain-induced transformation of retained austenite to martensite; this transformation result is accompanied by a volume expansion that generates plastic deformation and work hardening of the



surrounding ferrite phases. In fact, during the first phase of the deformation process, the hard phases dispersed in soft ferrite, i.e. bainite and thermal activated martensite, produce an increasing of the density of dislocations and therefore a high initial value of the work hardening rate. This phenomenon determines a high initial slope in the flow stress curve of the material. Furthermore, in TRIP steels, during the whole deformation process, at increasing of the strain level, the retained austenite progressively transforms itself to the martensite. This phenomenon determines a high work hardening rate and therefore flow stress curve slope; this is also the case for higher strain values. The persistence of the high work hardening rate may be attributed to the formation of stress induced martensite and the accumulation of dislocations in the soft ferrite matrix. Therefore, this strain-induced transformation determines high uniform elongation and also high strength of the material; furthermore it delays the onset of necking and increases the crash energy absorption capability of the material. Finally, the martensitic transformation generates inside the material a compression stress that confers high fatigue resistance (Kumar Srivastava et al. [4], Wang et al. [5]).

2.2 BH effect

The BH phenomenon consists of the increasing of yield properties of material after the paint baking treatment. The deforming process of working parts is always experimentally simulated by prestrain. The BH properties are therefore evaluated considering the difference between the yield stress after baking and the flow stress corresponding to a selected percentage of prestrain before the BH treatment. This treatment consists of the aging of the material at 443°K for 30 minutes. Many factors, such as the bainite phase-transformation, increasing of the carbon content in the retained austenite, decreasing of the retained austenite content and increasing of the dislocation density in ferrite matrix, influence the yielding phenomenon of tensile prestrained and baked trip steel sheets.

It is possible to distinguish different contributions inside the yield variation connected to the paint baking treatment. Initially there is an increment of yield stress produced into the ferrite matrix due to an activate diffusion of the solid solute, which determines a hindrance of dislocation movement. Upon longer aging times, carbides precipitate out the C atmospheres around the dislocations, resulting in an increase in both yield stress and ultimate tensile strength. Another contribution of yield increment is produced from increasing of the carbon content in the retained austenite during baking and the produced solid solute strengthening effect determines the strength of the retained austenite. It also needs to be remarked that during the baking treatment, a decrease in the amount of the retained austenite due to the austenite transformation to bainite, which is more stable at the given temperature, appears. Each contribution on the yield properties of material is connected on the amount of each phase. During the BH treatment the amount and therefore the yield contribution of the martensitic phase does not change.



3 The existing numerical models

The existing numerical models consider these particular multiphase steels as a composite material, and therefore start from the phenomenological laws that describe the mechanical behaviour of each existing phase. The interaction between the martensite and austenite phases is examined using the Gladman-type mixing law and foresees the assumption of the partition stress and strain mechanism between the two phases. The kinetics of the strain induced transformations are modelled using the Olson-Cohen equations. This approach allows one to simulate the mechanical behaviours of TRIP steels, but does not consider the main aspect connected to the BH effect, and therefore the results are unable to predict this important aspect of TRIP steels. The other most used numerical models to simulate the mechanical behaviours of TRIP steels are the Johnson-Cook, the Ludwig and the Zhao models or variants of these. Each numerical model has a specific applicability range that is coupled with the determination of strain ranges in which the fitting capability of the model decreases. These models also do not consider the physical aspect connected to the BH effect (Shan et al. [6], Liu et al. [7], Li et al. [8], Bouquerel et al. [9]).

4 The ANN technique

The ANN approach constitutes a regression analysis method in which a flexible non linear function is fitted to the experimental data. This tool is able to capture complex relationships characterizing phase transformations, without requiring mathematical descriptions of phenomena.

The Bayesian framework applied to the neural model is able to take into account the fitting uncertainty. This method calculates a probability distribution of the set of neural network weights and provides the outputs error bars, defining the applicability range of the neural model. Furthermore, the significance of the input variable is automatically quantified.

Considering the Kolmogorov theorem, the complexity of each system can be captured with a neural network model containing a single hidden layer; the flexibility of the model is attained operating on the number of the hidden units. The general model formulation considering a feed-forward architecture with one hidden layer and i hidden units is:

$$y_k = \sum_i w_{ki}^{(2)} h_i + \theta_k^{(2)}, \quad (1)$$

where

$$h_i = \tanh\left(\sum_j w_{ij}^{(1)} x_j + \theta_i^{(1)}\right), \quad (2)$$

x_j are the inputs, y_k are the outputs, θ are the bias corresponding to each neural node, w are the neural weights and the superscript (1) refers to the hidden layer, whereas the superscript (2) refers to the output layer. Eqn (1) expresses the output of the neural model, whereas eqn (2) expresses the transfer function. The



combination of several hyperbolic tangents confers to the model the ability to capture the non linear relationship between inputs and outputs.

The number of input, output and hidden nodes and their connections defines the architecture of the neural model. The Bayesian framework foresees that the weights and biases of the network are assumed to be random variables with specified distributions and provides a method to improve the generalization capability of the neural network, usually called regularization.

The backpropagation algorithm is able to train multilayer feed-forward networks with differentiable transfer functions to perform function approximation, pattern association, and pattern classification. There are several backpropagation training algorithms; among them, the Bayesian regularization algorithm consists of a modification of the Levenberg-Marquardt training algorithm to produce networks that generalize well, reducing the difficulty of determining the optimum network architecture.

The Bayesian regularization involves modifying the performance function, which normally is the sum of the squares of the network errors on the training set. The formulation of the Bayesian performance function is depicted in eqn (3):

$$MSE_{reg} = \gamma MSE + (1 - \gamma) MSW, \quad (3)$$

in which MSE_{reg} is the modified performance function, γ is the performance ratio, MSE is the typical performance function mean squared error given by:

$$MSE = \frac{1}{N} \sum_{i=1}^N (e_i)^2 = \frac{1}{N} \sum_{i=1}^N (t_i - y_i)^2, \quad (4)$$

in which $t_i - y_i$ represents the difference between the target value and the output value and MSW is the mean of the sum of the squares of the network weights:

$$MSW = \frac{1}{n} \sum_{i=1}^n (w_j)^2. \quad (5)$$

The determination of the optimum value for the performance ratio parameter (γ) allows one to generate a network that best fits the training data. In effect, if this parameter is too large, it may get overfitting and if the ratio is too small, the network will not adequately fit the training data.

The described network architecture has been implemented using the MATLAB neural network toolbox that provides some routines that automatically set the regularization parameter. The Bayesian regularization works well if the input and the target data are ranged in $[-1;1]$. Therefore, the inputs and the targets have been normalized within the range $[-1;1]$ before training as follows:

$$x_{norm} = 2 \frac{x - x_{min}}{x_{max} - x_{min}} - 1, \quad (6)$$

where x_{norm} is the normalized value of each parameter and x , x_{min} and x_{max} are respectively the measured, the minimum and the maximum values for the

considered parameter. In order to avoid the possibility of overfitting data, the experimental data are randomly divided into two groups respectively called the training set and the test set. The model has been implemented considering the only training data set constituted by 75 pct of the experimental data and it has been tested considering the test data set constitute by 25 pct of the experimental data (De Cooman [10], Cetinel et al. [11], Dobrzanski and Trzaska [12], Garcia et al. [13], Das et al. [14]).

5 Model application and results

The topological definition of the selected neural model started from the individuation of the main parameters that influence the selected forecasting outputs: the BH index and the UTS value. The strong influence of the two thermal treatments able to confer to the material the TRIP effect was considered, selecting as input of the neural network the temperatures and the times of both the IA treatment and the IBT treatment. The paint baking treatment was taken into account, choosing as an input the prestrain value, considering that the BH index is a function of the selected prestrain level. The operating parameters of the paint baking treatment were considered as constant and equal to 443°K and 30 minutes. The variability of the chemical composition of steel was considered, inserting among the input the volume fraction of the retained austenite achieved after the IA end the IBT treatments. Each designed neural model therefore has six input parameters, as depicted in table 1. The considered outputs were the BH index and the UTS value. The Bayesian regularization used gives good results if the input and the target data are ranged in $[-1;1]$; for this reason, the inputs and the targets have been normalized, highlighting the maximum and the minimum values of each considered input and output.

The fitting capability of the neural model was investigated, designing different neural networks containing a variable number of the hidden units.

Table 1: Variation ranges of input and output parameters.

		Max	Min
Inputs	T_{IA} (°K)	1086	1031
	t_{IA} (s)	600	120
	T_{IBT} (°K)	733	643
	t_{IBT} (s)	960	120
	Prestrain (pct)	20	0
	V_{ret} (pct)	16	4
Outputs	BH (MPa)	80	50
	UTS (MPa)	1050	790



The selection of the best number of the hidden neurons has been made using a pruning algorithm that uses sensitivity analysis to quantify the relevance of inputs and hidden units proposed by Engelbrecht [15]. The obtained best performance allowed one to select the model with a complexity level able to optimize the forecasting capability of the neural network. The set of data useful for defining the training and the testing of each neural model were collected considering a wide experimental campaign, previously conducted, to highlight the influence of the IA and IBT operating parameters on the UTS and the BH properties of TRIP steel (Barcellona et al. [16, 17]). In order to enlarge the training and the test data set, experimental results also derived from literature data have been considered (Zhang et al. [18], Timokhina et al. [19], Wang et al. [20], Pereloma et al. [21], Kvačakj and Mamuzić [22]). In order to highlight the trend of performance data at the varying of the number of the hidden neurons, eight neural networks differing in the number of the hidden neurons have been displayed in their training and testing phases. The detailed topology of each neural network is reported in table 2, in which the performance results are also summarized in terms of the correlation coefficient R between the forecasted and the experimental outputs.

In order to achieve a better readability of the obtained results, the outputs of each neural network have been post-processed; the linear regression between the network response and the target data allowed one to evaluate the fitting capability of the model to the experimental data in the training and in the testing phases. The evaluation of the regression coefficient R provided the degree of correlation between the experimental and the foreseen data.

Twenty-two hidden units offers a sufficient complexity level to best fit the experimental data. In effect, the observation of the values of the R coefficient of two outputs in the training phase evidenced that a lower number of hidden units is insufficient to best fit the experimental data, but the fitting capability increases with the increasing of the hidden neurons and it attains the maximum in the neural network model 6-22-2.

Table 2: Outputs correlation coefficients R of the training and the testing phases.

Neural Networks	$R_{\text{training BH}}$	$R_{\text{testing BH}}$	$R_{\text{training UTS}}$	$R_{\text{testing UTS}}$
6-5-2	0.495	0.397	0.523	0.497
6-7-2	0.872	0.823	0.891	0.823
6-10-2	0.883	0.842	0.918	0.882
6-14-2	0.885	0.844	0.917	0.885
6-20-2	0.919	0.897	0.920	0.902
6-22-2	0.944	0.943	0.965	0.963
6-24-2	0.943	0.932	0.958	0.950
6-27-2	0.921	0.914	0.928	0.915



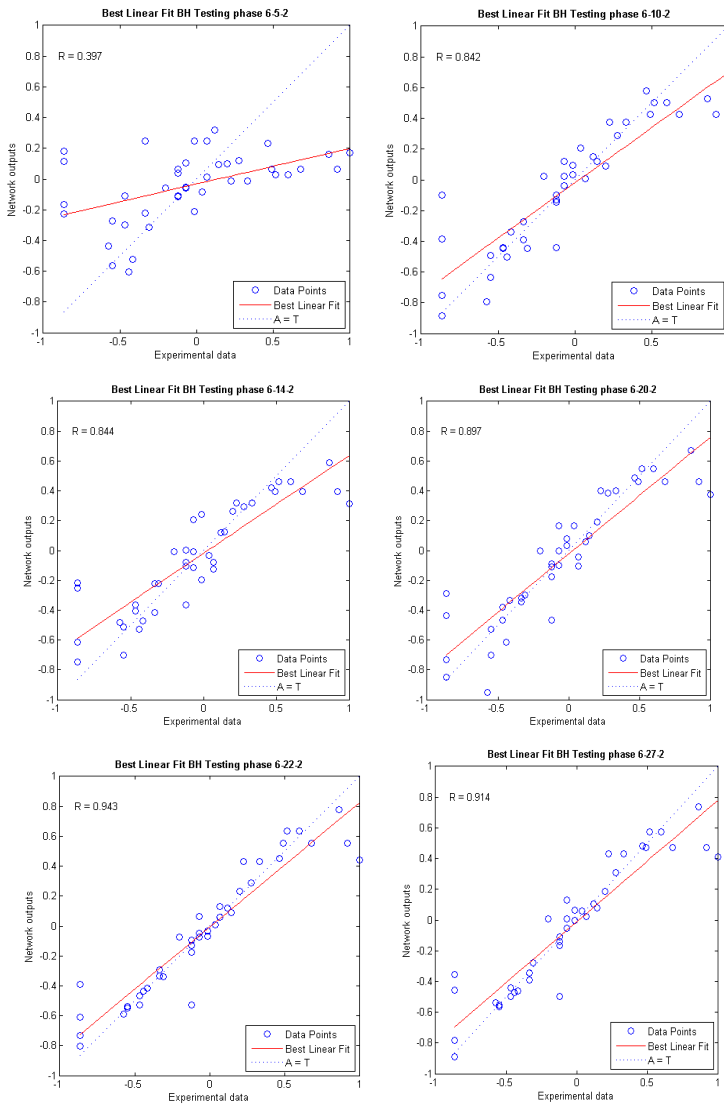


Figure 1: Linear regression between the network response and the target in the testing phase for the BH output parameter.

This optimum of performances was found for both the considered outputs. The interpolation capability of the forecasting tool was also investigated in the testing phase by the evaluation of the performance coefficient R ; a light decreasing of the fitting capability in respect to the training phase has been observed.



This difference becomes almost pointless for the best neural model. This tendency has been observed for both outputs.

The designed neural model shows better forecast ability for the UTS values, but the difference in the R values of the two output parameters tends to decrease when the number of neurons in the hidden layer approaches the best number of hidden neurons.

The image visualization of the results of the regression analysis in the testing phase, as depicted in figure 1, allowed one to evaluate how the forecasted data differs from the experimental data, and it directly shows the dispersion effect produced by the neural model in respect to the best fitting condition, represented by the 45° inclined line.

6 Conclusions

The main focuses of the automotive market are to guarantee safety and comfort while maintaining the light weight of the cars and preserving a good combination of strength and formability. These goals are achieved by the development of TRIP steels that posses the BH effect. In this research an ANN with a Bayesian framework able to predict the BH and the mechanical properties of the TRIP steels was designed. The neural approach allowed one to overcome the lack of prediction capability of the existing numerical models. The main obtained results are summarized as follows.

- The selection of the best number of the hidden neurons has been made using a pruning algorithm that uses sensitivity analysis to quantify the relevance of input and hidden units proposed by Engelbrecht.
- In order to highlight the trend of performance data at the varying of the number of the hidden neurons, eight neural networks differing in the number of the hidden neurons have been displayed in their training and testing phases.
- The outputs of each neural network has been post-processed; the linear regression between the network response and the target data allowed one to evaluate the fitting capability of the model to the experimental data in the training and in the testing phases.
- The observation of the values of the R coefficient of the outputs in the training phase evidenced that a low number of hidden units is insufficient to best fit the experimental data, but the fitting capability increases with the increasing of the hidden neurons and reaches the maximum in the neural network model 6-22-2. This optimum of performances was found for both the outputs.
- The interpolation capability of the forecasting tool was investigated by the evaluation of the performance coefficient R in the testing phase. A light decreasing of the fitting capability in respect to the training phase has been observed. This difference becomes almost pointless for the best neural model and this tendency has been observed for both the outputs.



- The designed neural model possesses better forecast ability for the UTS values, but the difference in the R values of the two output parameters tends to decrease when the number of the hidden units approaches the best number of hidden neurons.
- The graphic visualization of the results of the regression analysis allowed one to evaluate how the forecasted data differ from the experimental data and the degree of dispersion from the best fit condition.

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Transient and steady-state heat conduction analysis of two-dimensional functionally graded materials using particle method

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Abstract

The moving-particle semi-implicit (MPS) method, one of the particle methods, is an effective numerical simulation method for incompressible inviscid flows with free surfaces. The discretization scheme of the particle method can be utilized for discretizations of gradient, divergence and Laplace operators in the partial differential equations such as the diffusion equation and the wave equation. In recent years, advanced materials known as Functionally Graded Materials (FGMs) have drawn considerable interest. These FGMs are expected to be highly heat resistant materials that can be used under high temperature and high temperature gradient conditions. Because of this, it is important to investigate the temperature distributions in the FGMs. The purpose of this work is to present a numerical analysis of the heat conduction for two-dimensional FGMs where the thermal conductivity is a function of the spatial coordinates using the particle method. Analytical solutions and finite element solutions are compared with the present results, and the validity of the present method is shown.

Keywords: particle method, functionally graded materials, heat conduction, transient analysis, steady-state analysis.

1 Introduction

In recent years, in the field of numerical simulations, the moving-particle semi-implicit (MPS) method has been attracting much interest [1]. The MPS method, one of the particle methods, is the leading numerical-analysis technique that is also capable of treating, and has been used to investigate, complicated



phenomena such as incompressible inviscid flows with free surfaces and the collapse of a column of water [2]. Advanced materials known as Functionally Graded Materials (FGMs) have drawn considerable interest [3]. These FGMs are expected to be highly heat resistant materials that can be used under high temperature and high temperature gradient conditions. In this case, it is important to investigate the temperature distributions in the FGMs. It is usually difficult to obtain an analytical solution for heat conduction problems with complex geometries and complex thermal boundary conditions. Therefore, a numerical analysis technique is very important. Sladek proposed a method for transient heat conduction analysis in FGMs using the meshless local boundary integral equation [4]. Also Wang developed a meshless numerical method to analyze problems of transient heat conduction in FGMs [5]. Hamza-Cherif solved transient temperature fields in axisymmetric FGM cylinders under various boundary conditions using an h-p finite element method [6]. Dai discussed different material thermal property functions affecting temperature distributions in two-dimensional FGMs using the method of lines [7].

To the best of the author's knowledge, no numerical solutions for heat conduction problems in FGMs by the particle method have been reported. The purpose of this our investigation is to perform analysis of transient and steady-state heat conduction analysis of two-dimensional FGMs using the particle method. In this work, the thermal conductivity or the thermal diffusion coefficient of FGMs is a function of the spatial coordinates. Moreover, although a particle method belongs to the category of meshless methods, the formulations for numerical analysis are mathematically simple, unlike the integral equation method. First, the basic discrete equations for transient and steady-state heat conduction analysis of FGMs are derived. For a few numerical examples, analytical solutions and finite element solutions are compared with the present results. The effects of the radius of interaction and number of particles are also discussed. We obtained good agreement between our present results and those of others with respect to the temperature values and temperatures distributions. This agreement shows the validity of the present method.

2 Heat conduction equation in FGMs

In the Cartesian co-ordinate system, the two-dimensional equation governing the heat conduction problem of FGMs without internal heat generation is given by eq. (1) or eq. (2),

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) \quad (1)$$

or

$$\frac{\partial T}{\partial t} = \nabla \cdot (D \nabla T) \quad (2)$$



where, t is time, $T = T(x, y)$ is the temperature function, and $\lambda = \lambda(x, y)$ denotes the thermal conductivity and is a function of spatial coordinates, $\rho = \rho(x, y)$ is the mass density, $c = c(x, y)$ is the specific heat, and $D(x, y) = \lambda(x, y) / \rho(x, y) c(x, y)$ is the thermal diffusion coefficient respectively.

3 Discretization of gradient and Laplacian

From eq. (2), the following expression is obtained

$$\frac{\partial T}{\partial t} = (\nabla D) \cdot (\nabla T) + D \nabla^2 T. \quad (3)$$

From the above equation, the discretization of the gradient vectors and Laplacian operator are needed [1,2]. The discretization of the gradient vector of a scalar function $\phi(x, y)$ at the i -particle is given by

$$\langle \nabla \phi \rangle_i = \frac{d}{n_i} \cdot \sum_{j \neq i} \left[\frac{\phi_j - \phi_i}{|\mathbf{r}_j - \mathbf{r}_i|^2} (\mathbf{r}_j - \mathbf{r}_i) w(|\mathbf{r}_j - \mathbf{r}_i|) \right] \quad (4)$$

where ϕ_i, ϕ_j are the values of scalar function $\phi(x, y)$, $\mathbf{r}_i, \mathbf{r}_j$ are the position vectors of i -particle and j -particle respectively, $|\mathbf{r}_j - \mathbf{r}_i|$ is the distance between i -particle and j -particle, n_i is the particle density, d is the dimensional number which equals 2 in the two-dimensional problems, the function w is the weighted function and $\sum$ means summation with respect to $j \neq i$. The weighted function w is given as follows,

$$w(r) = \begin{cases} \frac{r_e}{r} - 1 & (0 \leq r < r_e) \\ 0 & (r_e \leq r) \end{cases} \quad (5)$$

where, r is the distance between two particles, and r_e is the radius of the interaction. Hence, if r is less than r_e , there is interaction between two particles. The particle density n_i is given as follows,

$$n_i = \sum_{j \neq i} w(|\mathbf{r}_j - \mathbf{r}_i|). \quad (6)$$

The discretization of the Laplacian operator of the scalar function $\phi(x, y)$ at the i -particle is given by



$$\langle \nabla^2 \phi \rangle_i = \frac{2d}{\Lambda n_i} \cdot \sum_{j \neq i} [(\phi_j - \phi_i) w(|\mathbf{r}_j - \mathbf{r}_i|)] \quad (7)$$

where, Λ is a constant given by the following expression

$$\Lambda = \frac{\sum_{j \neq i} |\mathbf{r}_j - \mathbf{r}_i|^2 w(|\mathbf{r}_j - \mathbf{r}_i|)}{\sum_{j \neq i} w(|\mathbf{r}_j - \mathbf{r}_i|)} . \quad (8)$$

4 Basic discrete equation

Applying Euler's explicit method to the term on the left hand side of eq. (3), and discretization of the gradient vector and Laplacian operator on the right side, the basic discrete equation for the transient heat conduction can be obtained as follows,

$$\begin{aligned} T_i^{s+1} = & T_i^s + \Delta t \cdot \sum_{j \neq i} \frac{2d}{\Lambda n_i} [D_i(T_j^s - T_i^s) \cdot w(|\mathbf{r}_j - \mathbf{r}_i|)] \\ & + \Delta t \cdot \left(\sum_{j \neq i} \frac{d}{n_i} \left[\frac{T_j^s - T_i^s}{|\mathbf{r}_j - \mathbf{r}_i|^2} (\mathbf{r}_j - \mathbf{r}_i) \cdot w(|\mathbf{r}_j - \mathbf{r}_i|) \right] \right. \\ & \left. \cdot \sum_{j \neq i} \frac{d}{n_i} \left[\frac{D_j - D_i}{|\mathbf{r}_j - \mathbf{r}_i|^2} (\mathbf{r}_j - \mathbf{r}_i) \cdot w(|\mathbf{r}_j - \mathbf{r}_i|) \right] \right) \end{aligned} \quad (9)$$

where the upper subscript s is the time step number and Δt is the time increment. The dot inside the parenthesis of the third term on the right hand side denotes the inner product. The basic discretized simultaneous equation for the steady state heat conduction is given by,

$$\begin{aligned} & \sum_{j \neq i} \frac{2d}{\Lambda n_i} [D_i(T_j - T_i) \cdot w(|\mathbf{r}_j - \mathbf{r}_i|)] \\ & + \left(\sum_{j \neq i} \frac{d}{n_i} \left[(T_j - T_i)(\mathbf{r}_j - \mathbf{r}_i) \frac{w(|\mathbf{r}_j - \mathbf{r}_i|)}{|\mathbf{r}_j - \mathbf{r}_i|^2} \right] \right. \\ & \left. \cdot \sum_{j \neq i} \frac{d}{n_i} \left[(D_j - D_i)(\mathbf{r}_j - \mathbf{r}_i) \frac{w(|\mathbf{r}_j - \mathbf{r}_i|)}{|\mathbf{r}_j - \mathbf{r}_i|^2} \right] \right) = 0 \end{aligned} \quad (10)$$



5 Numerical examples

In order to demonstrate the efficiency and accuracy of the proposed particle method, we first considered steady-state heat conduction problems, and then transient heat conduction in FGMs.

5.1 Steady-state analysis

In the first examples, a square FGM is considered as shown in Fig.1. On both opposite sides parallel to the x -axis, heat insulation conditions are imposed, and on the lateral sides, two different temperatures are prescribed. Initial temperature of the whole region is zero.

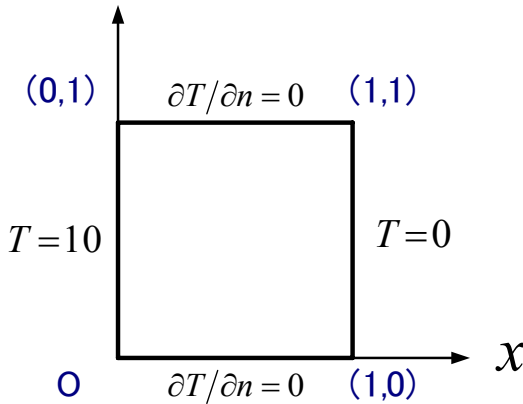


Figure 1: Geometry and boundary conditions.

In numerical calculations, 11 particles are located along x -axis and y -axis respectively for a total of 121 particles. The radius of interaction r_e in eq. (5) is twice the minimum distance between two particles.

Particles on the boundary have interaction between only inner particles, no prescribed temperatures are imposed and heat insulation conditions are satisfied automatically.

5.1.1 Example 1

The distribution of thermal conductivity of the FGM is assumed as,

$$\lambda(x) = A \exp(Bx), \quad (11)$$

where λ is the thermal conductivity and A and B are constants [8]. In case $A = 1, B = -2, 0, 2$, the distribution of the thermal conductivity is shown in Fig.2. The case of $B = 0$ corresponds to an isotropic material.



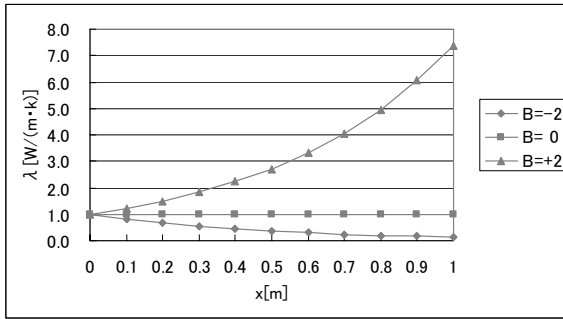


Figure 2: Thermal conductivity of eq. (11).

The temperature distributions simulated by the present method and exact solutions along the line $y = 0.5$ in FGM are shown in Fig.3 [8]. For each value of constant B , the numerical results are in good agreement with the analytical solutions.

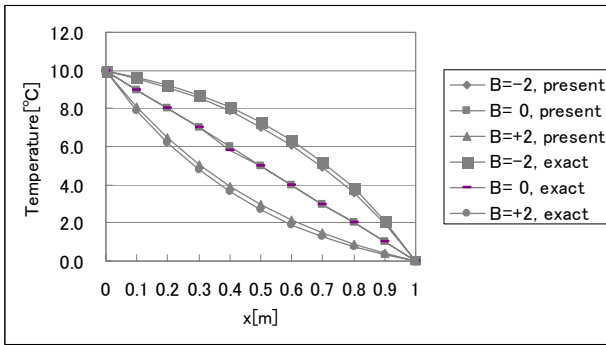


Figure 3: Distribution of steady-state temperature.

5.1.2 Example 2

Thermal conductivity in the material changes according to the following equation,

$$\lambda(x, y) = 1 + 2 \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \quad (12)$$

where the side-length of the square is $L = 1$ m [8]. In this material, the thermal conductivity changes in x -axis and y -axis directions. The distribution of the thermal conductivities along $y = 0.1$ and $y = 0.5$ are presented in Fig.4. The temperature distribution obtained by the present method and a FEM solution along the line $y = 0.5$ are presented in Fig.5 [8]. In this case, both are in good agreement.



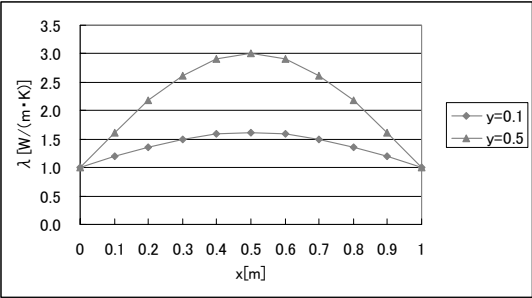


Figure 4: Thermal conductivity of eq. (11).

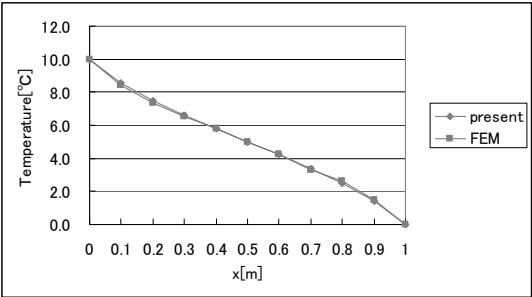


Figure 5: Distribution of steady-state temperature.

5.2 Transient analysis

Carrying out the transient simulation until the steady state is achieved, the results are compared with analytical solutions obtained by Fourier transform.

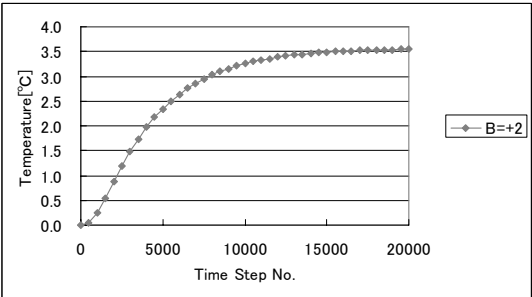


Figure 6: Time variation of temperature.

In the numerical calculations we, for convenience, use a square with side-length $L = 1$ m, take the thermal conductivity as $B = 2$ (eq. (11)) and the thermal conductivity $\rho c = 1000$. Take 11 particles along x -axis and y -axis respectively so a total of 121 particles are used. The radius of interaction in eq. (5) is twice

the minimum distance between two particles and $\Delta t = 1.0 \times 10^{-2}$ s time increment is used. The variation of temperature at the central point (0.5, 0.5) is presented in Fig.6, and the field of the stationary temperature along $y = 0.5$ at time step 20,000 with the analytical solution of steady-state is shown in Fig.7. Because of the convenient thermal capacity, these results have no physical meaning. The temperature reached steady-state at about 15,000 time steps and there was excellent agreement between the results of the proposed method and the exact solution by steady-state analysis.

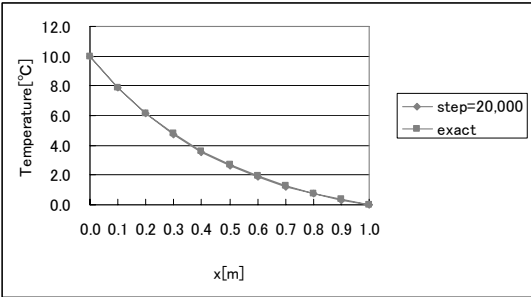


Figure 7: Stationary temperature distribution.

5.3 Effect of number of particles

In this section, number of particles affecting the accuracy of the steady-state solutions is examined. The thermal conductivities of eq.(11) with $B = 2$ and eq. (12) are analyzed. The geometry, boundary conditions, and the interaction radius of the problem are the same as above. The temperature distributions along $y = 0.4$ under eq.(11) analysis using 6×6 , 11×11 , and 16×16 particles respectively are shown in Fig.8. In each case, the accuracies of the results are guaranteed even for the 6×6 particles.

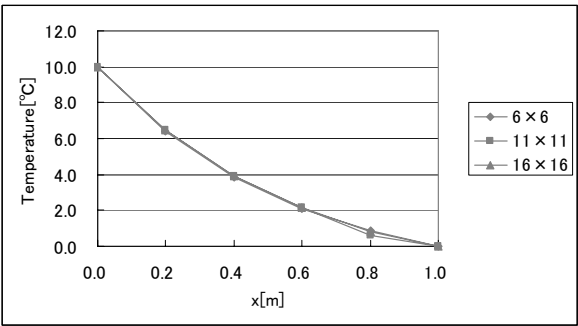


Figure 8: Relationships between temperature and number of particles under eq. (11).



5.4 Effect of radius of interaction

Via parameter analysis with respect to the radius of interaction in the weighted function eq. (5), the influence of these radii on the accuracies of the steady-state results was investigated. The geometry, the distribution of thermal conductivity and boundary conditions is the same as in the above section. Figure 9 shows the relationships between the temperature distributions along $y = 0.5$ and the radius of interaction for variation from 5 times to twice the minimum distance between two particles.

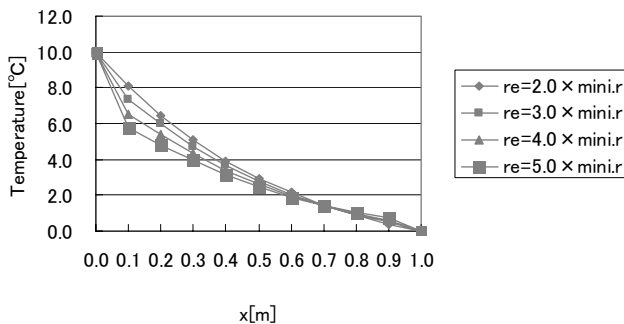


Figure 9: Relationships between temperature distributions and radius of interaction under eq.(11).

Accuracy in the case where the interaction radius is twice the minimum distance between two particles is good, but accuracy falls off with increase in the interaction radius. In reference [1], radius of interaction from 4 times to twice the minimum distance between two particles is recommended.

6 Conclusion

In this paper, the transient and steady-state analysis of heat conduction for FGMs using the particle method is presented. The basic discrete equations for heat conduction analysis in FGMs are formulated by the discretizations of gradient and Laplace operators in the heat conduction equation. Solving a few two-dimensional problems in FGMs, most of the results correlate well with the exact solutions or those obtained by the finite element method and the validity of the present method is shown. And also, according to the parameter analysis with respect to the number of particles and the radius of interaction in the weighted function, accurate solutions are obtained for even a comparatively small number of particles, and the recommended interaction radius is twice the minimum distance between two particles.



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A unique computational algorithm to simulate probabilistic multi-factor interaction model complex material point behavior

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Abstract

The Multi-Factor Interaction Model (MFIM) is used to evaluate the divot weight (foam weight ejected) from the launch external tanks. The multi-factor has sufficient degrees of freedom to evaluate a large number of factors that may contribute to the divot ejection. It also accommodates all interactions by its product form. Each factor has an exponent that satisfies only two points—the initial and final points. The exponent describes a monotonic path from the initial condition to the final. The exponent values are selected so that the described path makes sense in the absence of experimental data. In the present investigation, the data used was obtained by testing simulated specimens in launching conditions. Results show that the MFIM is an effective method of describing the divot weight ejected under the conditions investigated.

Keywords: weight, comparisons, cumulative distribution, probabilistic sensitivities, local optimization.

1 Introduction

The simulation of complex material behavior resulting from the interaction of several factors (such as temperature, nonlinear material due to high stress, time dependence, fatigue, etc.) has been mainly performed by factor-specific representations. For example, entire text books are devoted to plasticity, creep, fatigue and high strain rate to mention only a few. Investigators have derived equations that describe material behavior for each factor-specific effect. Suppose we visualize that the material behavior is a continuum represented by some



surface. Then, we can think of some representation which describes that surface which is inclusive of all participating factors that affect material behavior either singly or interactively in various combinations. To that end, research has been a continuing activity at NASA Glenn Research Center (GRC) for about thirty years. It started with a primitive form of the Multi-Factor Interaction Model (MFIM) representation for describing complex composite behavior in polymer matrix composites (Chamis *et al.* [1]). It was extended to metal matrix composites (Chamis and Hopkins [2]) and continued to be evolving during the National Aerospace Plane and the High Speed Research Programs (Chamis *et al.* [3]). The result of all this research is the development of the MFIM to represent complex material point behavior by a single equation (Tong *et al.* [4], Boyce and Chamis [5]). The development of this equation starts with the premise that, if we are to quantify the range of factors affecting material point properties, we need a description of point behavior (Minnetyan [6], Chamis and Minnetyan [7]). In this context, it is reasonable to consider that behavior constitutes an n-dimensional space (Point Behavior Space (PBS)) where each point on that surface represents a specific aspect of complex behavior. It is further reasonable to assume that PBS can be described by an assumed interpolation function. One convenient interpolation function is a polynomial of product form because mutual interactions among different factors can be represented by the overall product, and includes those cross products which are present in common algebraic polynomials.

2 Multi-factor interaction model

In this investigation, PBS is assumed to be described by the model shown in the following equation:

$$\frac{P}{P_0} = \left[1 - \frac{x_1}{x_{1f}} \right]^{ex1} \left[1 - \frac{x_2}{x_{2f}} \right]^{ex2} \left[1 - \frac{x_3}{x_{3f}} \right]^{ex3} \dots \left[1 - \frac{x_n}{x_{nf}} \right]^{exn} \quad (1)$$

where $\frac{P}{P_0}$ is the ratio of predicted effected property to some arbitrary original

Property P_0 ; $\frac{x_i}{x_{if}}$ is the ratio factor (design variable that is known to influence

the initial property) to some arbitrary final condition; $ex1$ is an exponent which can be set to some default value (say 0.5), and n is the total number of factors. The factor final condition x_f has to be set to a value that is a bit larger than the maximum value of the selected factor (i.e. $x_f > x_i$). Note as well that the factors are normalized so that the model can represent anything that a user wants it to represent. Note also that the exponent is different for each factor. The exponents are selected so that the model represents some data. The only restriction is that the exponents must satisfy the initial and final conditions for each factor. The



final condition can be an intermediate point in cases where the surface may require it. Illustrative examples are presented in the paper that shows correlation with measured data and different applications.

In this investigation, PBS is assumed to be described by the MFIM shown in the following equation:

$$\frac{W}{W_0} = \left[1 - \frac{VD}{VD_f} \right]^{-0.282} \left[1 - \frac{VH}{VH_f} \right]^{-0.131} \left[1 - \frac{FH}{FH_f} \right]^{-1.189} \tag{2}$$

Table 1: Probabilistic results compared with test data from cryo ingestion tests.

Void diameter VD, in.		Void depth VH, in.		Foam over void FH, in.		Test divot weight, lb	MFIM divot weight, lb	Actual difference, (Test- MFIM), lb
MFIM	Test	MFIM	Test	MFIM	Test			
1.1249	1.1250	0.5000	0.5000	0.5000	0.5000	0.0019	0.0059	-0.0040
1.6248	1.6250	0.5000	0.5000	0.5000	0.5000	0.0034	0.0073	-0.0039
0.8749	0.8750	0.2500	0.2500	0.7499	0.7500	0.0039	0.0052	-0.0013
1.1249	1.1250	0.5000	0.5000	0.9999	1.0000	0.0081	0.0061	0.0020
1.3749	1.3750	0.7499	0.7500	0.7499	0.7500	0.0051	0.0072	-0.0021
1.8748	1.8750	0.7499	0.7500	0.7499	0.7500	0.0055	0.0099	-0.0044
0.8749	0.8750	0.2500	0.2500	1.2499	1.2500	0.0072	0.0054	0.0018
2.1229	2.1250	0.1250	0.1250	2.4998	2.5000	0.0810	0.0833	-0.0023
2.1235	2.1250	0.6249	0.6250	1.9998	2.0000	0.0471	0.0488	-0.0017
2.1191	2.1250	1.1249	1.1250	1.4999	1.5000	0.0272	0.0330	-0.0058
1.8748	1.8750	1.6450	1.7500	1.2499	1.2500	0.0172	0.0271	-0.0099
1.3749	1.3750	1.6450	1.7500	1.2499	1.2500	0.0221	0.0196	0.0025
1.1249	1.1250	1.4999	1.5000	1.4999	1.5000	0.0182	0.0127	0.0055
1.1249	1.1250	0.1000	0.1000	2.0998	2.1000	0.0240	0.0220	0.0020
1.3749	1.3750	0.1000	0.1000	2.0998	2.1000	0.0301	0.0280	0.0021

In this solution, the exact ratio for each factor as provided in the test has been used in the MFIM model. The final condition for each factor was calculated as 120% of the maximum value that was given in the test data. The reference weight W_0 was set to 0.0060. The results from the MFIM simulation are presented in table 1. As shown in the table, the maximum absolute difference between the test and MFIM prediction is 0.0099 lb and the minimum absolute difference is 0.0013. The divot weight results obtained from the MFIM simulation are compared to the test data in figure 1 for the void diameter and for the void height in figure 2. The use of MFIM replicated the test with reasonable accuracy. The values used in this part of the probabilistic evaluation are given in table 2. The probabilistic vectors for design 1/10,000 and 9999/10,000 are given in table 3. The cumulative distribution function of the divot weight is shown in figure 3. The corresponding probability density function is shown in figure 4.

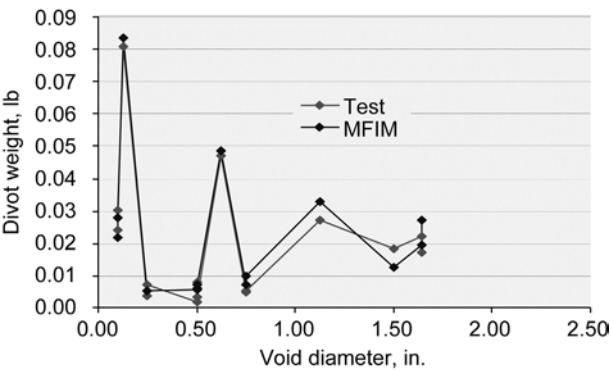


Figure 1: MFIM divot weight as a function of void diameter. (Cylindrical voids—cryo ingestion test).

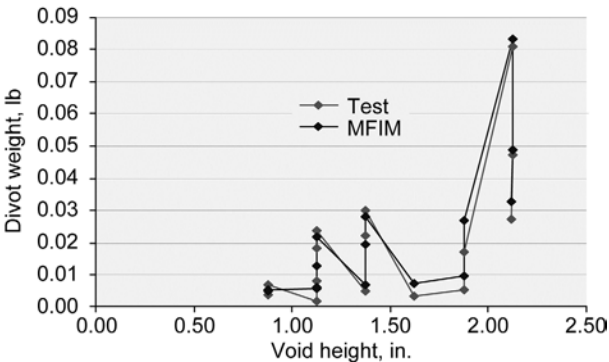


Figure 2: Probabilistic MFIM evaluation of divot weight (cylindrical voids—void ingestion test).

Table 2: Variable values used in the probabilistic evaluation.

Primitive variable	Mean	Coefficient of variation	Distribution type
Void diameter VD, in.	1.1250	5%	Normal
Void height VH, in.	0.5000	5%	Normal
Foam height over void FH, in.	1.0000	5%	Normal

The respective probabilistic sensitivities are shown in figure 5. It can be seen in the summary of these results (tables and figures) that the probabilistic evaluation provides the most complete information.

The results presented in table 1 require additional discussion on how the MFIM results were obtained. Each line requires an optimization simulation as follows:

Find the values of the exponents and the corresponding vectors so that the predicted weight is close to the test weight.



Table 3: Probable design vectors at 1/10,000 and 9999/10,000 probabilities probabilistic MFIM evaluation of divot weight (cylindrical voids-cryo ingestion test).

Primitive variable	Starting vector	0.0001 Probability	0.9999 Probability
Void diameter VD, in.	1.1250	0.9477	1.3152
Void height VH, in.	0.5000	0.4543	0.5357
Foam height over void FH, in.	1.0000	0.9620	1.0288

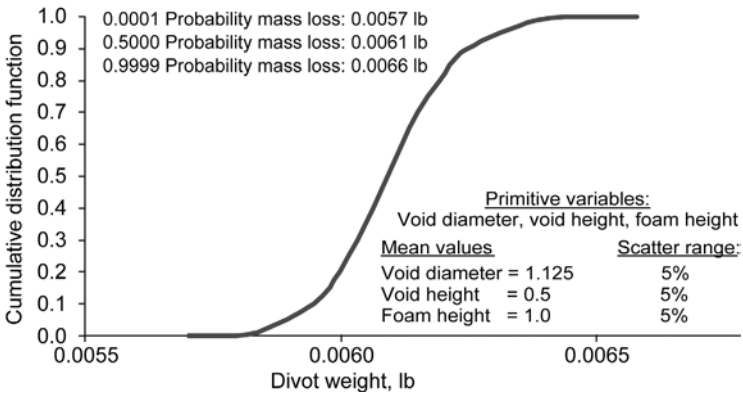


Figure 3: Preliminary MFIM probabilistic cumulative distribution function of divot weight for the cryo ingestion test (cylindrical voids).

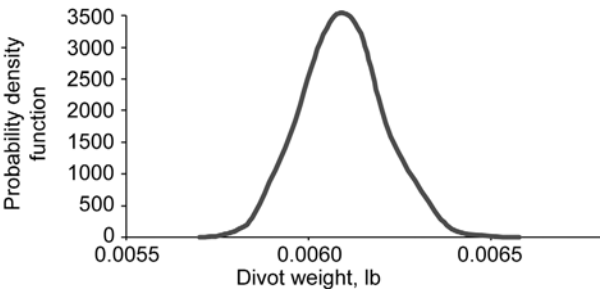


Figure 4: Preliminary MFIM probability density function of divot weight for the cryo ingestion test (cylindrical voids).

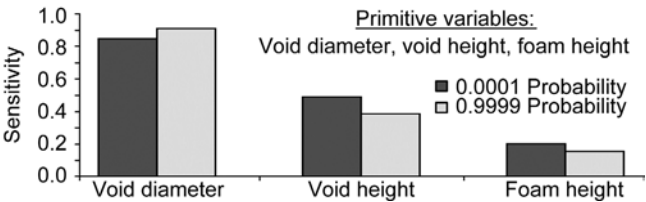


Figure 5: Preliminary MFIM probabilistic sensitivities of divot weight for the cryo ingestion test (cylindrical voids).

Optimize $e_{x1}, \dots, e_{xn} \ni W_{\text{predicted}} \approx W_{\text{test}}$ and all vectors are constrained to approximate their test values. The optimization was run as many times as there are rows in table 1. Then the different exponents were fitted by a least squares algorithm to obtain the exponent values listed in eqn (2).

The probabilistic results are interesting. The cumulative distribution function shows the typical s-curve shape with a divot weight and almost a bell curve for the probability density function, figure 3. From the cumulative distribution function it can be seen that the divot weight is about 0.0057 lb. for a probability, figure 4, of 1/1000 and 0.0066 lb. for a probability of 9999/10,000. The probability density function reads about 0.0057 to about 0.0066.

The probability sensitivities factors are plotted in figure 5 as was already mentioned. It can be seen in this figure that the order is: void diameter, void height, and foam height above the void. The magnitudes are about 0.8, 0.5, 0.2, respectively for probability level of 0.0001.

3 Application of MFIM to predict foam divot in PAL ramp of the external tank

One advantage of MFIM is that can be an effective tool where little or no information exist about a particular process or behavior. The question that would arise at this stage is what type of foam divot weight one would expect if the two variables model was applied to component specific natural voids of the External Tank (ET). The tank was dissected to determine the component specific voids in the foam. As a reminder, the foam used in the thermal protection system of the external tank is based on the application process that was in place prior to the Columbia shuttle accident. To demonstrate the effectiveness of MFIM, the reduced model shown in eqn (3) was put to use to hypothetically estimate foam divot weight based on existing voids in the PAL Ramp region of the ET. The voids from dissecting the PAL Ramp of the ET were grouped as cylindrical and slot type voids. The MFIM model of eqn (3) will address only the cylindrical voids.

$$\frac{W}{W_0} = \left[1 - \frac{VD}{VD_f} \right]^{-0.032} \left[1 - \frac{VH}{VH_f} \right]^{-0.091} \quad (3)$$

The exponents in the MFIM model were evaluated to be of (−0.032 and −0.091) based on the simulation of divot in the thermal vacuum test that was discussed earlier. The assumption here is that only two factors are present. Note that the maximum void diameter was around 0.9 in. and the maximum void height was around 0.3 in. The final condition VD_f and VH_f are the largest dissected void diameter and void height found in the PAL Ramp of the ET. The preliminary calculations are summarized in table 4. The void diameter effect on the divot weight is shown in figure 6. The void height (void depth) effect on the divot weight is depicted in figure 7. MFIM, unlike any other computational model, MFIM is capable of simulating very complex behavior of functional

responses. That is evident in the plots presented in figures 6 and 7, where the response (divot weight) took on many fluctuating trends. The analysis presented is hypothetical. The MFIM calculated divot weight requires a reference value W_0 where it can be selected, for example, as a mean value of part specific historical divot weights. In this case, it was assigned a mean value of 0.0276 lb.

Table 4: Application of MFIM to the preliminary prediction of divot weight in the PAL ramp of the external tank (cylindrical voids).

Void diameter VD, in.	Void height VH, in.	MFIM-divot weight $W = (W_0 = 0.0276 \text{ lb})$
0.2500	0.0500	0.0284
0.28	0.1	0.0290
0.3	0.2	0.0309
0.3	0.03	0.0282
0.3	0.1	0.0290
0.35	0.05	0.0285
0.35	0.15	0.0299
0.35	0.05	0.0285
0.4	0.05	0.0286
0.4	0.1	0.0292
0.4	0.02	0.0283
0.4	0.1	0.0292
0.5	0.1	0.0294
0.6	0.29997	0.0659
0.7	0.1	0.0300
0.7	0.29997	0.0667
0.89991	0.15	0.0394

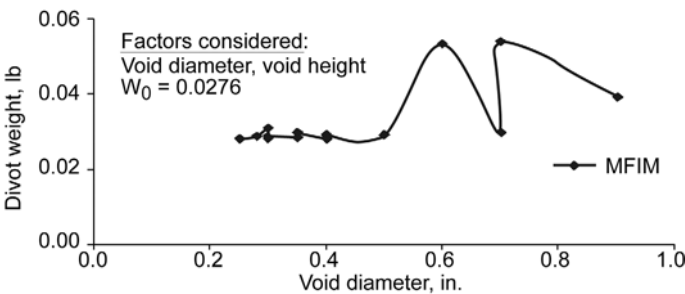


Figure 6: Preliminary MFIM prediction of divot weight with void diameter for the PAL Ramp of ET (cylindrical voids).

With the completion of the task of estimating the deterministic divot weight, it would be important to evaluate the probabilistic distribution and assess the influence of the foam void physical dimensions on the divot weight. The probabilistic evaluation of the divot weight for the PAL Ramp of the ET (assuming effects of thermal vacuum test) is described herein. As in the case of the deterministic model, the probabilistic MFIM model consists of the same two factors: void diameter and void height. The mean values for the void diameter and void height are, respectively, 0.434 and 0.112. The standard deviations for the void diameter and void height are 0.11 and 0.03 in. The probabilistic



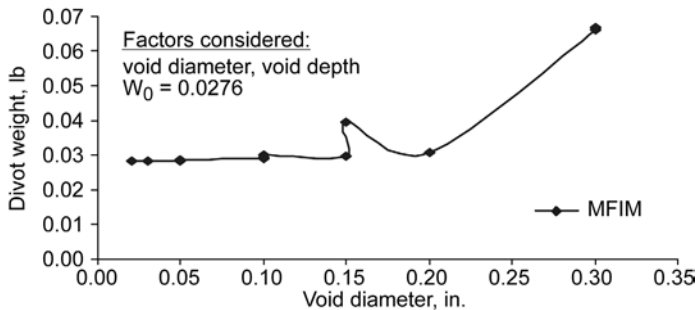


Figure 7: Preliminary MFIM prediction of divot weight with void diameter for the PAL Ramp of ET (cylindrical voids).

distribution type for the two independent variables, void diameter and void height, is assumed to be Lognormal for computational convenience.

The cumulative distribution function for the divot weight is shown in figure 8. The scatter in the divot weight is estimated to be around 0.007 lb. Based on the assumed uncertainties the divot weight is 0.0289 lb at a cumulative probability of 1/10,000 while it is 0.0296 lb at a cumulative probability of 9999/10,000. The cumulative distribution function presented in figure 8 indicates that the majority of the divots would have values close to the mean. Very few divots would have weights under 0.023 lb and above 0.0298 lb. The Probability Density Function (PDF) of the divot weight is presented in figure 9. The PDF analysis indicates that a scatter of 7 standard deviations can be achieved for the PAL Ramp anticipated divot weight. The values of the void diameter and void height at the 1/10,000 and 9999/10,000 probabilities are tabulated in the insert in figure 8.

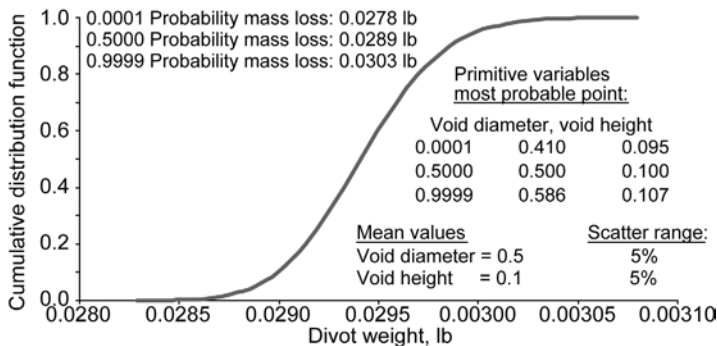


Figure 8: Preliminary MFIM probabilistic cumulative distribution function of divot weight for the PAL Ramp of ET (cylindrical voids).

An important byproduct of the probabilistic evaluation is the probabilistic sensitivities. Those are shown in figure 10. The sensitivity analysis indicates that the void diameter dominates. The void height has about 1/4 of the significance in the divot weight. Unlike traditional statistical analysis, the probabilistic analysis



can yield the design vectors that would produce a specific divot weight and also can result in calculating the design vectors that would produce near zero divot weight. Additionally, the sensitivity analysis can set the stage for eliminating from the test matrix the variables that have minimum or no effect on the divot weight. That could cut the cost and time of running additional tests using variables that would not contribute to the divot or expulsion of foam. The major conclusion from predicting computationally of divot weight is that the MFIM can be used effectively.

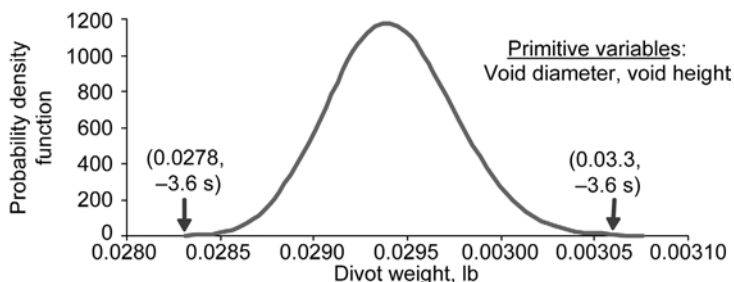


Figure 9: Preliminary MFIM probability density function of divot weight for the PAL Ramp ET (cylindrical voids).

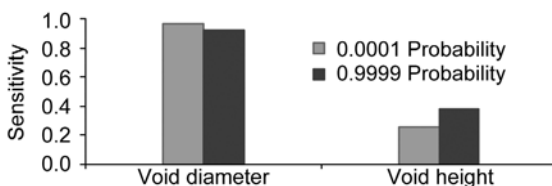


Figure 10: Preliminary MFIM probabilistic sensitivities of divot weight for the PAL Ramp of ET (cylindrical voids).

4 MFIM with seven factors

We now describe the effectiveness of the MFIM as applied to seven factors. Table 5 summarizes the deterministic results with the factors shown in the equation at the bottom of the table. It is noted in this table that the comparison is given on all the factors where the computed result is compared with the test result on the same line. The weight is compared in the last two columns of the table. To evaluate the probability the factors are normalized in shown in table 6. The probabilistic values of these factors are shown in table 7 for two probabilities 0.0001 and 0.9999. These values were obtained by asking the fast probability integrator to calculate the factors in the two probabilities. If one of the vectors was very much smaller or very much larger, then it would have been proof that these low and high probabilities were not possible and changes in the probabilities would have been required. As can be verified by visual inspection, the low and high probability values are reasonable and the probabilistic evaluation is appropriate.



Table 5: Foam mass loss as predicted by multifactor interaction model (MFIM*). [Simulating mass loss in thermal vacuum test (cylindrical voids).]

Void diameter, VD/VD_f		Void depth, VL/VL_f		Foam thickness, FT/FT_f		Foam height, FH/FH_f		Foam surface Temperature, FST/FST_f		Pressure inside void, PR/PR_f		Time to fail, t/t_f		Mass loss, lb, M	
MFIM	Test	MFIM	Test	MFIM	Test	MFIM	Test	MFIM	Test	MFIM	Test	MFIM	Test	MFIM	Test
0.1948	0.202	0.2085	0.208	0.4284	0.156	0.816	0.104	0.2664	0.237	0.5996	0.667	0.756	0.386	0.00040	0.00044
.1272	.101	.22	.208	.4577	.156	.821	.104	.2693	.455	.5625	.556	.825	.495	.00021	.00022
.198	.202	.3889	.417	.6639	.260	.833	.104	.4347	.222	.5595	.611	.636	.352	.00040	.00044
.1986	.202	.2106	.208	.6206	.208	.77	.208	.5107	.707	.5646	.667	.604	.583	.00132	.00132
.101	.101	.2088	.208	.8295	.208	.235	.208	.2633	.833	.5646	.667	.808	.833	.00041	.00044
.199	.202	.3937	.417	.6218	.313	.766	.208	.5088	.671	.5633	.611	.606	.569	.00151	.00154
.1014	.101	.416	.417	.7378	.313	.673	.208	.268	.833	.5891	.833	.72	.732	.00041	.00044
.6492	.631	.8226	.833	.35	.833	.55	.833	.6401	.533	.5555	.686	.55	.522	.10249	.10318
.8237	.833	.8237	.833	.3508	.833	.553	.833	.6425	.284	.5555	.639	.552	.434	.14397	.14506
Final condition is set to 120 percent of largest primitive variable															
Mass loss at reference condition $M_0 = 0.038$ lb															

*MFIM model:

$$\frac{M}{M_0} = \left[1 - \frac{VD}{VD_f}\right]^{-0.5} \left[1 - \frac{VH}{VH_f}\right]^{-0.5} \left[1 - \frac{FT}{FT_f}\right]^2 \left[1 - \frac{FH}{FH_f}\right]^2 \left[1 - \frac{FST}{FST_f}\right]^{-2} \left[1 - \frac{PR}{PR_f}\right]^{-1.5} \left[1 - \frac{t}{t_f}\right]^{-1.5}$$

Table 6: Probabilistic MFIM Modeling of Foam Mass Loss. [Thermal vacuum test cylindrical voids; Mean mass loss: 0.00151 lb.]

Primitive variable	Normalized mean	Actual mean	Coefficient of variation, percent	Distribution type
Void diameter, VD , in.	0.199	0.99	5	Normal
Void depth, VH , in.	.394	0.94	5	Normal
Foam thickness, FT , in.	.622	2.98	5	Normal
Foam height over void, FH , in.	.766	1.84	5	Normal
Foam surface temperature, FST , °F	.509	393.81	5	Normal
Pressure inside void, PR , psi	.563	10.14	5	Normal
Time to fail, t , sec	.606	89.45	5	Normal

Table 7: Primitive variables design vectors at 0.0001 and 0.9999 probabilities.

Primitive variable	Starting vector	0.0001 probability	0.9999 probability
Void diameter, VD , in.	0.985	0.984	0.99
Void depth, VH , in.	.94	.941	.95
Foam thickness, FT , in.	2.98	3.94	2.25
Foam height over void, FH , in.	1.84	1.95	1.68
Foam surface temperature, FST , °F	393.81	384.62	416.67
Pressure inside void, PR , psi	10.14	9.92	10.69
Time to fail, t , sec	89.45	91.93	84.44



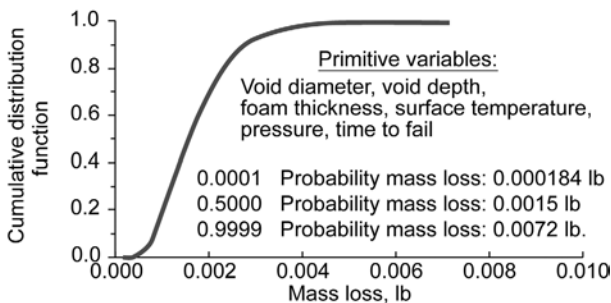


Figure 11: Probabilistic MFIM foam mass loss thermal vacuum test (cylindrical voids).

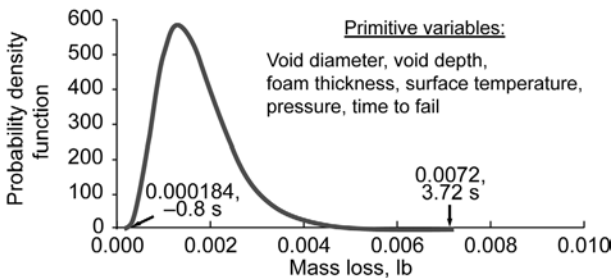


Figure 12: Probability density function with MFIM mass loss thermal vacuum test (cylindrical voids).

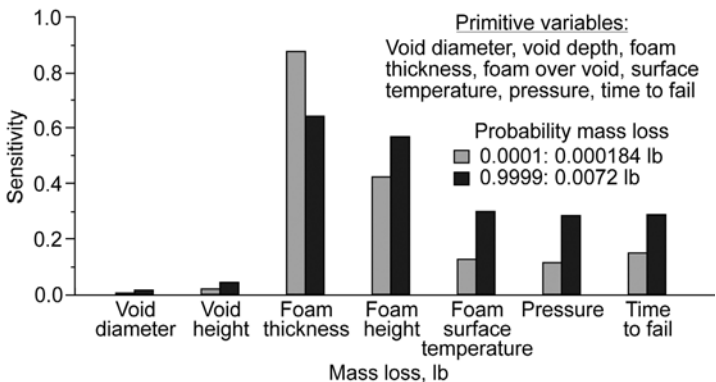


Figure 13: Probabilistic sensitivities—MFIM foam mass loss thermal vacuum test (cylindrical voids).

The CDF is plotted in figure 11. It is seen in this figure that the CDF has somewhat of an exponential distribution. This kind of a distribution is practical by the use of the fast probability algorithm. In the figure inserts the names of the factors are listed as well as three values of the CDF at probability 0.0001, 0.50, and 0.9999. As can be deduced from the respective weights in this plot, there is



substantial weight difference. The corresponding PDF is plotted in figure 12. Observe that the low probability value is given with respect to a standard deviation. The high probability is also given with its respective value and standard deviation. This looks like a gamma type distribution input function of the combined factors input.

The respective sensitivity factors are summarized in figure 13. It can be seen in this figure that dominant factors in a decreasing order are: foam thickness, foam height, while foam surface temperature, void internal pressure and time to fail are about of equal magnitude. The results of this last example illustrate the effectiveness of the multifactor interaction model; and even more importantly, the effectiveness of the fast probability algorithm that made the results practical with respect to computational time.

5 Conclusions

The Multi-Factor Interaction Model (MFIM) is a very effective way to represent factors which influence material behavior. In this investigation, MFIM was applied to predict the foam divot weight in the external tank during its ascent cycle. Factors with two, three, and seven terms were evaluated and compared with test results that were obtained from tests of simulated conditions during the ascent of launching vehicles. The comparisons were very satisfactory considering the relative small divot weight. Results also were obtained on what values the factor needs to be in order to ascertain divot weights at very low and very high probabilities. The exponents of the factors were obtained by a local optimization. The overall conclusion is that the MFIM in conjunction with the fast probability integration algorithm is very effective and practical for evaluating the MFIM and matching experimental data.

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Section 2

Mechanical characterisation and testing

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Evaluation of dynamic connection designs for road safety barriers

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Abstract

Bolted road safety barrier connections utilise slotted holes that are perpendicular to the direction of the safety barrier beam. Typically, eight M16 bolts are needed in a lap joint configuration to make each connection. The design of the lap joint connection has remained unchanged for several years.

Previous research work has successfully determined the performance characteristics of the bolted connections at quasi-static velocities. Performance improvements at quasi-static velocities have been identified. Therefore, representative test coupons using different design configurations to that of the original test coupon were examined at dynamic velocities.

The laboratory test results show that improvements can be made if the current lap joint design were to be changed. Performance improvements such as the amount of energy that the connection was able to absorb and the maximum connection system force were observed.

Keywords: safety barrier, crash performance, fastener, connection, dynamic performance.

1 Introduction

The performance of road safety barrier connections is not directly linked to advances in vehicle technology. The UK government has recently released a specification for road restraint systems that has resulted in the transfer of design responsibility to industrial safety barrier manufacturers (BSI [1]).

Whilst there has been a great incentive to improve the prospect of occupant survivability through improvements to the vehicle design (Birch *et al* [2]), it would seem safety barrier designs have remained stagnant in the UK for several decades. The vehicle fleet found on the road has evolved, vehicles in use today



cover a wide range of sizes, more than ever before, and there is a need to use different materials for certain parts of roadside hardware (Tabei *et al* [3]).

The use of bolted joints to connect structural members together and to transfer in-plane forces between them has been widely employed in civil, mechanical and aeronautic structures (Su and Siu [4]). Bolted connections are extensively used in roadside safety barriers and their characteristics can directly affect the performance of the whole roadside barrier system. Corrugated beam safety barriers use double row bolted lap joints to make the connection between beam lengths. When an errant vehicle impacts the safety barrier system, each connection joint moves differently in relation to the distance from the impact point. When redirecting the vehicle away from the impact area, the safety barrier absorbs a significant amount of energy. Much of the impact energy is transmitted along the length of the barrier system. In general, bolted joints are mechanical connections between two components that will slip and allow for movement of one of the components in relation to the other along a specified direction (Reid and Hiser [5]). However in the case of corrugated beam safety barrier connections the slot is perpendicular to the barrier direction to aid with the construction of the barrier system. Tabei and Wu [3] report that in the experimental testing of the safety barrier system, it is observed that some bolted connections are subjected to very high forces that cause the bolts to shear through the corrugated beam. This could be compared to plane out shear reported by Kulak *et al.* [6]. Yet the joint does move prior to deformation of the connecting members upon impact of an errant vehicle, and this occurs because the slotted hole is significantly larger than the bolt diameter as well as due to plastic deformation of the actual safety barrier material (Bayton *et al.* [7]). Failure in bolted connections are similar to an “unbuttoning” effect that occurs after the connection has slipped i.e. moved and taken up all of its manufacturing tolerances (Oberg *et al.* [8]). Other failure modes include crushing of plate or bolt shank, tearing of the plate to the margin and tearing between fasteners (Oberg *et al.* [8]).

Dynamic tensile testing at different velocities was undertaken. Representative connection coupons were used to understand the energy absorbing properties of different connection designs when compared to the current four bolt connection design.

This study presents some initial results as to the increased performance that could be gained from subtle changes in design for the production of road safety barrier connections.

2 Experimental

The material used in the manufacture of the safety barrier beams is a structural steel known as S275. The composition of this steel grade is given in Table 1 (BSI [9]).

The S275 grade used for the test programme has a minimum yield strength of 275MPa in accordance to BS EN 10025-1-2004 Hot rolled products for structural steels (BSI [9]).



Table 1: Chemical composition of S275 steel grade (BSI [9]).

Steel Grade	C Max.	Mn Max.	P Max.	S Max.	Si Max	N1,2 Max	Nb Min- Max	V Min- Max
S275	0.25	1.60	0.05	0.05	0.50	-	-	-
Notes: 1. It is permissible to exceed the specified values provided that for each increase of 0.0015 nitrogen the phosphorous maximum content will be reduced by 0.005%; the nitrogen content of the ladle analysis, however, shall not be more than 0.012%. 2. The maximum value for nitrogen does not apply of the chemical composition shows a minimum total aluminium content of 0.020% or if sufficient other nitrogen-binding elements are present. The nitrogen-binding elements shall be mentioned in the inspection document. 3. Values are in weight percentages.								

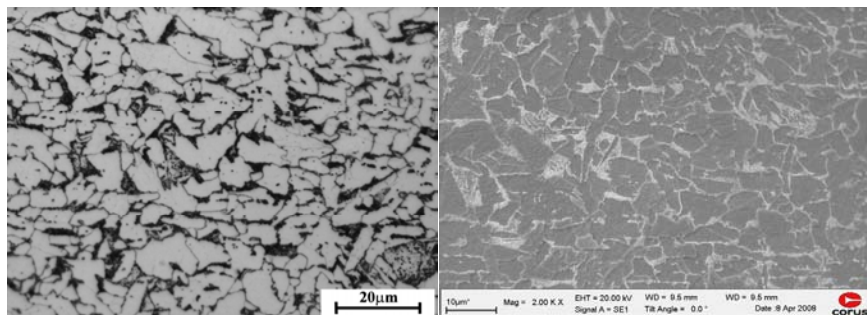


Figure 1: Light optical and SEM micrographs of CMn S275 steel grade.

With the equipment that was available a dynamic velocity of 2.5ms^{-1} was chosen in order to conduct tests with a certain amount of focus on a typical reality based strain rate. Additionally Dieter [10] states that a strain rate of 10^{-1} to 10^2 s^{-1} should be used for dynamic tension or compression testing.

All of the equipment used in the subsequent tests was supplied by Corus RD&T. In particular the following instruments were employed.

- MAND high rate tensile machine capable of a velocity of 2.5ms^{-1} .
- Resistance strain gauges with a measuring area of $5\text{mm} \times 1.5\text{mm}$.
- Strain gauges used in half bridge configuration with data logging equipment.
- Calibrated torque wrench.
- High speed video camera.

To ensure that there was as increased test accuracy, the quasi-static tests conducted previously also acted as a calibration exercise for the high rate testing. This is because the high rate tensile machine could not be fitted with a load cell to record the forces incurred during the test. The results from the calibration tests provided a basis on which to accurately calculate the Maximum Connection System Force (MCSF) for each connection.

Each bolt was tightened using an elevated torque setting of 100Nm to give better preload accuracy and allow for the effect of friction between the nut and bolt threads as well as the washer faces [8,11,12].

The connection configuration was assembled for test as shown in Figure 2. This was the basic configuration. Other designs were based on variations of this design. A matrix of the tested design configurations is shown in Table 2.

Connections with the bolt shank locked out against the edge of the slots were tested. In effect, optimum connections were tested without any undesired features such as loose bolts or connections that were able to move prior to plastic deformation of the connection material.

The containment section of the table refers to the depth of material between the edge of the first slot and the edge of the test coupon. Normally this dimension is 21.5mm however this was increased for the High Containment (HC) coupon to 31.5mm. Other design variables included the addition of an extra bolt in the centre of the existing four bolt coupon. Also the slots were removed and clearance holes were used. The spacing (216mm) between two bolt groups was reduced to 108mm. Therefore this represented four alternatives to the current connection design.

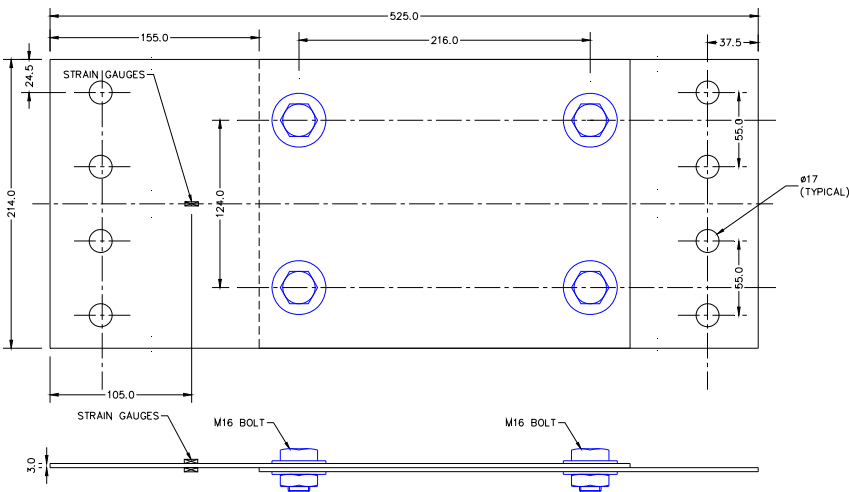


Figure 2: Four bolt connection test coupon.

Table 2: Connection configuration test matrix.

Testing Matrix	Machine Cross Head Speed	Variables		
		Containment	Gauge	Material
Coupon	2500mm/sec			
Std. Four Bolt	✓	NC	3.00	S275
Std. Four Bolt	✓	HC	3.00	S275
Five Bolt	✓	NC	3.00	S275
Four Bolt Reduced	✓	NC	3.00	S275
Four Bolt (Holes)	✓	NC	3.00	S275



3 Results

The fifteen tests that were conducted are summarised in Table 3 for the dynamic tensile testing. The Maximum Connection System Force (MCSF) has been presented along with the absorbed energy. Two failure modes were observed in the test coupons. Oberg *et al.* [8] and Nethercott [13] observed several typical failure modes for mechanically fastened connections and the failure modes of these test coupons can be defined as either plane out shear or tearing of the slot. Both failure modes occur after rotation of the bolts and local out of plane buckling of the connection members (Birch and Alves [2]). The connections could be defined both as shear connections and friction grip connections based on the observed failure mode path (Nethercott [13]). The observed failure modes are shown in Figure 3.

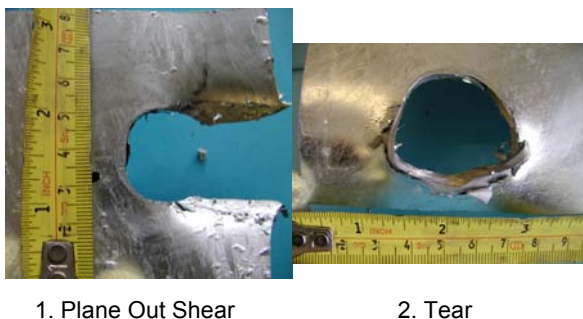


Table 3: Observed connection failure modes.

Safety barrier connections are dynamic connections. Consequently, it is important not only to record the load versus displacement of each connection test but to calculate the amount of energy that the connection can absorb. Using the trapezoidal rule to calculate the area under the graph plot curve the amount of energy absorbed in Joules is recorded (Cox [14]).

The Normal Containment (NC) coupons surprisingly recorded better results than the High Containment (HC) coupons. The lowest results were from the test coupon where the two bolt groups were brought closer together by reducing the spacing to 108mm. The amount of energy that the reduced spacing bolt group could absorb was also reduced.

The graph plots shown in Figure 5 shows the Maximum Connection System Force (MCSF) along with the amount of energy that each connection design was able to absorb. The error bars show the standard deviation of the mean.

The linear displacement is greater for the high containment coupon. This is because of the greater slot to margin dimension of 31.5mm instead of the standard normal containment coupons that have a slot to margin dimension of 21.5mm.

Table 4: Connection dynamic results.

Connection Type	Test Coupon Number	Maximum Connection System Force (kN)	Absorbed Energy (J)	Failure Mode (T=Tear POS=Plane Out Shear)			
4 Bolt NC	1	239.28	1609	POS	POS	POS	POS
4 Bolt NC	2	237.07	1572	T	POS	POS	T
4 Bolt NC	3	241.5	1694	POS	POS	POS	POS
Mean		239.28	1625				
4 Bolt HC	1	223.57	1482	T	T	T	T
4 Bolt HC	2	211.48	1709	T	T	T	T
4 Bolt HC	3	201.42	1194	T	T	T	POS
Mean		212.16	1462				
4 Bolt Reduced	1	193.56	1180	T	T	POS	POS
4 Bolt Reduced	2	143.81	incomplete	Void Test			
4 Bolt Reduced	3	194.57	1240	T	POS	T	POS
Mean		194.07	1210				
4 Bolt Holes	1	231.02	1585	POS	POS	POS	POS
4 Bolt Holes	2	237.67	1382	POS	POS	POS	POS
4 Bolt Holes	3	247.74	1370	POS	POS	POS	POS
Mean		238.81	1446				
5 Bolt	1	224.78	1596	POS	POS	POS	POS
5 Bolt	2	233.84	1523	POS	POS	POS	POS
5 Bolt	3	250.96	1923	POS	POS	POS	T
Mean		236.53	1681				

4 Discussion

The failure modes for each connection are similar to those experienced within structural steel work members. Kulak *et al.* [6] conducted work into failure modes of structural connections with respect to load as a function of displacement. There were two distinct features of the load displacement curve, one being the transfer of the load by friction and the other by bearing of the bolts onto the member’s cross section. In the graph plots shown in Figure 4 in particular, the phenomenon can be clearly seen. The transition between the two joint characteristics occurs in all of the test coupon types around the load of 50kN and at a linear displacement of 2.5mm. This is where the graph plots oscillate slightly. Steel shear connections are designed to transfer the load from one member to another (Astaneh-Asl [15]). Research by Ray *et al* [16] showed the same failure modes for a corrugated safety barrier beam tensile tested at quasi-static velocities



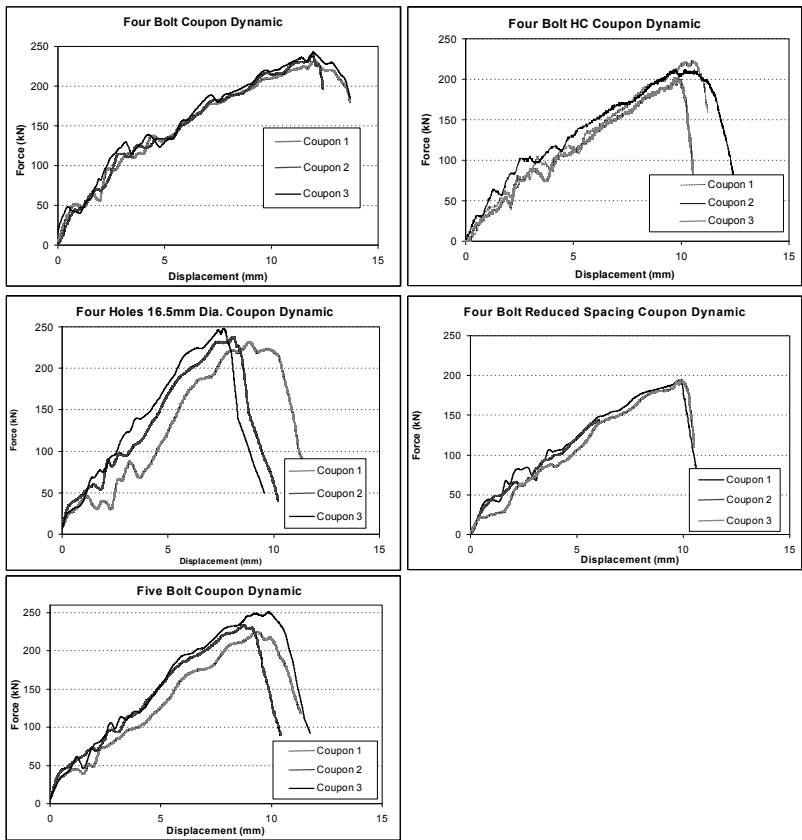


Figure 3: Dynamic force vs. displacement for connection test coupons.

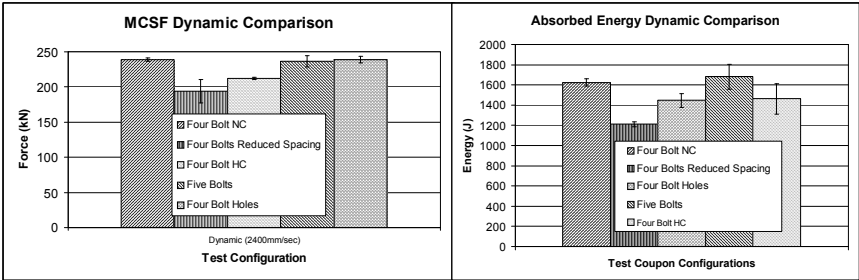


Figure 4: Connection performance comparisons.

Principally the five bolt connection returns the highest absorbed energy. However it is similar in MCSF to the standard four bolt and four bolt holes coupon. Looking at the force/displacement graph for the five bolt connection, it can be seen that the maximum load is reached within a reduced displacement



when compared to the standard four bolt coupons. This means that there is less connection slip for a given displacement. Connection slip is defined as the movement in a connection when friction is overcome and the bearing of the component parts is initiated (Kulak *et al.* [6]). With this mind any slip between connecting members will affect the smooth transfer of load between members.

The test coupon that uses clearance holes ($\varnothing 16.5\text{mm}$) instead of the standard safety barrier slots ($27\text{mm} \times 29\text{mm}$) gives the best connection performance for a four connection coupon. The increased cross sectional area would account for better performance but additionally the clamping force being exerted on the connection members would also be increased. Distortion of the connecting members upon tightening of the bolts was not evident in this particular coupon. The graph plot for this specific coupon, shown in Figure 4 demonstrates that the coupon reaches its maximum load with a very small displacement. This indicates that the bolt shanks come to bear on the section members almost instantaneously.

Finally the high containment coupon does not perform well in the dynamic tests. The graph plot in Figure 4 shows how the force/displacement curve is “flattened” considerably. The failure modes of the high containment test coupons consistently show that the tear failure mode was the predominant failure path. It may be the case that this failure mode leads the connection into a sequence of failure events that result in the connection being weaker overall.

The connection with a reduced spacing between the two bolt groups did not compare well to the other connections in terms of performance in the laboratory tests. Reducing the spacing between the bolt groups led to a reduction in absorbed energy as well as MCSF. Although the failure modes were consistent with the other test coupons, the point at which the two bolt groups come to bear on the connecting plates occurs sooner and the failure mode can be initiated earlier than with the other test coupon samples

5 Conclusion

In total, eighteen test coupons have been analysed to give an indication of the benefits that could be obtained from modifying the design of the road safety barrier lap joint connection. This paper gives an indication of the properties that may increase the performance of safety barrier systems. The following conclusions can be drawn from this study.

1. The five bolt connection absorbs more energy than any four bolt design.
2. Removing the slots and adding clearance holes increases connection strength.
3. Reducing the spacing between bolt groups is detrimental to connection performance.
4. Emphasis is also on the quality of the mechanical fastener components to stop the “tear” failure mode.
5. Failure mode can affect the linear displacement prior to failure in the connection. As a result this affects the amount of energy that can be absorbed.



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Characterization of dynamic tensile and shear strength of safety bolts in light collision safety devices of a train

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Abstract

This paper introduces design strategy to develop safety bolts in light collision safety devices under dynamic tensile and shear loading conditions. The light collision safety device is an energy absorbing one for low speed collision of a train. An energy absorbing scenario in the device has several sequential stages. Tension and shear bolts are the key components which make the sequential energy absorbing scenario operated by a series of failures at the specific collapse load. Exact failure loads of tension and shear bolts at crash conditions were determined in aid of finite element analysis considering the dynamic material properties of component materials. Failure loads of tension and shear bolts designed were verified with experiments using tension and shear type jig sets at quasi-static and dynamic loading conditions. Strain gages were attached to both the parallel section of tension bolts to measure the load response acting on tension bolts and the jig set to measure the load responses acting on shear bolts. The quasi-static and dynamic experiments as well as the numerical analysis explained above predicted the load capacities of tension and shear bolts accurately for the crashworthiness design.

Keywords: tension bolt, shear bolt, light collision safety device, crash test, finite element analysis.

1 Introduction

The crashworthiness of trains is now a major concern since a crash accident of a train leads to a fatal disaster accompanying loss of human lives and properties



although the train accident is less frequently reported than car accidents [1]. In order to design a reliable Light Collision Safety Device (LCSD) satisfying the standard for the train crashworthiness to minimize passenger injuries and fatalities, a thorough systematic approach is required based on improved energy management concepts and design involving new structural arrangements of higher absorbing capacity in a controlled manner [2]. LCSD is employed as an energy absorber in low speed collision. Repairing charges can be remarkably decreased while passenger safety is also secured by absorbing most crash energy in LCSD. The energy absorbing mechanism of LCSD [5] is operated sequentially in each energy absorber by corresponding levels of load as shown in Fig. 1. The coupler is the first energy absorber whose load-carrying capacity is 1,000 kN and the second energy absorber is an expansion tube whose driving force is over 1,500 kN. The tension bolts are installed between the first and second energy absorber and make the energy absorbing mechanism to be sequential to the levels of load [3]. A single tension bolt sustains the tensile load of 375 kN respectively since four tension bolts are designed to carry the load of 1,500 kN. After the energy absorption of the expansion tube, LCSD should be detached from the train when the carrying load is over 2,000 kN after eight shear bolts are broken. A single shear bolt sustains the shear load of 250 kN respectively since eight shear bolts are designed to carry the load of 2,000 kN. The maximum load of the designed tension and shear bolts should be verified in dynamic loading conditions experimentally. The load responses are measured with strain gages attached to the parallel section of the tension bolt and the shear type jig set and calibrated by the reference load cell. Since the safety bolts designed undergo dynamic tensile and shear deformation, the dynamic material properties of the base material, SCM440H, should be provided in order to take account of crashworthiness design of both kinds of safety bolts. This paper demonstrates that the maximum load of tension and shear bolts in the quasi-static test is distinguishably different from that in the dynamic tensile and shear tests.

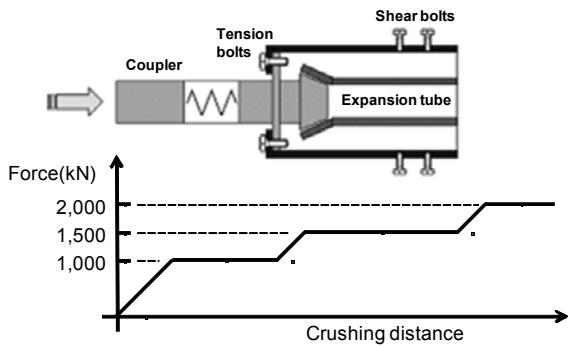


Figure 1: Energy absorbing mechanism of light collision safety devices.

2 Design of safety bolts and jig systems

2.1 Tension bolts

The tension bolt designed has the central diameter of 21 mm, the gage length of 30 mm and the total length of 190 mm as shown in Fig. 2. The material of tension bolts is SCM440H after heat treatment. The material is heated up to 850°C and held for 3 hours. After the heat treatment, the material is tempered three times at 600°C for 5 hours. Stress–strain curves of SCM440H are shown in Fig. 3, which shows lower strain rate sensitivity than that of conventional steels [6–8]. Strain gages are attached on the parallel region which is machined intentionally for load measurement. The load signal is calculated from the strain gage signal by synchronizing with the load signal from a quasi-static universal testing machine. Strain gages are located oppositely to each other in order to compensate a bending effect by constructing a half bridge circuit.

2.2 Tension type jig system

The maximum carrying load of the tension bolt designed should be investigated by impact tests since the tension bolt designed undergoes high speed deformation during train crash. For the reason, a High Speed Crash Tester is needed to perform crash tests of the tension bolts as shown in Fig. 4. The maximum speed of the High Speed Crash Tester is 20 m/sec and the mass of a carrier is 250 kg. The crash speed is adjusted to 9.5 m/sec (34.2 km/h) which is almost same as the targeting train speed. A tension type jig system shown in Fig. 5 converts a compressive loading condition to a tensile loading condition since the tension bolts experience tensile loading. The jig system consists of two parts: fixed frame; and movable frame. Fixed frame of the jig system is fixed on the wall by bolting as shown in Fig. 5 and has four main columns which sustain crash loads. The movable frame slides smoothly on the four holes bored in the fixed frame. The tension bolt specimen locates between the fixed frame and the movable frame being fastened by a spanner. Cylindrical buckles are inserted into four columns between two thick plates to sustain pre-tension. Pre-tension of the

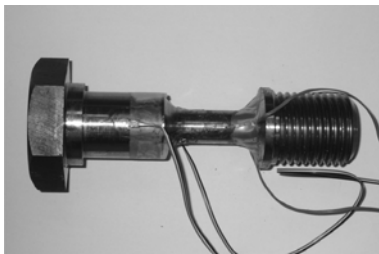


Figure 2: Designed tension bolt.

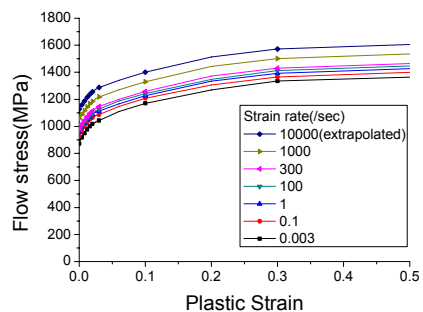


Figure 3: Strain rate dependent stress–strain curves of SCM440H.



Figure 4: High speed crash tester.

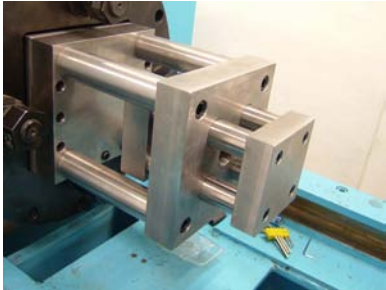


Figure 5: Tension type jig system.

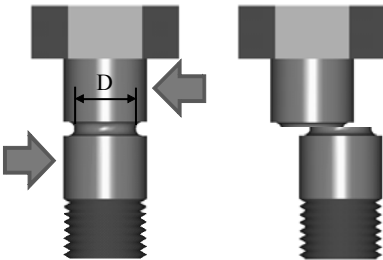


Figure 6: Deformation mechanism of a shear bolt.



Figure 7: Prepared shear bolts.

tension bolt is continuously monitored by checking the strain signal from a signal conditioning amplifier. After applying designated amount of pre-tension the main controller of the High Speed Crash Tester triggers the carrier with a speed of 9.5 /sec. The strain gages attached on the both sides of a specimen measure the load signal accurately. The deformed shapes are continuously taken with 7,000 frames/sec by a high speed camera.

2.3 Shear bolts

Basic shapes of shear bolts are commercial standard bolts except they have a narrow groove as shown in Fig. 6. The flat region right below the bolt head is longer than that of conventional bolts since shear bolts need a narrow groove where shear deformation takes place. The basic dimensions of the designed shear bolt are based on the M30 standard bolt. The outer diameter of the shear bolt is 30 mm. Two kinds of shear bolts were prepared by the size of a groove whose diameter, D , is 20 and 22 mm respectively. The gap of a groove is 4 mm for all shear bolts. The material for shear bolts is SCM440H after heat treatment which is same as the material for tension bolts. Stress-strain relations were obtained by high speed material tests up to the strain rate of 1,000/sec and estimated by modified Johnson-Cook model [4] up to the strain rate of 10,000/sec. The maximum strain rate locates at the center of a groove and is around 3,000/sec at finite element analyses. For the reason, the upper bound of strain rates in piecewise linear data was determined to be 10,000 /sec which can cover the



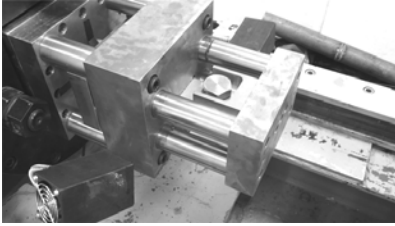


Figure 8: Shear-off jig system.

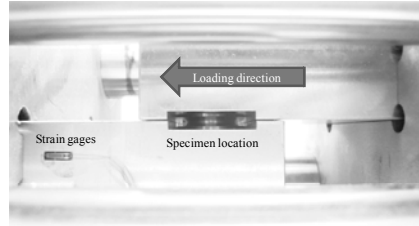


Figure 9: Shear loading mechanism.

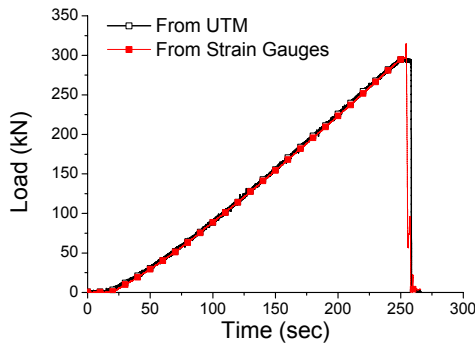


Figure 10: Strain gage output voltage versus load signal from UTM.

maximum strain rate during high speed shear deformation. Shear bolts were prepared by turning as shown in Fig. 7.

2.4 Shear-off jig system

The shear bolts are used to install LCS to the front head of a train. The shear bolt fails when the crush load exceeds the designated load of 250 kN. Design of the shear-off jig system is obviously simple for quasi-static shear-off tests, but becomes very complicated for dynamic crash shear-off tests since a crash test needs sufficient loading speed, crash energy and reliable measurement system. Therefore, the shear-off jig system should be carefully designed and verified for a corresponding crash condition. The shear-off jig system in Fig. 8 converts compressive loading to shear loading. A carrier of the crash tester impacts the end of the shear-off jig and the polyurethane pad stops the moving jig after the fracture of the shear bolt. A half bridge circuit of strain gages is devised for a load measurement since the load measurement using load cells sustaining the full jig system has a severe load ringing problem. The strain gages are attached to both sides of a lower jig which is fixed on the left side as shown in Fig. 9. Load calibration of an output signal from strain gages is performed in a quasi-static UTM (Universal Testing Machine) by comparing an output signal from strain gages with the load signal from UTM as shown in Fig. 10. Two signals are in proportion and the scale factor is obtained by dividing the load signal by the

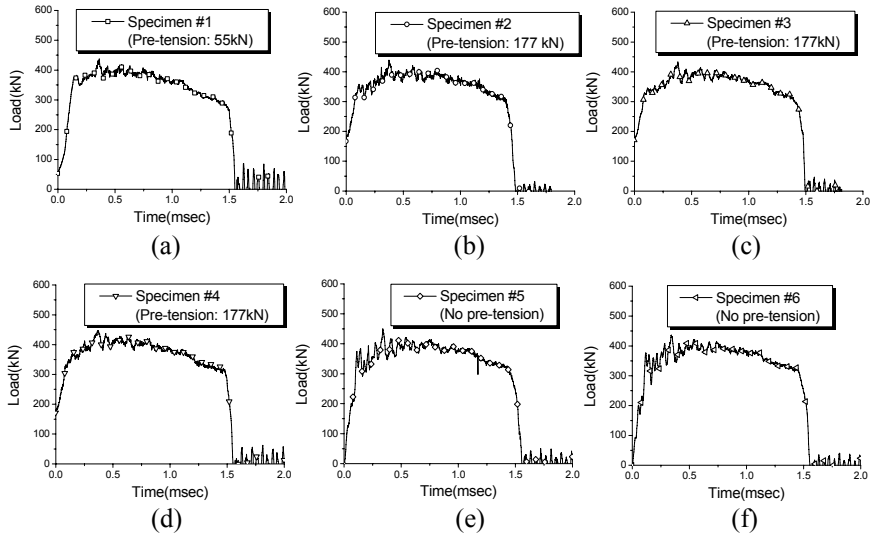


Figure 11: Load-time curves in the crash tests of tension bolts: (a) specimen #1(pre-tension: 55 kN); (b) specimen #2(pre-tension: 177 kN); (c) specimen #3(pre-tension: 177 kN); (d) specimen #4(pre-tension: 177 kN); (e) specimen #5(no pre-tension); (f) specimen #3(no pre-tension).

output signal from strain gages. The shear-off jig system can perform both quasi-static and dynamic shear-off tests using the same load measurement method.

3 Experimental and numerical results

3.1 Tension bolts

3.1.1 Experimental results

Six testing results are shown in Fig. 11 and Table 1 with respect to an applied pre-tension. Pre-tension denotes tension force applied during fastening tension bolts. The load curve of specimen #1 starts from 55 kN since the pre-tension is 55 kN in this case. Crash test results of specimens without pre-tension are shown in Fig. 11(e) and (f). The load response shows elastic region, yield point, ultimate tensile strength, necking and fracture finally. The load signal has no load oscillation but a minor noise since the strain gages attached to the tension bolt measure the load acting on the cross section of the tension bolt. Duration of the total deformation of tension bolts is 1.53 msec which is an extremely short time compared to whole energy absorption procedure of LCSD. The load at the yield point of the tension bolt is about 350 kN for all cases and the averaged maximum load is 410.4 kN as shown in Table 1. The amount of pre-tension has effects on neither maximum loads nor impact durations of the tension bolt. Total displacements of specimens are about 11 mm, that is, total elongation of 33%. Necking occurs at between 0.5 msec and 1.0 msec from sequential deformed



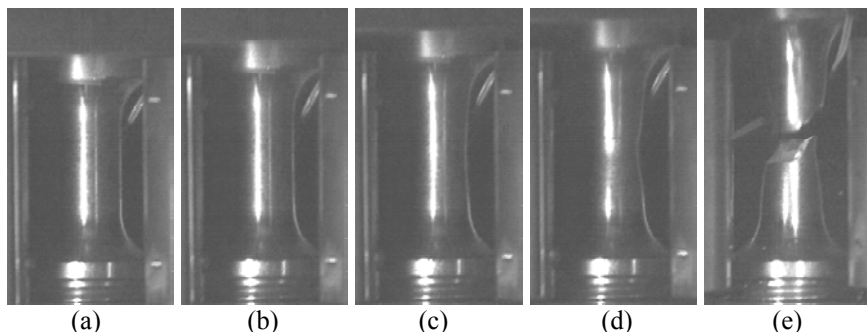


Figure 12: Deformed shapes during crash test of a tension bolt: (a) 0 msec; (b) 0.5 msec; (c) 1.0 msec; (d) 1.5 msec; (e) after fracture.

Table 1: Crash testing results of tension bolts.

Specimen number	Pre-tension (kN)	Maximum load (kN)	Duration (msec)
1	55	413.9	1.55
2	177	407.9	1.49
3	177	406.4	1.49
4	177	427.5	1.55
5	0	401.2	1.55
6	0	405.3	1.55
Average		410.4	1.53

shapes Fig. 12. The maximum load in crash tests is 9.4% higher than the originally designed maximum load of 250 kN which is in an acceptable range for application to LCSD.

3.1.2 Numerical results

Finite element analysis of the tension bolt was performed to verify crash test results. Finite element mesh system has 18,186 nodes and 16,644 brick elements as shown in Fig. 13. Finite element simulation was carried out using LS-DYNA 3D. A piecewise linear model at the different strain rates was adopted in order to consider the strain rate hardening effect as shown in Fig. 3. The right side of the tension bolt was fixed and the bolt head was impacted by a barrier which has a mass of 250 kg at a speed of 9.5 m/sec. Fig. 14 shows the load response and energy absorption of both the numerical analysis and the experiment. The load response in the numerical analysis coincides with the experimental result closely. The maximum load at the numerical analysis is 408.5 kN while the averaged maximum load at the experience was 410.4 kN. The load curve after the maximum load in the numerical simulation shows slightly higher than that in the experiment. Post necking behavior of the tension bolt is inevitably unstable and stress-strain relations are less reliable than that at the pre-necking region. The

element is deleted from the calculation when the plastic strain reaches 0.52. The energy absorption of a single tension bolt is 3,647.2 J at the experiment and 3,785.3 J at the numerical simulation which is less than 1% of absorbing energy for light collision safety devices while most of the crash energy is absorbed in the coupler and the expansion tube. The deformed shapes at each time step during the numerical simulation are shown in Fig. 15. The deformed shapes and contours of the plastic strain explain that necking occurs at the center of a gage region at about 0.5 msec and the fracture occurs at the center due to localized necking. In conclusion, the tension bolts can carry out the role of a mechanical fuse successfully regardless of the amount of pre-tension.

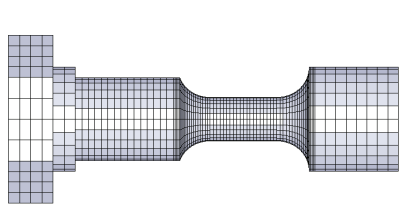


Figure 13: Finite element model of the tension bolt.

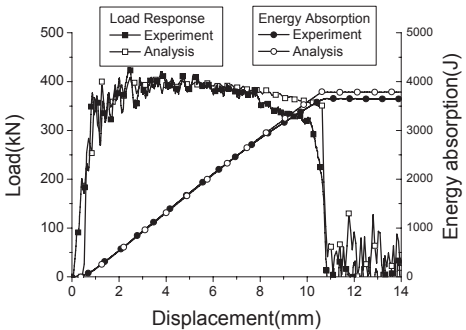


Figure 14: Comparison of load responses and energy absorption between experiment and analysis.

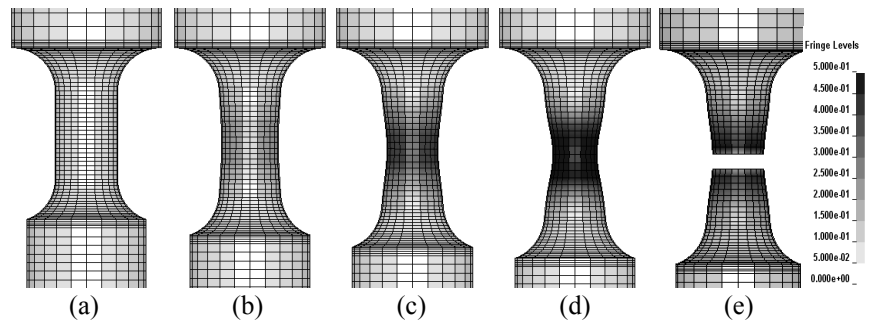


Figure 15: Deformed shapes of tension bolts in finite element analysis: (a) 0 msec; (b) 0.5 msec; (c) 1.0 msec; (d) 1.5 msec; (e) after fracture.

3.2 Shear bolts

3.2.1 Experimental results

Quasi-static shear tests are performed with a static UTM whose maximum capacity is 50 tonf. The shear-off jig system is installed upon the bed of UTM. A



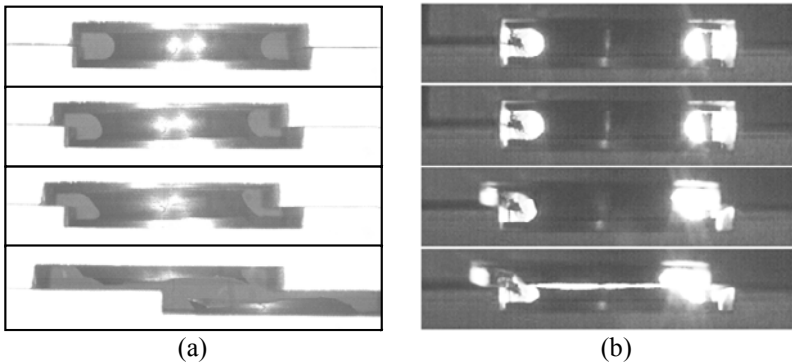


Figure 16: Deformed shapes during shear deformation: (a) quasi-static shear tests; (b) dynamic shear tests.

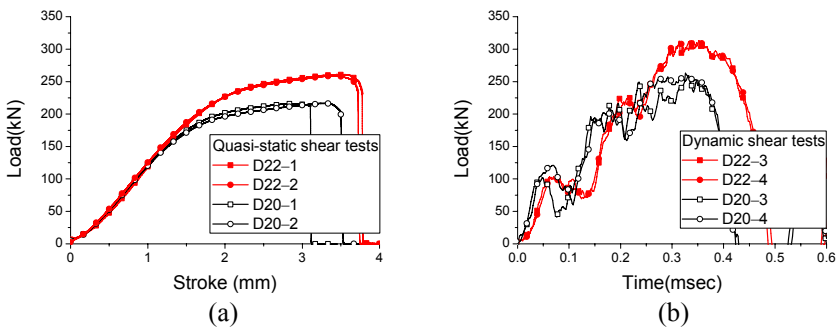


Figure 17: Load responses of the designed shear bolts: (a) quasi-static shear tests; (b) dynamic shear tests.

data acquisition board on PC captures the signals for the load and displacement from a strain conditioning amplifier and a linear displacement transducer. Sequential deformed shapes during shear deformation are shown in Fig. 16. Deformed shapes show that the specimen is slanted during shear deformation by 7° which is measured by image processing of the third picture of Fig. 16(a). The load responses during quasi-static and dynamic shear tests are shown in Fig. 17. The maximum loads of shear bolts are 259.6 kN for D22 specimens and 216.1 kN for D20 specimens. The total stroke until failure is about 3.8 mm for D22 specimens and 3.5 mm for D20 specimens. Deformed shapes after quasi-static and dynamic shear tests are shown in Fig. 18. The specimen, D20-1, shows abnormal fracture at quasi-static deformation. The abnormal fracture seems to be affected by initial defects in the original specimen. D22 shear bolts seem to satisfy targeting shear-off load while D20 shear bolts cannot satisfy targeting shear-off load in quasi-static shear tests. Dynamic shear tests are still needed to evaluate the crashworthiness of the shear bolts since the targeting shear load of 250 kN, should be evaluated in crash conditions. Dynamic shear tests were performed in the High Speed Crash Tester of a horizontal-type. The shear-off jig system is fixed on the wall horizontally. The mass of a moving carrier is 250 kg

Table 2: Maximum shear load in quasi-static and dynamic shear tests.

Test method	Min. diameter (mm)	Specimen number	Max. shear load (kN)
Quasi-static shear tests	22	D22-1	260.7
		D22-2	258.4
	20	D20-1	215.7
		D20-2	216.5
Dynamic shear tests	22	D22-3	312.1
		D22-4	313.2
	20	D20-3	259.2
		D20-4	262.9



Figure 18: Deformed specimens after quasi-static and crash tests.



Figure 19: Typical fracture surface after dynamic shear tests: (a) D22; (b) D20.

and the crash speed is 9.5 m/sec. The deformed shapes are continuously taken by a high speed camera with 7,000 frames/sec. Load responses are obtained from the strain conditioning amplifier at the sampling rate of 500 kHz as shown in Fig. 17(b). The load responses at dynamic shear tests are highly reliable after 0.2 msec since the load oscillation caused by load ringing phenomena decreases after 0.2 msec. The maximum shear-off loads in dynamic shear tests are 312.6 kN for D22 specimens and 261.1 kN for D20 specimens. Both D22 and D20 specimens show clear fracture surfaces after quasi-static and dynamic shear tests as shown in Fig. 19. Duration of dynamic shear tests is ranged from 0.43 to 0.49 msec and the total stroke is ranged from 3.9 mm to 4.5 mm. Consequently, D20 shear bolts satisfy design criteria, the maximum shear load and clear fracture surface, at the crash speed of 9.5 m/sec.

3.2.2 Numerical results

Finite element analysis of the shear bolt was performed to verify crash test results. The material properties used are piecewise linear stress–strain curves shown in Fig. 3. The loading direction is not perfectly aligned, but has an inclined angle of 7 degree for quasi-static shear tests and 2 degree for dynamic shear tests according to image analyses. For the reason, the bottom side of the shear region is fixed and the velocity boundary condition is applied on the top of the shear region with the inclined angle. The effective plastic strain at fracture is 0.52 which is same as that for the tension bolt analysis. Finite element mesh system has 12,032 brick elements as shown in Fig. 21. Sequential deformed shapes are shown in Fig. 22. The elastic region of experimental load–displacement curves in Fig. 23 is corrected in accordance with the numerical load–displacement curves. Mechanical arrangement and elastic deformation of shear-off jig system cause disagreement of the elastic region between experiments and FEA. Fig. 23(a) shows FEA results in comparison to quasi-static shear test results. The maximum load from FEA coincides with that from the experiment as well as the fracture point. FEA results for the dynamic shear test are also in coincidence with the experimental results in the maximum load and fracture point. The maximum shear load for the D20 shear bolt is 216.1 kN for the experiment and 218.2 kN for FEA in quasi-static shear tests while the

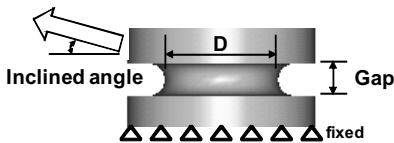


Figure 20: Boundary conditions for shear analysis.

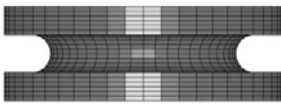


Figure 21: Finite element model of the shear bolt.

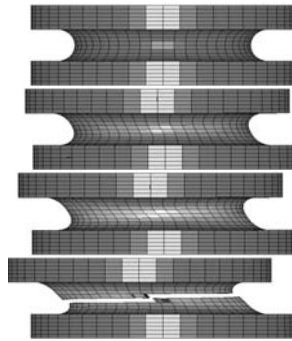
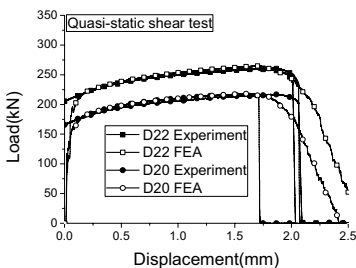
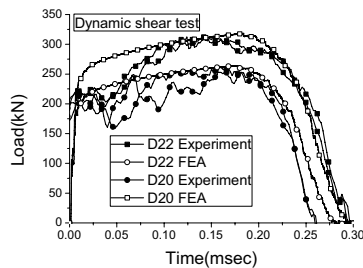


Figure 22: Sequential deformed shapes.



(a)



(b)

Figure 23: Load–time curves from experiments and FEA: (a) quasi-static shear tests; (b) dynamic shear tests.



maximum shear load for the D20 shear bolt is 261.1 kN for the experiment and 264.2 kN for FEA in the dynamic shear test. Numerical simulation with dynamic material properties of SCM440H precisely predicted the experimental result.

4 Conclusion

Crash test results of the tension bolt designed showed the maximum load of 410.5 kN and the absorbed energy of 3785.3 J while the target load was 375 kN. The tensile testing devices were designed to perform the crash tests of tension bolts at the High Speed Crash Tester. The load measuring system using strain gages was calibrated in a proper manner and carried out measurement of load responses successfully. It is noted that the amount of applied pre-tension had no effects on the maximum load. The shear bolts for Light Collision Safety Devices were designed and evaluated by quasi-static and dynamic shear tests. The designed shear bolts, D20 specimens, showed the maximum shear load of 216.1 kN for quasi-static shear tests and 261.1 kN for dynamic shear tests while D22 specimens showed the maximum shear load of 259.6 kN for quasi-static shear tests and 312.6 kN for dynamic shear tests. The maximum shear load of D20 specimens is 261.1 kN which is 4.4% larger than the targeting shear-off load. Accordingly, D20 shear bolts with a material of SCM440H operate sufficient function in Light Collision Safety Devices. The numerical simulation for the tension and shear bolts with dynamic material properties of SCM440H predicted the experimental results closely.

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Mechanical properties of a baseline UHPC with and without steel fibers

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Abstract

Personnel of the Geotechnical and Structures Laboratory, US Army Engineer Research and Development Center, conducted a series of laboratory experiments to investigate the strength and constitutive property behavior of baseline ultra-high-performance composite concrete (Cor-Tuf) with and without steel fibers. A total of 23 mechanical property tests were successfully completed for each Cor-Tuf concrete. The property tests included hydrostatic compression, unconfined compression (UC), triaxial compression (TXC), unconfined direct pull (DP), uniaxial strain, and uniaxial-strain-load/constant-volume-strain loading tests. Results of the TXC tests exhibited a continuous increase in maximum principal stress difference with increasing confining stress. A compression failure surface was developed from the TXC and the UC test results. The results for the DP tests were used to determine the unconfined tensile strength of the concretes, which was less than 10% of the unconfined compression strength. The Cor-Tuf with the steel fibers exhibits slightly greater strength with increased confining pressure than the Cor-Tuf without steel fibers. Overall, the results from all of the compression tests for both Cor-Tuf concretes were very similar.

Keywords: ultra-high-performance concrete, steel fibers, high pressure mechanical response.

1 Introduction

Cor-Tuf is the nomenclature given to a family of ultra-high-performance concretes (UHPCs) developed at the Geotechnical and Structures Laboratory



(GSL), U.S. Army Engineer Research and Development Center (ERDC). UHPCs are distinguished by their high compressive strengths (ranging from 190 to 244 MPa in the case of the Cor-Tuf cylinders). The Cor-Tuf concrete composition was designed to develop ultra high compressive strength while maintaining workability and production economy. Cor-Tuf can be broadly characterized as a reactive powder concrete, which is composed of fine aggregates and pozzolanic powders, but does not include coarse aggregates like those found in conventional concrete. The mixture proportion for Cor-Tuf is in table 1.

Table 1: Cor-Tuf mixture composition.

Material	Product	Proportion by weight
Cement	Lafarge, Class H, Joppa, MO	1.00
Sand	US Silica, F55, Ottawa, IL	0.967
Silica flour	US Silica, Sil-co-Sil 75, Berkeley Springs, WV	0.277
Silica fume	Elkem, ES 900 W	0.389
Superplasticizer	W.R. Grace, ADVA 170	0.0171
Water (tap)	Vicksburg, MS municipal water	0.208
Steel fibers ¹	Bekaert, Dramix® ZP305	0.310

¹ Steel fibers used in Cor-Tuf1 material only.

For comparative purposes, two preparations of Cor-Tuf were produced for this study, i.e., Cor-Tuf1 contained steel fibers, and Cor-Tuf2 did not. The steel fibers in Cor-Tuf1 were a Dramix® ZP305 product from Bekaert Corporation. Personnel with the GSL Impact and Explosion Effects Branch conducted mechanical property tests for both preparations of Cor-Tuf. The test specimens were cut to the correct length, and the ends were ground flat and parallel to each other and perpendicular to the sides of the core in accordance with procedures in ASTM D 4543 [1]. The prepared test specimens had a nominal height of 110 mm and a diameter of 50 mm. A total of 23 successful quasi-static mechanical property tests were conducted on Cor-Tuf1 and on Cor-Tuf2. The mechanical property tests consisted of hydrostatic compression (HC), unconfined compression (UC), triaxial compression (TXC), unconfined direct pull (DP), uniaxial strain (UX), and uniaxial-strain-load/constant-volume-load (UX/CV) tests. Table 2 contains the average values of wet density, water content, dry density, and air voids content from each preparation of Cor-Tuf.

Table 2: Average composition properties for test specimens.

Cor-Tuf Mix	Wet Density Mg/m ³	Water Content, %	Dry Density, Mg/m ³	Air Voids Content, %
1	2.557	2.73	2.490	8.3
2	2.328	3.24	2.256	11.3



2 Mechanical property tests

All of the mechanical property tests were conducted with axial strain rates on the order of 10^{-4} to 10^{-5} per second and times to peak load on the order of 5 to 30 minutes. Undrained isotropic compressibility data were obtained during the hydrostatic loading phases of the TXC tests and from HC tests. Shear and failure data were obtained from UC tests, unconsolidated-undrained TXC tests, and DP tests. One-dimensional compressibility data were obtained from undrained UX tests with lateral stress measurements. One type of undrained strain path test was conducted during the test program. The strain path tests were initially loaded under uniaxial strain boundary conditions to a prescribed level of stress or strain. At the end of the UX loading, a constant axial-to-radial-strain ratio (ARSR) of -2.0 was applied. The ARSR = -2.0 path is a constant-volume-strain-loading path; these tests will be referred to as UX/CV tests. The term unconsolidated undrained signifies that no pore fluid (liquid or gas) was allowed to escape or drain from the membrane-enclosed specimens.

2.1 Test devices and instrumentation

Three sets of test devices were used in this test program. The axial load for all of the UC tests was provided by a 3.3 MN loader. The application of load was manually controlled with this test device. No pressure vessel was required for the UC tests; only a specimen base and top cap, load cell, and vertical and radial deformeters were necessary.

DP tests were performed using end caps that were attached to the unconfined specimens with a high-modulus, high-strength epoxy. A manual hydraulic pump was used to pressurize a chamber, which then retracted a piston and produced tensile loading in the test specimen. Measurements for the loading of the specimen were recorded by the load cell.

All of the remaining tests were conducted in a 600-MPa-capacity pressure vessel, and the axial load was provided by an 8.9-MN loader. With the 8.9-MN loader and associated hydraulic pump, the application of load, pressure, and axial displacement were regulated by a servo-controlled data acquisition system. This servo-controlled system allowed the user to program rates of load, pressure, and axial displacement in order to achieve the desired stress or strain path. Confining pressure was measured externally to the pressure vessel by a pressure transducer mounted in the confining fluid line. A load cell mounted in the base of the specimen pedestal was used to measure the applied axial loads.

The vertical deflection measurement system consisted of two linear variable differential transformers (LVDTs) mounted vertically inside the pressure vessel on an instrumentation stand and positioned 180-degrees apart. They were oriented to measure the displacement between the top and base caps, thus providing a measure of the axial deformations of the specimen. In addition, a linear potentiometer was mounted externally to the pressure vessel, so as to measure the displacement of the piston through which axial load was applied. This provided a backup to the internal LVDTs in case they exceeded their



calibrated range. Two radial deflection measurement systems were used in this test program. One lateral deformer consisted of an LVDT mounted on a hinged ring; the LVDT measured the expansion or contraction of the ring [2]. This lateral deformer was used for smaller ranges of radial deformation when the greatest measurement accuracy was required. The second lateral deformer consisted of two strain-gaged spring-steel arms mounted on a double-hinged ring; the strain-gaged arms deflect as the ring expands or contracts. This lateral deformer was used when the greatest radial deformation range was required, and therefore, it is less accurate than the LVDT.

3 Comparisons of test results

Measurements of posttest water content for each test specimen were conducted in accordance with procedures given in ASTM D 2216 [1]. Based on the appropriate values of posttest water content, wet density, and grain density, values of dry density and air voids content of the test specimens were determined.

3.1 Hydrostatic compression test results

Undrained bulk compressibility data were obtained from the HC tests and during the hydrostatic loading phase of the TXC tests. The pressure-volume data from the HC tests conducted on each concrete are compared in fig. 1. The figure legend identifies the test number, and the second number designates whether the test specimen is Cor-Tuf1 or Cor-Tuf2. The initial dry densities of Cor-Tuf1 HC test specimens were 2.510 and 2.523 Mg/m³, while the initial dry densities of Cor-Tuf2 HC test specimens were 2.286 and 2.312 Mg/m³. The test specimens for each material with the lower densities (test 3-1 for Cor-Tuf1 and test 3-2 for Cor-Tuf2) were more compressible than the test specimens with the higher densities. The HC compressibility for Cor-Tuf1 and 2 are very similar, with Cor-Tuf2 displaying a slightly greater compressibility. This implies that the steel fibers in Cor-Tuf1 slightly reduced its compressibility compared with that of Cor-Tuf2. During the transition from loading to unloading, the pressure was held constant, and the deformations were monitored. When the deformation rate decreased significantly, the pressure was decreased. Specimens of both concretes displayed increases in the volumetric strains during the transition, which is an indication that the concretes are susceptible to creep. Based on the data from the HC tests, the initial elastic bulk modulus for Cor-Tuf1 is 25.2 GPa and is 22.7 GPa for Cor-Tuf2.

3.2 Triaxial compression test results

Compression shear and failure data were successfully obtained from results of the UC tests and the unconsolidated-undrained TXC tests. The UC tests were performed in accordance with ASTM C 39 [1] and are a type of TXC test without the application of confining pressure. No attempt was made to capture the post-peak (or softening) stress-strain behavior during the UC tests. Fig. 2



presents plots of the stress-strain data (principal stress difference versus axial strain) from the UC tests for each concrete. The UC test results are very sensitive to small changes in the dry density and specimen structure, which cause variations of the initial loadings and peak strengths. The mean unconfined compressive strengths of Cor-Tuf1 and Cor-Tuf2 were 237 and 210 MPa, respectively.

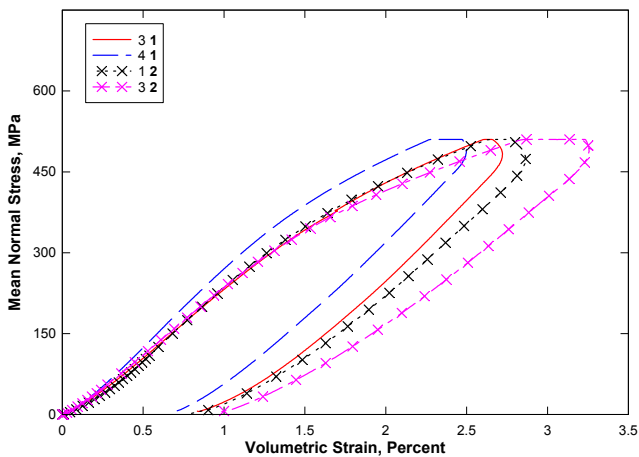


Figure 1: Pressure-volume responses from HC tests.

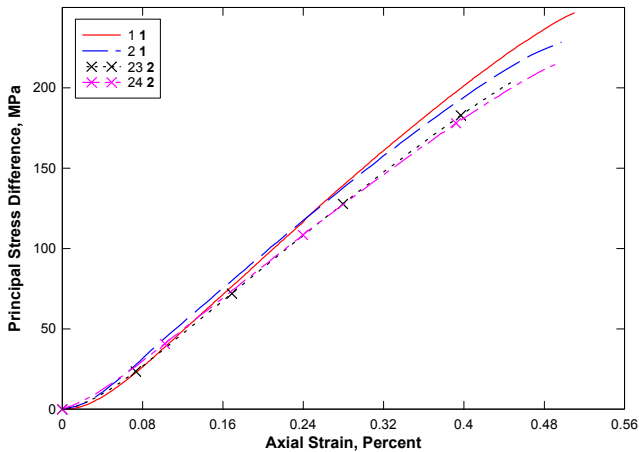


Figure 2: Stress-strain data from UC tests.

For comparison purposes, stress-strain data from selected TXC tests conducted with constant confining pressures of 10, 20 and 50 MPa are plotted in fig. 3, while stress-strain data from selected TXC tests with constant confining



pressures of 100, 200, and 300 MPa are plotted in fig. 4. The legend for symbols in these two figures includes the test number, the level of confining pressure, and the number label for Cor-Tuf. For plotting purposes, the axial and volumetric strains at the beginning of the shear phase were set to zero, i.e., only the strains during shear are plotted. A few comments should be made concerning the unloading results. The final unloading stress-strain responses at axial strains approaching 15 percent are less reliable than the unloadings at axial strains of less than 11 percent. The internal vertical deformeters go out of range at axial strains of approximately 11 percent. After that, an external deformeter with less resolution is used to measure axial displacement.

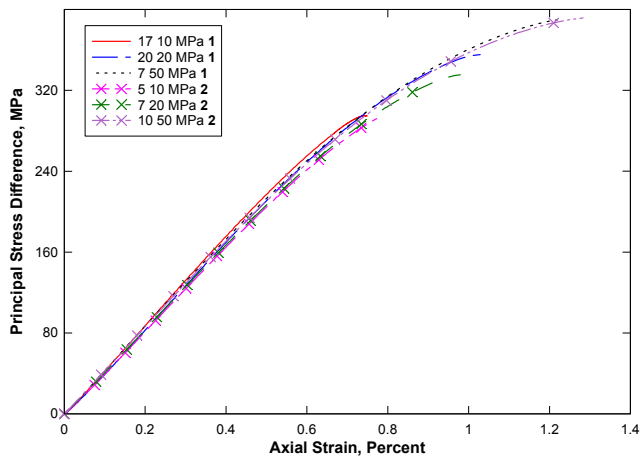


Figure 3: Stress-strain data from selected TXC tests at constant confining pressures between 10 and 50 MPa from Cor-Tuf1 and Cor-Tuf2.

The peak strengths of the test specimens for Cor-Tuf1 and 2 are very similar for confining pressures between 10 and 50 MPa (fig. 3). Cor-Tuf1 clearly displays increases in strength over Cor-Tuf2 with confining pressures of 100 MPa and greater (fig. 4). The increased strength of Cor-Tuf1 is a result of the steel fibers and the density of the test specimens.

Fig. 4 illustrates both the brittle and ductile nature of Cor-Tuf1 and Cor-Tuf2. At confining pressures of 100 MPa and below, Cor-Tuf1 and Cor-Tuf2 test specimens behave in a brittle manner, i.e., the material strain-softens. At confining pressures above 100 MPa, Cor-Tuf1 and Cor-Tuf2 behave in a ductile manner, i.e., the stress-strain data exhibit strain hardening. The initial compaction then dilation during shear is displayed in the volumetric strain responses (fig. 5) for Cor-Tuf1 and 2 at confining pressures of 100 MPa and above.

The failure data and the compression failure surfaces for both concretes developed from the UC and TXC test results are plotted in fig. 6 as principal stress difference versus mean normal stress. The recommended failure surfaces for Cor-Tuf1 and Cor-Tuf2 are initially the same. However, as the confining



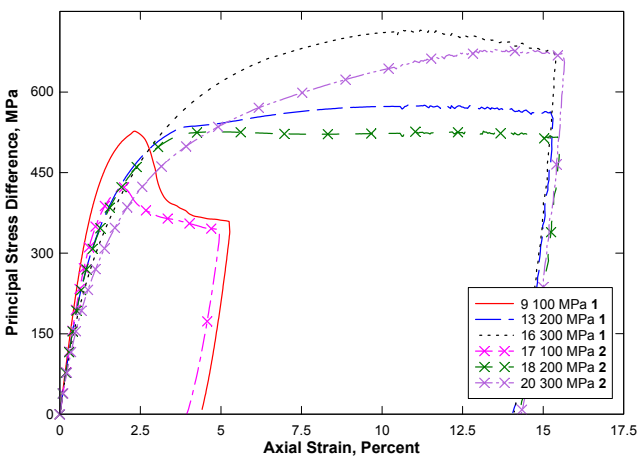


Figure 4: Stress-strain data from selected TXC tests at constant confining pressures between 100 and 300 MPa from Cor-Tuf1 and Cor-Tuf2.

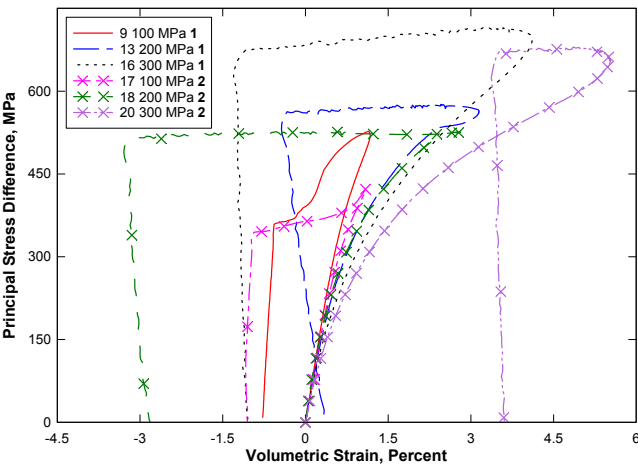


Figure 5: Stress difference-volumetric strain responses during shear from selected TXC tests at confining pressures between 100 and 300 MPa from Cor-Tuf1 and Cor-Tuf2 concrete.

pressure increases, the failure surface for Cor-Tuf1 becomes slightly greater than the failure surface for Cor-Tuf2. The response data from the 300 MPa TXC tests indicate that both Cor-Tuf1 and Cor-Tuf2 have not reached void closure. Concrete materials can continue to gain strength with increasing pressure until all of the air porosity in the specimen is crushed out, i.e., when void closure is tests and under hydrostatic loading conditions. The failure surface will have a minimal slope after void closure is achieved.



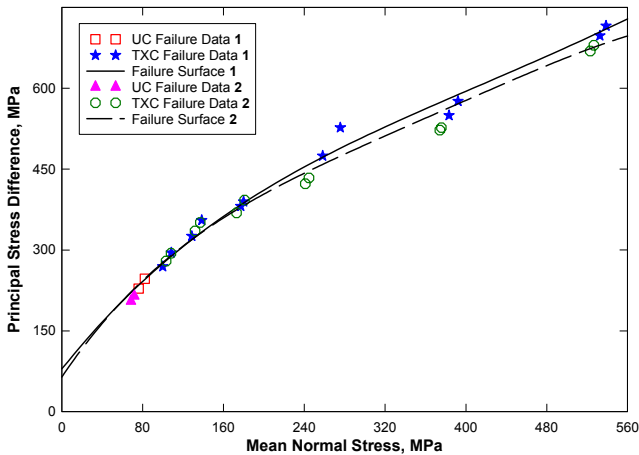


Figure 6: Failure data from UC and TXC tests and the failure surfaces for both materials.

3.3 Direct pull test results

Results from the DP tests are plotted in fig. 7. The average tensile strength from the Cor-Tuf1 DP tests was at -5.58 MPa, while the Cor-Tuf2 DP test specimen failed at -8.88 MPa. There was only one test completed for Cor-Tuf2, because the high strength epoxy failed in two tests before the test specimens fractured. The average tensile strength of Cor-Tuf1 concrete is 2.4% of its average unconfined compression strength, while the tensile strength of the Cor-Tuf2 concrete is 4.2% of its average unconfined compression strength. According to ACI 318-02 [3], the tensile strength of concrete is normally assumed to be about 10 to 15% of the compressive strength. In this case, both Cor-Tuf1 and 2 have less tensile strength than generally assumed by ACI 318-02.

3.4 Uniaxial strain test results

Comparisons of the UX test results for the two concretes are in figs. 8 and 9. The stress-strain data are plotted in fig. 8 and the stress paths with the TXC failure surfaces in fig. 9. Cor-Tuf2 displays greater amounts of axial strain (fig. 8) than Cor-Tuf1; therefore, Cor-Tuf2 compresses more than Cor-Tuf1. The steel fibers and the densities of the Cor-Tuf1 test specimens reduce the compressibility of the test specimens.

From the UX stress-strain loading data in fig. 8, the initial constrained modulus of Cor-Tuf1 is 47.4 GPa, while the initial constrained modulus of Cor-Tuf2 is 43.1 GPa. An initial shear modulus of 16.7 GPa was calculated for Cor-Tuf1 concrete and 15.3 GPa for Cor-Tuf2 concrete based on each concrete's initial constrained modulus and bulk modulus (25.2 GPa for Cor-Tuf1 concrete and 22.7 GPa for Cor-Tuf2 concrete) determined from the HC tests. Any two moduli may be used to calculate any of the other elastic constants, e.g., Young's

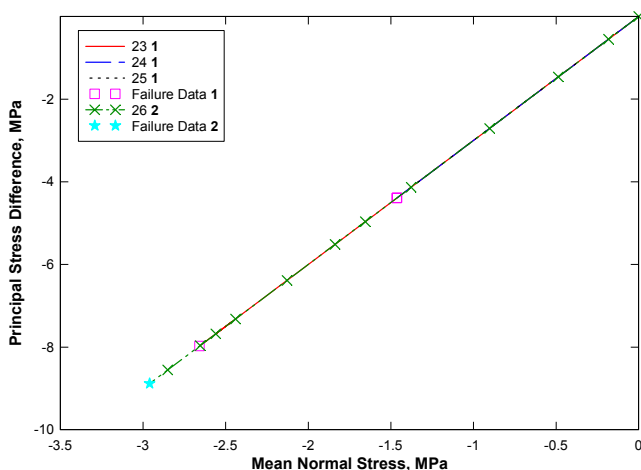


Figure 7: Stress paths from DP tests and the failure data for Cor-Tuf1 and Cor-Tuf2.

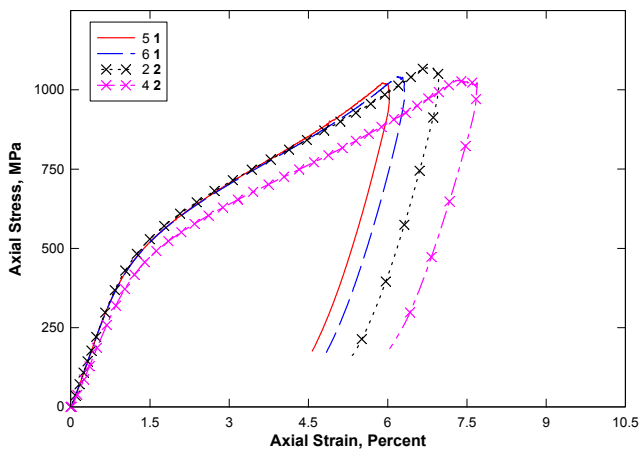


Figure 8: Stress-strain responses from UX tests.

modulus and Poisson’s ratio. The initial Young’s modulus for Cor-Tuf1 is 40.9 GPa and 37.5 GPa for Cor-Tuf2 concrete. The initial Poisson’s ratio is 0.23 for Cor-Tuf1 and 0.22 for Cor-Tuf2 concrete.

The stress paths for both concretes (fig. 9) are very similar; both concretes experience crushing of the cement bonds at approximately 300 MPa, and neither display full saturation.



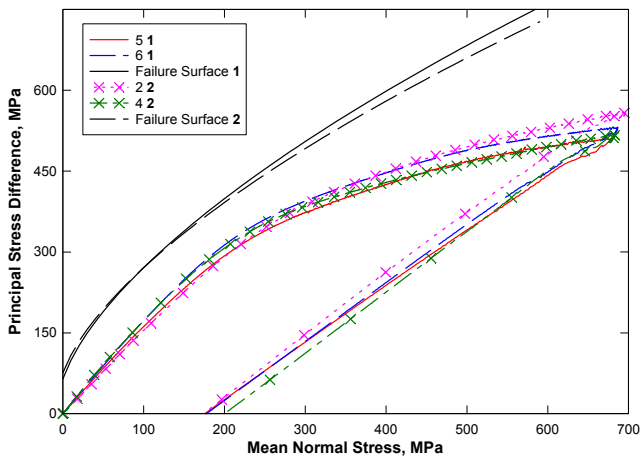


Figure 9: Stress paths from UX tests and the TXC failure surfaces for Cor-Tuf1 and Cor-Tuf2.

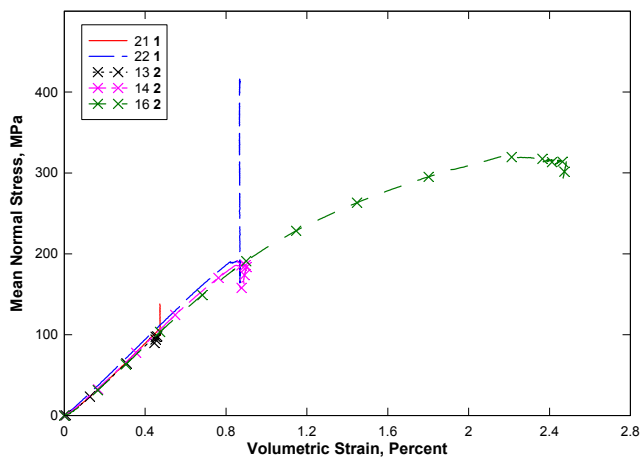


Figure 10: Pressure-volume data from the UX/CV tests for Cor-Tuf1 and Cor-Tuf2.

3.5 Strain path test results

One type of special strain path test was conducted. UX/CV refers to tests with uniaxial strain loading followed by constant volumetric strain loading (ARSR = -2.0). The UX/CV tests were loaded in UX to peak axial stresses of about 50 and 100 MPa for both materials. One Cor-Tuf2 test was loaded to 200 MPa in UX. Comparisons of the results of UX/CV strain-path tests conducted on the two concretes are shown in figs. 10 and 11. The pressure-



volume data are in fig. 10 and the stress-paths with the failure surface data are in fig. 11. Mechanical problems occurred during the CV portion of all the tests performed on Cor-Tuf2. The pressure volume data for Cor-Tuf1 (fig. 10) shows that the specimens were held at a constant volume. Cor-Tuf1 test specimen 22 and Cor-Tuf2 test specimen 14 displayed similar results until test specimen 14 was concluded because of a mechanical problem during the test.

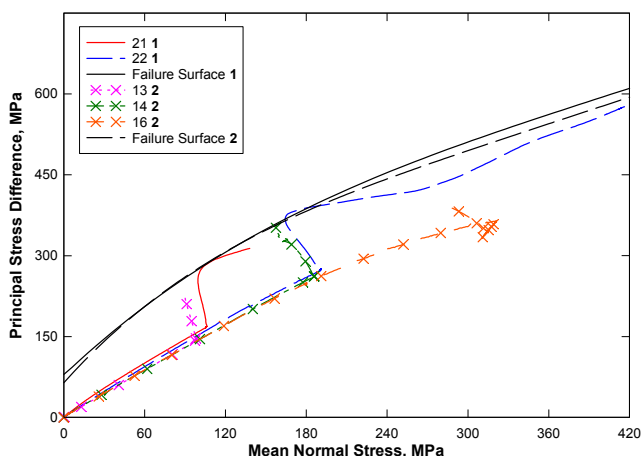


Figure 11: Stress paths from UX/CV tests and TXC failure surfaces for Cor-Tuf1 and Cor-Tuf2.

4 Conclusions

Personnel in the GSL, ERDC conducted a series of laboratory experiments to investigate the strength and constitutive property behavior of baseline ultra-high-performance composite (Cor-Tuf) concrete with and without steel fibers. A total of 23 successful mechanical property tests were conducted for each material.

The overall quality of the test data was very good. Cor-Tuf1 and Cor-Tuf2 concrete behave similarly, but Cor-Tuf1 exhibits greater strength with increased confining pressure, and Cor-Tuf2 displays greater compressibility. For both materials, creep was observed during the HC tests. Results from the TXC tests exhibited a continuous increase in principal stress difference with increasing confining stress. A compression failure surface was developed from results of TXC and UC tests. The results for the DP tests were used to determine the tensile strength of the concretes. By comparing the unconfined compression and unconfined tensile strengths, it is apparent that both concretes' tensile strengths are less than 10% of their unconfined compression strengths. The CV loading for Cor-Tuf1 followed closely along the TXC failure surface, which validates the failure surface. Overall, the results from all of the compression tests for the Cor-Tuf concretes were very similar. More tensile dominant tests are required to demonstrate the effects of the steel fibers in Cor-Tuf.



Acknowledgement

The tests described and the resulting data presented herein were obtained from research conducted jointly under the Scalable Technology for Adaptive Response and Defeat of Emerging Adaptive Threats Work Packages of the U.S. Army Corps of Engineers, Engineer Research and Development Center, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199. Permission to publish this paper was granted by the Director, Geotechnical and Structures Laboratory.

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A rheological comparison of hard grade binders with polymer modified bitumen under aged and unaged conditions

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Abstract

High ambient temperature and uncontrolled heavy axle loads are considered to be the root cause of premature failure of flexible pavements, especially rutting, in Pakistan. In order to combat rutting problems, 60/70 penetration grade bitumen modified with Elvaloy Terpolymer (PMB) has been used on various critical sections since 2001. Rheological characteristics of PMB, 60/70 and 40/50 penetration grade bitumen were studied using a dynamic shear rheometer at 25, 40 and 55°C. Short term aging effects were also studied in a rolling thin film oven test and the results of aged and unaged binders have been compared. The study revealed that the complex shear modulus of binders reduces significantly with an increase in temperature, while the phase angle increases, but at a lesser rate. Short term aging has showed relatively less influence on binder rheology than temperature.

Keywords: rheology, bitumen, aging, temperature.

1 Introduction

Pakistan has a total road network of 258,340 kilometers comprising 165,762 km of high type roads and 92,578 km of low type roads. The length of high type roads has increased by 40 percent since 1995–96 [1]. Over the past twenty years, road traffic (both passenger and freight) has grown significantly and loading is getting progressively worse due to the import of more powerful trucks with heavier wider bodies in Pakistan. One of the probable factors of increased road traffic is the decreased trend in railway use during the recent past. Consequently,



premature rutting in the form of shear flow in flexible pavements has been observed due to high ambient temperatures. The National Highway Authority (NHA), Pakistan, has been facing serious threats, such as frequent pavement failures, poor riding quality and high maintenance costs. Modifications of bitumen with polymers and the adoption of rigid pavement construction have increased the construction cost compared to that of conventional pavements. Among the other factors causing the premature failure of the flexible pavements, the properties of binders are believed to be the most important parameter. In order to cater for the growing axle load and to increase the performance of bituminous mixes, it is necessary to investigate the true prediction and evaluation of binder rheological parameters in parallel.

2 Literature review

Rheology is the study of the deformation and flow of bitumen that explains the elastic and viscous behavior of bitumen when subjected to a stress [2, 3]. Complex modulus (G^*) and phase angle (δ) are considered to be the principal rheological parameters, normally measured from a device known as Dynamic Shear Rheometer (DSR) [4]. The complex modulus is the peak-to-peak shear stress to absolute value of peak-to-peak shear strain and the phase angle is the angle in radian between a simultaneously applied stress and the resulting sinusoidal stress in a controlled strain testing mode [5].

A number of researches have reported on binder rheology in the past, but little information is available regarding the effects of polymers on binder rheology at different temperatures under aged and unaged conditions. Branthaver *et al.* [6] reported that a reduction in the weight and quantity of the non-polar molecules occurs under aging phenomenon, which is due to conversion of non-polar molecules to the polar carbonyl group. They further concluded that new polar sites will form association with other polar molecules, making the bitumen molecules, to which they attached; act as strong polar associating molecules.

It has been reported by Hunter [7] that the rutting tendency of a pavement is greatly influenced by the ratio of the complex modulus to the phase angle. In order to maximize the rutting parameters, a high value of ' G^* ' and low values of ' δ ' are required. In order to reduce the fatigue parameters, a low value of ' G^* ' and ' δ ' are required.

Tarefder *et al.* [8] investigated the most important factors affecting the rutting and performance grade (PG) of bitumen and determined that specimen type, test temperature and moisture has a significant influence on binder performance.

Kantipong and Bahia [9] compared the rutting performance of polymer modified bitumen with conventional bitumen and concluded that the overall performance of the polymer modified binder was better than that found in conventional bitumen.

Huang *et al.* [4] studied the rheological properties of unaged and aged asphalt-filler mixes and reported that the rheological properties of bitumen depend upon aging and temperatures, and both can be characterized separately



with the help of different models. Moreover, an increase in aging level corresponds to a decrease in temperature. They developed models that differentiate aging and temperature effects on phase angles.

It is necessary to evaluate the performance of bitumen at various temperatures, states of aging and modification before using the same in the flexible pavements. This study involves the short term aging of three asphalt binders using the rolling thin film oven test (RTFOT), physical smart pave MCR-301 and parallel plate test geometry dynamic shear rheometer (DSR). The RTFOT procedure was used to simulate aging during the mixing and placement of asphalt binders. A constant frequency of 10 rad/sec was selected to ensure that the measurements are within the region of linear behavior.

3 Objectives

The objectives of this study were:

1. To determine the rheological parameters of three bitumen types i.e. 60/70 & 40/50 penetration grade bitumen and polymer modified bitumen (PMB) at 25, 40, 55 °C.
2. To compare rheological parameters of modified bitumen with its base bitumen (60/70) and 40/50 penetration grade bitumen.
3. To study the effects of aging on bitumen that is normally used in Pakistan.

4 Experimental design

4.1 Materials

Two neat bitumens with penetration grade '60/70' and '40/50' and one modified binder (PMB) with base asphalt '60/70' were used for this study. The bitumen with the penetration grade '60/70' was modified with 1.6% Elvaloy® 4170 and 0.7% superphosphoric acid in Attock Refinery, Pakistan. The PG grading of PMB was developed at Mathy Technology and Engineering Services, USA, where in different trials a final blend was prepared that would be more suitable for the climatic conditions. When tested at 76°C, the final blend produced a Dynamic Shear Rheometer (DSR) value of 1.66kpa at 16 hrs and 1.3 kpa at 184 hrs after blending as reported in Table 1 [10].

The Australian test specification, test methods and US equivalents used for PMB have been reported in Table 2 [11].

Consistency tests were performed as per AASHTO standards on bitumen in order to determine conventional grading. The results of the consistency tests of PMB matched with the '40/50' pen. bitumen and hence, both were designated under the same penetration grade. The results of consistency tests have been reported in Table 3.



Table 1: Modification results of ‘60/70’ penetration grade bitumen with Elvaloy Terpolymer.

Asphalt	Control	C1	D	D1	E
Penetration grade “60/70”		500g	500g	500g	500g
Elvaloy 4170		1%	1.5%	1.75%	2%
SPA (super phosphoric acid)		0.2%	0.2%	0.2%	0.2%
Mix Temperature		190 ⁰ C	190 ⁰ C	190 ⁰ C	190 ⁰ C
Mix Time		3hrs	3hrs	3hrs	3hrs
Penetration (dmm) at 25 ⁰ C		39	36	42	42
DSR					
G*/sin (delta)	1.9567	1.3896	1.3443	1.103	1.7680
Phase Angle	86.2	72.50	62.90	57.80	57
Pass/fail	63.1	73.20	79.30	83.20	82.70
PG Grade	58c	70c	76c	82c	82c
Ring & Ball Softening point		141f/60 ⁰ C	160f/71 ⁰ C	162f/72 ⁰ C	169f/76 ⁰ C
Elastic Recovery 25 ⁰ C (20cm)		50%	72.5%	75%	78%
Ductility @25 ⁰ C		37cm	20cm	23cm	22cm
Absolute Viscosity 60 ⁰ C (poise)		9107	56946	112060	183474
Brookfield viscosity 165 ⁰ C (centipoises)		2590	4200	5040	8400
Torsional Recovery (%)		18	25	32	32

Table 2: Specifications limits of PMB.

Test Type	Australian test Specifications	Australian Test Methods	US Equivalent
Elastic consistency @ 60 ⁰ C, pa.s	1500 min,	MBT 21	Not Known
Stiffness @ 25 ⁰ C, kpa,	130 max,	MBT 21	Not Known
Brookfield Viscosity @ 165 ⁰ C, pa.s	0.75 max,	MBT 11	Not Known
Flash point ⁰ C	250 min,	MBT 12	ASTM D92
Loss on Heating, %	0.6 max,	MBT 03	ASTM
Mass			D1754
Torsional Recovery, @ 25 ⁰ C %	12 min,	MBT 22	Not Known
Softening point ⁰ C	60 min,	MBT 31	ASTM D36



Table 3: Consistency of bitumen results.

Test Description	Test Methods	Results and specifications			
			AASHTO M-20		
		PMB	60/70 grade	Pen. 40/50 grade	Pen.
Ductility @ 25°C (cm)	AASHTO D113	45	100 (100-minimum)	67 (100-minimum)	
Flash Point, COC (°C (°F))	AASHTO D92	>232	>232 (232-minimum)	>232 (232-minimum)	
Penetration @ 25°C (1/10 mm)	AASHTO D5	46	65 (60-70)	44 (40-50)	
Softening Point	AASHTO D 36	58	49 (50-minimum)	56 (60-minimum)	

5 Testing

Short term aging using RTFOT was carried out as per ASTM D 2872-97, which covers the determination of the effect of heat and air on a film of asphaltic materials. A total mass of 35 ± 0.1 g of a thin bitumen film was taken in a standardized bottle during this test and exposed to airflow at a rate of 4000 ± 200 ml/min, for 85 minutes, and at a constant temperature of $163 \pm 0.5^\circ\text{C}$. The residue from the bottle was then collected and homogenized.

The effects before and after this treatment were determined using DSR, which is capable of characterizing the viscous and elastic behavior of bitumen at low, medium, and high temperatures, which are anticipated in the area where the asphalt binder would have been used. Eighteen specimens (both aged and unaged) were tested, i.e. three specimens from each bitumen type. Specimens were prepared using the standard test methods for “Determining the Rheological properties of Asphalt Binders using a Dynamic Shear Rheometer” ASTM D 7175-08. The test specimens were maintained at the test temperature within $\pm 0.1^\circ\text{C}$ by heating and cooling the upper and lower plates.

6 Results and discussion

Bitumen is characterized by the time of loading, temperature and the dependency of the mechanical response to loading [12]. Bituminous binder aging may be caused by different factors, but the key component of concern for the RTFOT is the loss of volatiles. The loss of smaller molecules was observed to cause an increase in bitumen viscosity. This can best be simulated with the loss of volatiles in the binder during its manufacturing and placement process. The elevated temperature of this process ages the bitumen by driving off a substantial



amount of volatiles. The principal viscoelastic parameters determined for aged and unaged bitumen have been compared in Table 4 and shown graphically in Figures 1(a), 1(b), 2(a) and 2(b).

It can be seen from Figures 1(a), 1(b), 2(a) and 2(b) that the rheological properties of asphalt binders depend on the temperature and aging with RTFOT. The complex modulus decreases drastically with an increase in temperature, which may cause an increase in binder susceptibility to rut. The phase angle increases with the increase in temperature at a given frequency, resulting in the delayed response of the binder at high temperatures. The phase angle and complex modulus were further compared at three temperature conditions as shown in Figures 3 and 4. It was observed that with the increase in the phase angle, the complex modulus or the stiffness of binder reduces in both aged and unaged specimens.

Table 4: Comparison of rheological parameters for unaged and aged samples.

Bitumen Types	Temperature (°C)	Phase Angle (Ø °)		Mean Complex Modulus (G*) (kPa)		
		Un-aged	Aged on RTFO	Un-aged	Aged RTFOT	on
60-70	25	72.5	59.5	462	591	
	40	80.8	61.4	37	47	
	55	86.6	63.2	3	4	
40-50	25	74.7	63.5	995	1323	
	40	83.8	65.4	75	95	
	55	87.7	66.7	6	7	
PMB	25	66.9	58.2	875	1138	
	40	69.8	56.5	60	77	
	55	70.7	55.1	7	9	

7 Conclusion

Based on the results obtained in this research study, the following conclusions can be drawn;

- The complex shear modulus of binders reduces significantly with an increase in temperature, while the phase angle increases, but at a lesser rate.
- Short term aging influences relatively lesser on binder rheology than temperature.



- Bitumen with a '60/70' penetration grade was observed to be more sensitive to temperature and short term aging than other binders. At the same time, PMB was observed to be the least sensitive binder.
- Bitumen '60/70' pen. grade, modified with Elvaloy Terpolymer, showed better rheological parameters than '40/50' pen. grade under specified test conditions.

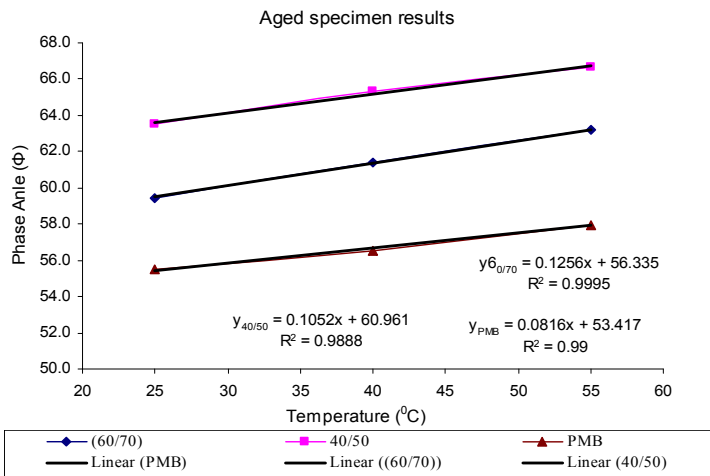
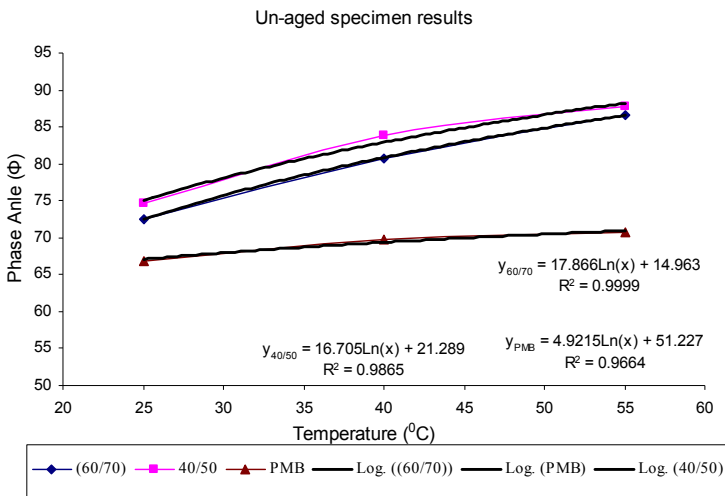
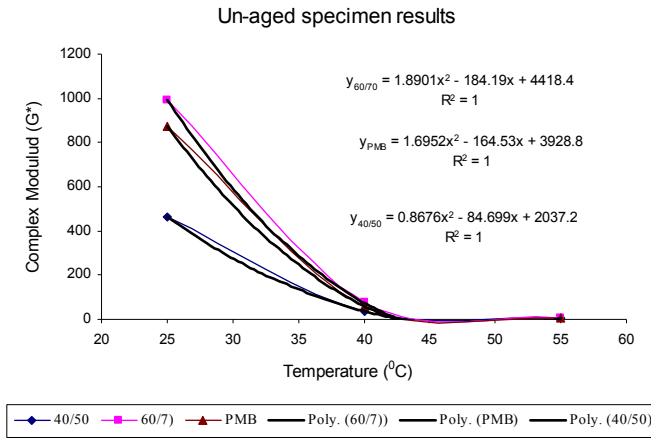
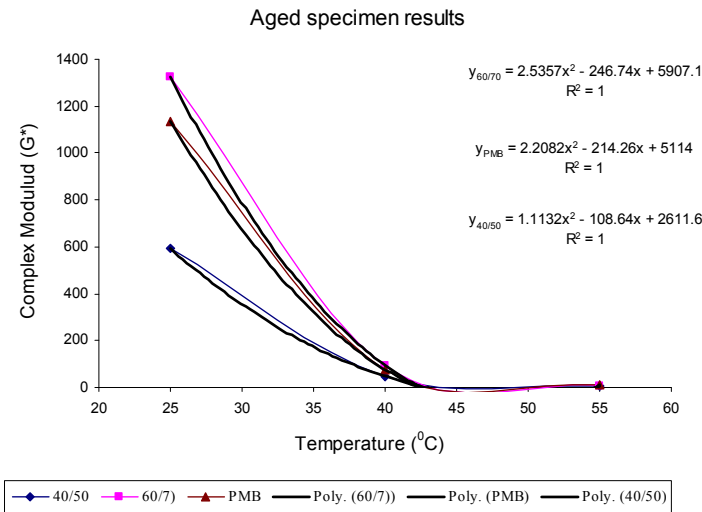


Figure 1: (a) Influence of temperature on phase angle (unaged specimens).
(b) Influence of temperature on phase angle (aged specimens).





(a)



(b)

Figure 2: (a) Influence of temperature on complex modulus (unaged specimens). (b) Influence of temperature on complex modulus (aged specimens).



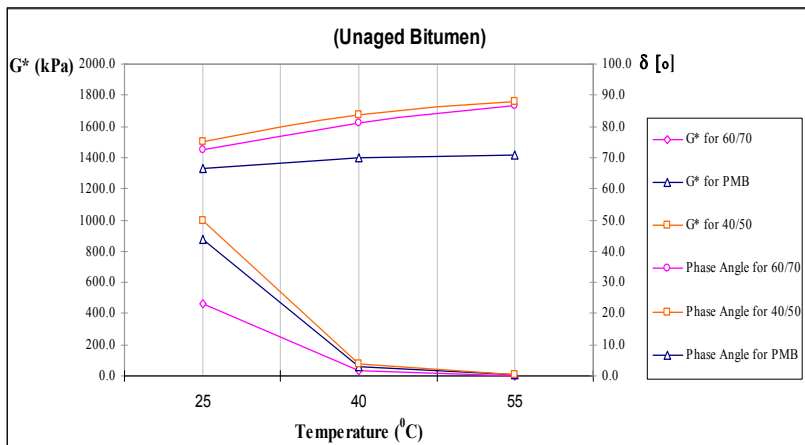


Figure 3: Variation in phase angle and complex modulus with temperature in aged bitumen.

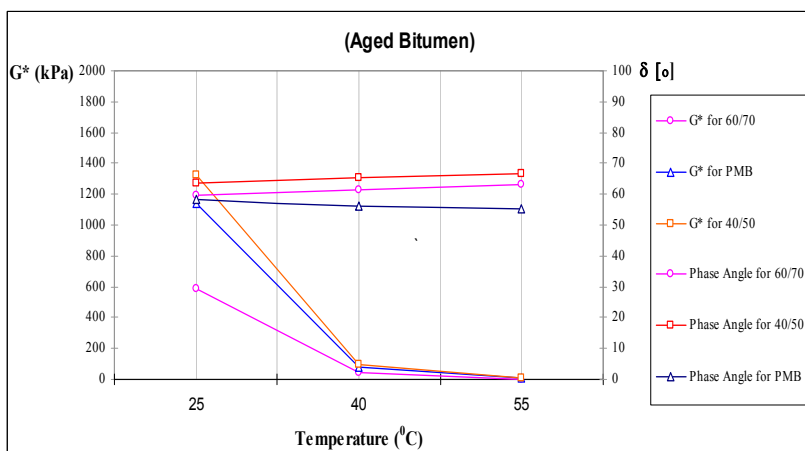


Figure 4: Variation in phase angle and complex modulus with temperature in unaged bitumen.

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Probabilistic model and experimental identification of screw-attachment in plasterboard

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Abstract

In this paper, one provides a robust modelling for the screw-attachment of large light partition wall between plasterboard (CPC) plate and metallic frame. The analysis of shear behaviour of this attachment under mechanic loads has been carried out by using an experimental approach taking into account the complexity of the mechanical systems. A deterministic model is then proposed to fit the experimental results. A mean model is identified using the experiments. Since there is variability in the experimental results and since the mean model corresponds to a rough approximation, there are uncertainties in the mean model which are taken into account with a parameter probabilistic approach. The probabilistic approach of uncertain parameters is constructed using the Maximum Entropy Principle under the constraints defined by the available information. The identification of unknown parameters of the probability model is performed using the experimental data which lead us to an optimization problem which has to be solved. Finally, the numerical results are presented and validated with experiments.

Keywords: screw attachment, plasterboard, probabilistic model, experimental identification.

1 Introduction

Nowadays, lightweight metal frames are widely used in construction. This type of frame has many advantages such as, rapidity construction and building flexibility, the facility of assemblage and of dismantling. They are used either as load-



bearing elements such as in residential, office or industrial buildings, or as non load-bearing elements in partition walls and suspended ceilings. In this research, we are concerned by the behaviour of a non load-bearing element. The chosen element is a large light partition wall with plasterboard using metallic frame. The plasterboard [cardboard-plaster-cardboard (CPC) multilayer] screwed with a metal frame on both sides, and are made of a body of plaster stickled with two sheets of cardboard on both sides. They are linked with the metal frame using screws. The dimension of a large light partition currently reaches more than 10 meters. Its mechanical and thermomechanical behaviour can be analyzed with computational models such as finite element models. Validation can be obtained using experimental tests. However, experimental tests cannot be carried out when the structural dimensions exceed those of the testing furnaces (generally up to three meters). Given the complexity of such a mechanical system, uncertainties exist in the system parameters. One very efficient way to take into account uncertainties in the computational model is using the probability theory. Some previous works have been carried out in this field and a deterministic and a probabilistic model for thermomechanical analysis of plasterboard plate submitted to fire load was proposed [8–10]. The present work is an extension to large light partitions. The work is focused on the screwed attachment between the plasterboard plate and the metallic frame. A full computational model of the structure with the attachments would require to introduce a multiscale nonlinear micro-macro model to describe the behaviour of the screw between the plasterboard plates and the metallic frame. Such a model would be very difficult to develop and a lot of data would be missing to perform efficient calculations. This is why we didn't try to develop such an approach and we have preferred to analyze a shear behaviour of the screw in the plasterboard plate using an experimental analysis and then fitting an equivalent constitutive equation with the experimental databases. The first section deals with a shear analysis of such an attachment under mechanical loads which is carried out by using an experimental approach. The experimental results were performed by the load-displacement curves. In the second section, a deterministic model is then proposed to fit the average experimental results. The parameters of this mean model are identified experimentally. Since there is variability in the experimental results due to materials and manufacturing processes, and since the mean model corresponds to a rough approximation, uncertainties in the mean model are taken into account using a probabilistic approach. The next section consists in developing the probabilistic model which is constructed using the Maximum Entropy Principle [4, 5] under the constraints defined by the available information. The identification of the unknown parameters of the probability model is performed again using the experimental data which leads us to the solution of the optimization problem to be solved. Finally, the numerical results are presented and validated with experiments.

Concerning the methodology used, the identification of the probabilistic model is performed in 2 steps. The first one is devoted to the first identification of the mean parameters of the shear behaviour for the screw attachment in minimizing a distance between the experimental average value and the average mean prediction.



The second one consists in identifying both the mean parameter and the dispersion parameter of the probabilistic model starting from the mean value identified in step one. This means that step one must be viewed as the primary computation step to perform the global identification in step 2.

In this paper the number of experiments is limited to a small number which is 10. It should be noted that such a number is always small due to the cost of experiments. In this condition, the variability observed with this small number of experiments is not representative of real statistical fluctuations which could be observed if a large number of experiments was available. A simply average deterministic function with known limits for variability can not be used. Such a deterministic approach would not allow the probability to reach the bounds to be known. This is the reason why a probabilistic approach is used and the probability model is constructed with the powerful Information Theory. Finally, the great interest of such an approach is to propose a practical design solution based on a probabilistic approach and not in an usual deterministic approach. With such an approach, a nonlinear structural statistical probabilistic analysis of large light partition walls with plasterboard screwed with metallic frames on both sides can be carried out to take into account large statistical fluctuations in due to the shear behaviour for the screw attachment.

2 Experimental analysis of the shear behaviour for the screw-attachment

2.1 Description of the experimental data

In order to analyze the shear behaviour of the screw-attachment, experiments have been carried out using the experimental setup shown in Fig. 1 consisting in imposing a relative displacement between the plasterboard plate and the metallic frame. A sensor directly measures the vertical relative displacement between the plasterboard plate at the screw level and the metallic frame while another load sensor measures the load applied to the sample.

The experiments have been carried out with 10 samples. The relative displacement at the screw level has been limited to $x_{\max} = 5.17mm$. This limit corresponds to the upper value for practical application (see Figure 2 left). Figure 2 displays the measurements obtained.

2.2 Analysis of the experimental results

The experimental results for the 10 samples are presented by 10 load-displacement curves (see Figure 2 left). Figure 2 right displays the averaging of the 10 experimental curves. It can be seen that the experimental averaging curve is monotone increase, and then a strictly concave function on interval $[0, x_{\max}]$. The mean





Figure 1: Photo of the experimental setup.

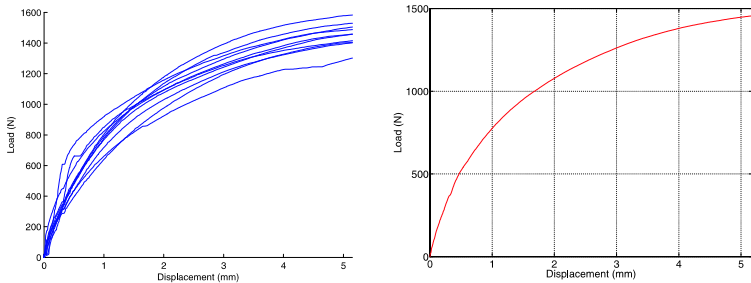


Figure 2: Experimental results of shear behavior of the screw-attachment. Load applied (vertical axis in N) as a function of displacement (horizontal axis in mm). 10 measures curves (left figure), averaging of the 10 curves (right figure).

model of the shear behaviour which is constructed in the next Section will satisfy this fundamental property. It can also be seen that for the same value of the displacement, corresponding loads is uncertain, and conversely. Hence, a stochastic modelling is used to take into account these uncertainties.



3 Mean model of shear behaviour of the screwed attachment and experimental identification of the mean model parameters

The mean model of shear behaviour is constructed as an algebraic function which fits the experimental averaging curve. Denoting x the relative displacement and y the applied load, the mean model is written as

$$y(x) = a[(x+b)^\alpha - b^\alpha] \quad (1)$$

In Eq (1) a , b and α are three positive real parameters. We introduce the vector parameter $\mathbf{r}$ such that $\mathbf{r} = (a, b, \alpha)$ which belongs to an admissible subset $\mathfrak{R}$. Parameter $\mathbf{r}$ is a parameter which has to be identified using the experimental averaging curve and which will be called the identification parameter of the mean model.

Since function $x \mapsto y(x)$ must be strictly concave in $[0, x_{\max}]$ with positive values and such that the relative displacement is zero if load applied is zero, it can be deduced that for all $\mathbf{r}$ in $\mathfrak{R}$ and for all $x \in [0, x_{\max}]$,

$$\begin{cases} y(x) \geq 0 \\ y(0) = 0 \\ y'(x) = \alpha a (x+b)^{\alpha-1} > 0 \\ y''(x) = \alpha(\alpha-1)a(x+b)^{\alpha-2} < 0 \end{cases} \quad (2)$$

From Eq. (2), it can easily be deduced that parameters a , b and α have to be such that

$$a > 0, \quad b > 0, \quad 0 < \alpha < 1 \quad (3)$$

which shows that $\mathfrak{R} =]0, +\infty[\times]0, +\infty[\times]0, 1[$.

The mean model is fitted with the experimental average curve using the mean-square method solving the following optimization problem

$$\underline{\mathbf{r}} = \arg \min_{\mathbf{r} \in \mathfrak{R}} \int_0^{x_{\max}} (y(x) - \underline{y}^{\text{exp}}(x))^2 dx \quad (4)$$

where $\underline{y}^{\text{exp}}$ is the experimental averaging curve.

4 Construction of the probability model to take into account uncertainties

As explained in Section 2, the variability of the experimental result are taken into account in modelling parameters a and b by two independent random variables A and B for which the mean values are $E\{A\} = \underline{a}$ and $E\{B\} = \underline{b}$ where E is the mathematical expectation. It should be noted that the independence hypothesis of random variables A and B is justified by the fact that no information variable



concerning the statistical dependence of A and B . In addition, α is not modelled by a random variable and $\mathbf{r} = (\underline{a}, \underline{b}, \underline{\alpha})$ will be considered as an updating deterministic parameter. Consequently, deterministic Eq. (1) is replaced by the random equation

$$Y(x) = A[(x + B)^\alpha - B^\alpha] \quad (5)$$

For physical reason, Y must be a second-order random variable which means that $E\{Y^2\} < +\infty$. It can be verified that this condition is satisfied if $E\{A^2\} < +\infty$ and $E\{B^2\} < +\infty$. From Eq. (5), it can be deduced that, if the applied load y is given, then the relative displacement x becomes a random variable X such that

$$X = \left(\frac{y}{A} + B^\alpha\right)^{\frac{1}{\alpha}} - B \quad (6)$$

Identically, for physical reason, X^α must be a second-order random variable for all $\underline{a}$ in $]0, 1[$ which means that $E\{X^{2\alpha}\} < +\infty$. Such a condition is satisfied if $E\{A^{-2}\} < +\infty$. In addition this last condition implies that $E\{A^2\} < +\infty$. The available information of random variable A are then: (i) its support is $]0; +\infty[$, (ii) its mean value $E\{A\} = \underline{a}$, (iii) $E\{A^{-2}\} < +\infty$. The maximum entropy principle with this available information yields for the probability density function $p_A(a)$ of A ,

$$p_A(a) = \mathbf{1}_{]0, +\infty[}(a) \frac{1}{\underline{a}} \left(\frac{1}{\delta_A^2}\right)^{\left(\frac{1}{\delta_A^2}\right)} \frac{1}{\Gamma\left(\frac{1}{\delta_A^2}\right)} \left(\frac{a}{\underline{a}}\right)^{\frac{1}{\delta_A^2}-1} \exp\left(-\frac{a}{\underline{a}\delta_A^2}\right) \quad (7)$$

where $\delta_A = \sigma_A/\underline{a}$ is the coefficient of variation of A , satisfying $\delta_A < \sqrt{\alpha/2}$, σ_A is the standard deviation of A , Γ is the Gamma function and where $\mathbf{1}_K(a) = 1$ if $a \in K$ and $= 0$ if $a \notin K$. For the random variable B , the available information are (i) its support is $]0; +\infty[$, (ii) its mean value $E\{B\} = \underline{b}$, (iii) $E\{B^2\} = \underline{b}^2(1 + \delta_B^2) < +\infty$. The probability density function is a truncated Gaussian function written as

$$p_B(b) = \mathbf{1}_{]0, +\infty[}(b) C_0 \exp(-\lambda_1 b - \lambda_2 b^2) \quad (8)$$

where $(C_0, \lambda_1, \lambda_2)$ are the value calculated by solving the system of equations

$$\begin{cases} C_0 \int_0^{+\infty} b \cdot \exp(-\lambda_1 b - \lambda_2 b^2) db = \underline{b} \\ C_0 \int_0^{+\infty} b^2 \cdot \exp(-\lambda_1 b - \lambda_2 b^2) db = \underline{b}^2 (1 + \delta_B^2) \\ C_0 \int_0^{+\infty} \exp(-\lambda_1 b - \lambda_2 b^2) db = 1 \end{cases} \quad (9)$$

Consequently, probability density functions p_A and p_B depend only on vector $\mathbf{r}$ and on dispersion vector parameter $\delta = (\delta_A, \delta_B)$ belonging to an admissible set Δ . Parameter δ allows the dispersion induced by uncertainties to be controlled.



5 Experimental identification of parameter

As explained in Section 4 there are two types of parameters which can be identified: the updating parameter $\underline{r}$ and the dispersion parameter δ . Below these two parameters are identified by using the 10 experimental curves $y^{\text{exp}, 1}(x), \dots, y^{\text{exp}, 10}(x)$ for $x \in [0, x_{\max}]$. The identification is performed in two steps. The first one consists in calculating $\underline{r}_0$ and δ_0 as the solution of the optimization problem based on mean-squared method. The second step consists in improving this first identification using the maximum likelihood method. This non convex optimization problem is solved around the optimal points $(\underline{r}_0, \delta_0)$ using the trial method.

6 Application and experimental validation

In this section, one presents the numerical application for the parameter identification and the validation with experimental data. The parameter of the mean model for shear behaviour screw attachment between plasterboard plate and the metallic frame defined in Section 3 is identified by minimizing the cost function defined in Eq. (4). The optimal parameter obtained is $\underline{r}_0^{\text{opt}} = (\underline{a}, \underline{b}, \alpha) = (16598.73; 0.215; 0.028)$. The comparison between mean model and average experimental result is presented in the figure 3.

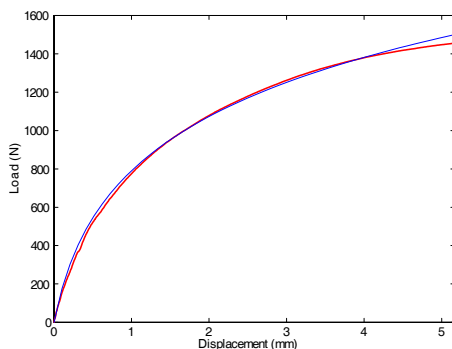


Figure 3: Comparison of the average experimental curve (thick solid line) with the mean model (thin solid line).

The stochastic model is then constructed by using Section 4. The vector-valued parameter $(\underline{r}, \delta) = (\underline{a}, \underline{b}, \alpha, \delta_A, \delta_B)$ is identified as explained in Section 5 and yields $\underline{r}^{\text{opt}} = (16210; 0.172; 0.0255)$ and $\delta^{\text{opt}} = (0.012, 0.2389)$. Figure 4 displays the confidence region for a probability level $P_C = 0.95$.



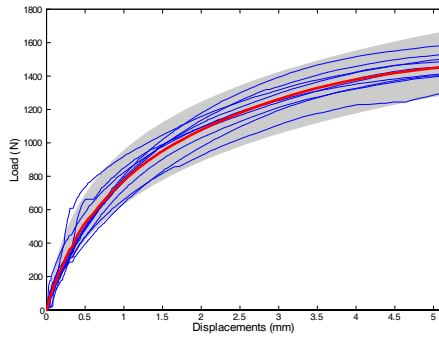


Figure 4: Maximum likelihood method. Comparison of the 10 experimental curves (ten thin solid lines) with (1) Average experimental data (thick solid line); (2) Confidence region of the optimal stochastic model (grey region).

7 Conclusion

In this paper, one has presented the construction and the experimental validation of a stochastic constitutive equation for screw-attachment. An experimental approach has been carried out to identify the shear behaviour of the attachment. A mean model then has been proposed to fit with the average experimental data. Due to data uncertainties and due to the variability of experimental data, a probabilistic model has been introduced to increase the robustness of the constitutive equation.

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Use of copper slag as a replacement for fine aggregate in reinforced concrete slender columns

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Abstract

The use of copper slag as a replacement for fine aggregate in construction will reduce damage to the environment due to the waste resulting from the copper manufacturing process and help in saving natural resources. In this research, the use of copper slag as a replacement for fine aggregate is investigated. Three slender reinforced concrete columns of 150x150x2500mm were tested for monotonic axial compression load until failure. The concrete mix included ordinary Portland cement, fine aggregate, 10mm coarse aggregate and copper slag. The ratios of copper slag to fine aggregate were 0%, 40% and 80%. Four-8mm diameter high yield steel bars were used as longitudinal reinforcement and 6mm diameter mild steel bars were used as stirrups. Three cubes, 100x100x100mm, three cylinders, 150x300mm, and three prisms, 100x100x500mm, were cast from the same mix of each specimen at the same time. Curing for the specimen and the samples was carried out using wet Hessian cloths for one week and then they were left under room temperature for about five weeks. Test results were judged by longitudinal steel strain, lateral displacement and failure load. The test results so far showed that up to 40% replacement of fine aggregate by copper slag does not have a significant effect on the load carrying capacity of the columns. Increasing the copper slag beyond this ratio accelerates the buckling, which leads to premature (before steel yields) failure load and a larger deflection.

Keywords: copper slag, fine aggregate, column, axial load, cylinder column.



1 Introduction

Aggregate is the main constituent of concrete, since it occupies more than 70% of the concrete matrix. In many countries there is a scarcity of natural aggregate that is suitable for construction, whereas in other countries the consumption of aggregate has been increased, in recent years, due to the increase in the construction industry. In order to reduce dependence on natural aggregate in construction, artificially manufactured aggregate and some industrial waste material can be used as an alternative. Since the beginning of the industrial revolution, slag, glassy materials and left over material when metals have been extracted from ores have been considered as waste. One such material is the copper slag that is produced during matte smelting and converting steps (Al-Jabri [1]).

Processed air-cooled and granulated copper slag has a number of favourable mechanical properties for aggregate use, including excellent soundness characteristics and good abrasion resistance. Some of the properties of copper slag are favourable for use as aggregate in asphalt paving applications (Queneau et al. [2]). The copper slag is generally similar to sand as far as maximum, minimum and average void ratios are concerned. The angle of friction of shearing resistance of the slag is generally higher than that of sands. This is because of angularity of the slag particles. Utilization of copper slag for applications such as a replacement for fine aggregate in concrete has the dual benefit of eliminating the costs of disposal, and lowering the cost of the concrete.

It appears that the slag can be used as a fill material; of course, slight variations in prosperities of the slag may be anticipated depending on the source (Das et al. [3]).

It has been estimated that for every ton of copper production about 2.2 ton of slag is generated and slag containing less than 0.8% copper is either discarded as waste or sold as a cheap product. Dumping or disposal of the copper slag causes environmental problems. Therefore, its use was explored by several investigators and they have utilized the slag in diversified ways, including the recovery of metal values and the preparation of value added products, such as cement, cement replacement in concrete, fill, ballast, abrasive, aggregate, glass, tiles etc (Shi and Meyer [4]).

Shoya et al [5] found no major differences in concrete compressive strength due the use of cooper slag as a replacement for fine aggregate. Resende et al. [6] reported a small reduction in concrete compressive and flexural strengths due to substitution of natural sand by copper slag. Workability was also reduced, although it stayed within reasonable limits.

Research is going on at Civil and Architectural Engineering Department, Sultan Qaboos University, to investigate the effect of partial and full replacement of fine aggregate with copper slag on the strength and behaviour of slender reinforced concrete columns. The column has a 150x150mm cross section and a length of 2500mm. The results found so far are presented in this paper.



2 Material used

Ordinary Portland cement (OPC), purchased from the Oman Cement Company, and natural fine and 10mm coarse aggregates, purchased from a nearby crusher in the Al-Khouth area, were used in this research. The copper slag was bought from the Oman Mining Company, which produces an average of 60,000 tons annually (Taha et al. [7]). Four 8mm diameter high yield bars were used as longitudinal reinforcement and 6mm diameter mild steel bars were use as stirrups with spacing of 150mm. Samples of three cubes of 150x150x150mm, three cylinders of 150x300mm and three prisms of 100x100x500mm were cast simultaneously with the specimen from the same mix. The samples were used to test the compressive and tensile strengths of the concrete. Table 1 shows the batch quantities of the mixes used for the three columns tested.

Table 1: Batch quantities.

Column No.	Water (kg)	Cement (kg)	10mm Aggregate (kg)	Fine aggregate (kg)	Copper slag (kg)
0% CS	30.8	52.2	154.3	96.8	0
40% CS	30.8	52.2	154.3	58.08	38.72
80% CS	30.8	52.2	154.3	19.36	77.44

3 Instrumentation and casting

Fig. 1 shows the steel strain gauges' labelling method. For each longitudinal bar, two strain gauges (A, B) were stuck opposite each other at the mid-span of the column. The letter (L) was used to identify the location of strain gauge, i.e. L2A means the number of the strain gauge that is stuck on longitudinal bar number 2 at location A. Two stirrups, one below and one above the mid-span of the column by 75mm, were strain gauged. Four strain gauges were stuck on each stirrup, one on each face of the column. The letters S and B/T were used to differentiate between the strain gauges, i.e. ST1 means the number of the gauge in the upper stirrup on face 1 of the column and SB4 means the gauge that is in the lower stirrup at face 4 of the column. To measure lateral deflection of the beam, a linear variable differential transducer LVDT was installed on each face at the mid-span of the column (Fig. 2). The concrete surface strain was measured using 100mm horizontal and 200mm vertical DEMEC gauges at mid-span.

After installing the steel strain gauges, the steel cage was prepared and inserted into a wooden mould. The strain gauges were numbered and casting of the specimen and the samples was carried out.



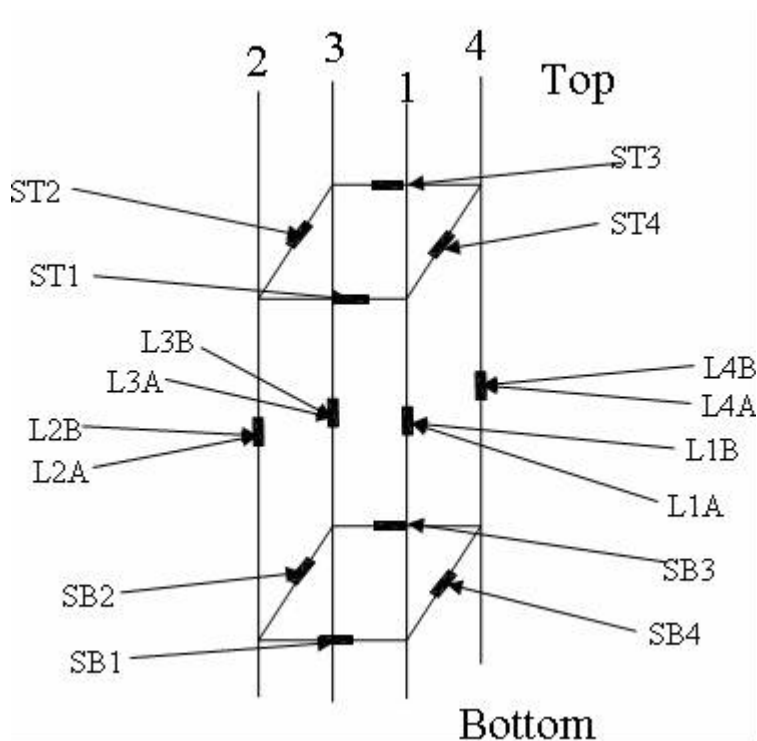


Figure 1: System of labelling the strain gauges.

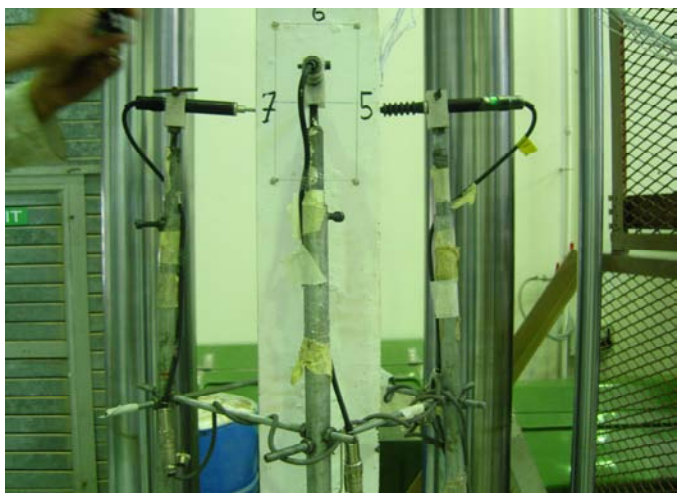


Figure 2: LVDT on each face at mid-span of the column.

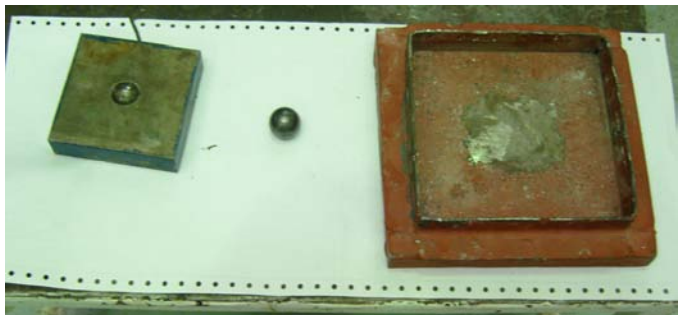


Figure 3: Base plate, ball and cap used at the bottom and top ends of the column.

Table 2: Average material properties.

Column No.	f_{cu} (N/mm ²)	f'_c (N/mm ²)	f_t (N/mm ²)	f_r (N/mm ²)	f_y (N/mm ²)	f_{yv} (N/mm ²)
0% CS	34.4	27.0	3.2	4.9	580	250
40% CS	33.9	26.3	2.9	4.3	580	250
80% CS	31.3	25.8	2.7	4.0	580	250
Average	33.2	26.37	2.93	4.4	580	250

4 Testing and results

After curing under wet Hessian cloths for one week, the specimen and the samples were left under room temperature for about four weeks before testing. The column was painted white and the DEMEC pins were fixed. The column was installed on a 5000kN DARTEC universal testing machine using a steel plate cap and a steel ball at each end to ensure the application of compressive axial load alone. Fig. 3 shows the cap and ball system used while Fig. 4 shows a typical column installed on a testing machine. The load was applied in increments of 50kN for the first three increments followed by reduced increments of 20kN until 210kN was reached and then by 10kN increments until failure. To allow for stable deformation to take place after each load increment, an interval of about one minute was used before recording the readings. The strain gauges and LVDTs were connected to a data logger while the DEMEC readings were taken manually. The cube, cylinder and prism samples were tested on the same day that the column was tested.

Table 2 shows the average cube and cylinder compressive strengths, the average cylinder splitting and prism flexural tensile strengths. It also gives the average yield strength of the reinforcement used. It is clear that a minor reduction in the concrete compressive and tensile strengths was reported due to the increase of the ratios of copper slag to fine aggregate.





Figure 4: Typical column installed on the 5000kN DARTEC testing machine.

Table 3: Failure loads of the columns.

Column No	Failure Load (kN)	L.F. Ratio
0% CS	552	0.97
40% CS	629	1.1
80% CS	472.1	0.83

4.1 Failure load

Table 3 shows the measured failure loads and the ratio of measured failure load to design load L.F. It is clear that the presence of up to 40% copper slag as a replacement for fine aggregate has resulted in some increase in the load carrying capacity. However, a high percentage of copper slag (80%) resulted in reduction



in the failure load of up to 17%. It was noticed during testing that a large presence of copper slag resulted in earlier buckling of the column, which led to earlier failure load than when the percentage of copper slag was low. The failure of the 0% CS column was more sudden with less time between the start of buckling and failure than columns with 40% and 80% CS.

4.2 Steel strain

Fig. 5 shows the ratio of the measured to yield longitudinal steel strain $\varepsilon/\varepsilon_y$ versus the measured load to design load ratios L.F. It is clear that as the percentage of copper slag increases the column stiffness decreases (more strain for same load). In spite of the lower load resisted, the steel strain in the 80% CS column reached near yield strain while less strain were recorded in the 0% CS ($\varepsilon/\varepsilon_y = 48\%$) and 40% CS ($\varepsilon/\varepsilon_y = 70\%$) before failure.

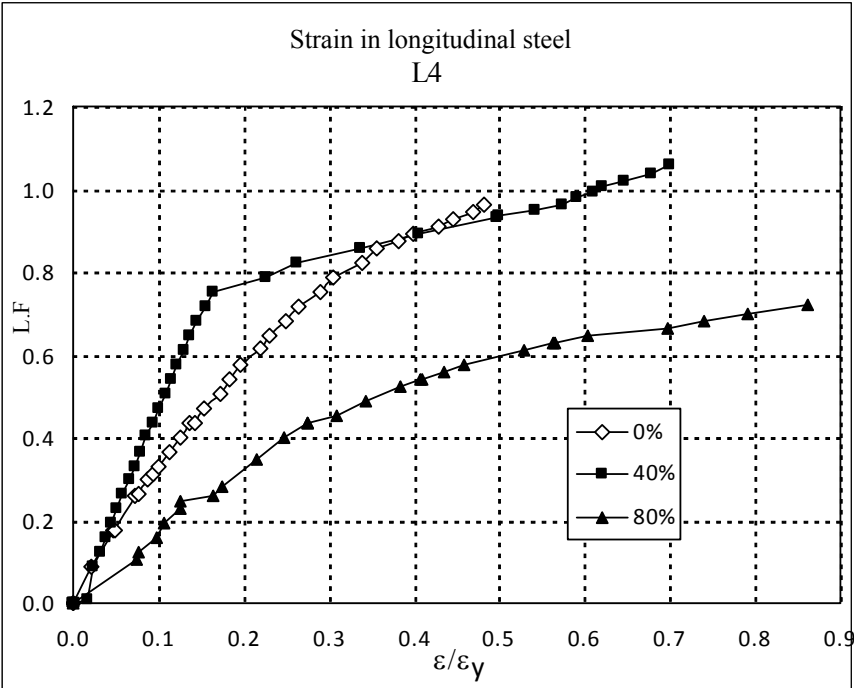


Figure 5: Strain in the longitudinal bars.

4.3 Lateral deflection

Table 4 shows the maximum measured displacement values in the four faces of the three columns with different copper slag to fine aggregate ratios. The positive values indicate extension. It should be mentioned that, for the purpose of safety, the LVDT readers were removed immediately after the signs of buckling, which



means some readings were not recorded. Fig. 6 shows a typical load versus displacement trend in the tested columns. It is clear that there were no major differences in deflection values between 0% CS and 40% CS while the 80% CS column recorded much more displacement. This indicates that the high percentage of copper slag leads to more ductile behaviour.

Table 4: Effect of copper slag on lateral displacements.

Column	Front face Disp. (mm)	Rear face Disp. (mm)	Right face Disp. (mm)	Left face Disp. (mm)
0% CS	-2.3	2.2	-0.1	0.2
40% Cs	-2.7	2.7	-0.92	1.05
80% CS	-10.2	9.8	-1.4	1.65

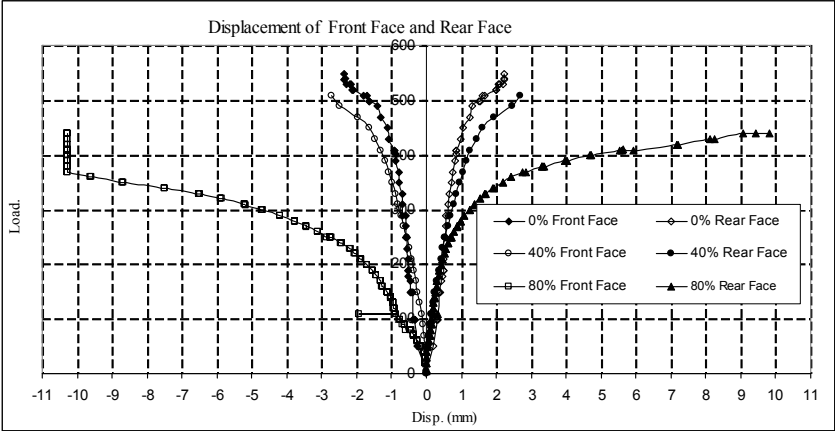


Figure 6: Typical lateral deflection in the tested columns.

5 Conclusions and recommendations

The use of copper slag as a replacement for fine aggregate is environmentally helpful due to the reduction in the waste produced from the copper manufacturing process and saving the natural fine aggregate. The results collected so far showed that increasing the ratio of copper slag as a replacement for fine aggregate reduces the column failure load and increases deflection. The difference was more pronounced in the 80% CS column. The steel in this column (80% CS) reached near yield strain, while other columns experienced lower strain ratios, which indicates that a larger load was carried by the reinforcement than the concrete in the case of 80% CS. Further study on the effect of copper slag on concrete strength, as well as structural behaviour, is needed. At Sultan



Qaboos University, tests on the concrete strengths and slender columns' behaviour, which have different percentages of copper slag as a replacement for fine aggregate, are in full swing.

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Characterization of field-dependent elastic modulus and damping in pure nickel and iron specimens using a new experimental system

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Abstract

The main objective of this work is to characterize the dependence on the applied magnetic field of both the Young's modulus (ΔE -effect) and the specific damping capacity ($\Delta \Psi$ -effect) in pure nickel and iron specimens. The high quantity of direct and indirect information they provide requires very precise and accurate results, which can be achieved by means of a recently developed experimental set-up. The experimentally measured ΔE - and $\Delta \Psi$ -effects in pure nickel and iron are in good agreement with magnetic domain theory and they show better magnetoelastic behaviour of nickel in comparison to iron.

Keywords: magnetoelasticity, elastic modulus, damping, iron, nickel.

1 Introduction

The main objective of this work is to characterize the dependence on the applied magnetic field of both the Young's modulus (ΔE -effect) and the specific damping capacity ($\Delta \Psi$ -effect) in pure iron and nickel specimens.

This kind of research in these metals has been previously developed by Chen *et al.* [1], but applied to torsional stress and measuring magnetostriction. In this work we will stress the samples axially and will focus our attention into the two significant magnetoelastic effects previously mentioned.

The reason for measuring these magnitudes lies in the high quantity of direct and indirect information they can provide: directly, both of them show the influence of the magnetic field and stress in acousto-elastic measurements and



performances of magnetic materials; indirectly, the ΔE -effect provides significant details about anisotropy and domain structure [2] and the $\Delta\Psi$ -effect can also be used as a tool for probing internal stress in ferromagnetic materials [3]. Thus, more precise and accurate results regarding these magnitudes can be valuable for researchers.

Before we start presenting the achieved results it is advisable to properly define the magnitudes we desire to characterize in this work. Regarding the ΔE -effect, when tension is applied to any ferromagnetic sample, two different types of deformations appear: elastic (ε_{ll}), fully described by Hooke's law, and magnetoelastic (ε_{ml}), an additional strain caused by the constitution of its magnetic domains [4]. Hence, the Young's modulus for a specific applied magnetic field will be called E_H , so the complete ΔE -effect is described in terms of the ratio

$$\frac{\Delta E}{E} = \frac{E_S - E_D}{E_D} = \frac{\varepsilon_{ml}}{\varepsilon_{ll}} \quad (1)$$

with E_D and E_S being the demagnetized and saturated Young's moduli, respectively. The $\Delta\Psi$ -effect requires a more careful explanation. If we take into account the fact that macroscopic and microscopic eddy currents only influence damping of ferromagnetic materials for frequencies on the order of 300kHz or higher [4], the full damping will be given by magnetomechanical hysteresis losses. This term depends on both the amplitude of the oscillation and the applied external magnetic field, but it is independent of frequency. So, the specific damping capacity for a specific magnetic field and stress will be called $\Psi_{H,\sigma}$, which lets us describe the $\Delta\Psi$ -effect for a constant stress σ in terms of the ratio

$$\frac{\Delta\Psi_\sigma}{\Psi_\sigma} = \frac{\Psi_{S,\sigma} - \Psi_{D,\sigma}}{\Psi_{D,\sigma}} \quad (2)$$

with $\Psi_{D,\sigma}$ and $\Psi_{S,\sigma}$ being the demagnetized and saturated specific damping capacity for such stress σ .

2 Experimental set-up

Pure crystalline bars of iron and nickel were obtained from the Godfellow Corporation. Their purities, sizes and other relevant data can be found in Table 1.

Table 1: Information about the tested specimens.

Material	Purity (%)	Length (mm)	Diameter (mm)	Density (kg/m ³)
Iron	99.99	100	6	7874
Nickel	99.90	110	10	8912



The field-dependent elastic modulus and specific damping capacity of these materials were obtained by means of a novel experimental system for automatic measurement based on laser Doppler vibrometry, which also makes it possible to include stress-dependence studies. This experimental system, which is depicted in the sketch of the fig. 1, was developed by Morales and recently published in [5].

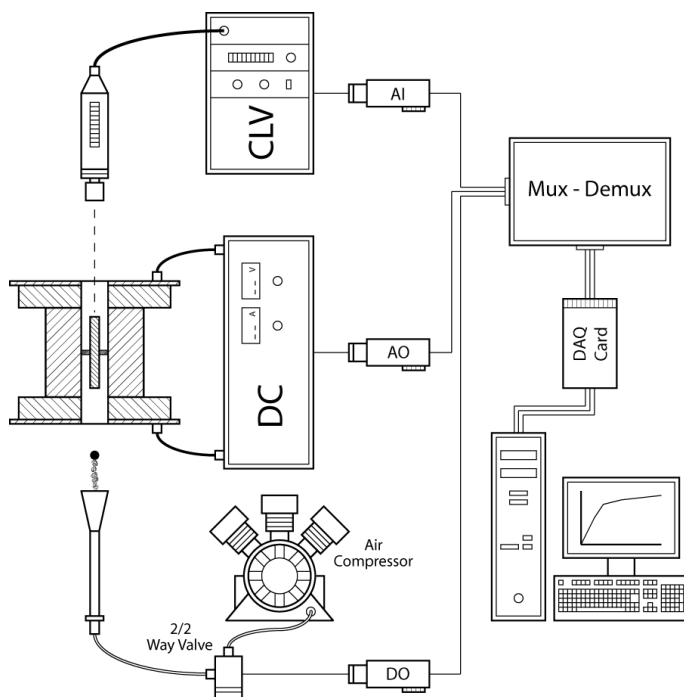


Figure 1: Sketch of the experimental system developed by Morales *et al.* [5].

Basically, the ferromagnetic samples are magnetized by a solenoid in whose inner space the specimen is placed. This solenoid combines both a straight coil and a pair of Helmholtz coils, which compensate for the inhomogeneity of the straight component. In order to generate the magnetic field necessary to achieve the desired magnetization throughout the sample, a dc supply feeds the appropriate current intensity. The exciting system is responsible for generating an automatic free longitudinal oscillation in the specimen: it consists of a barrel in which a lead pellet is placed, while a 2/2 way valve and a relay regulate the necessary compressed air flow for the shot. On the other hand, the basis of the measuring system is a Polytec compact laser vibrometer based on LDV technology (laser Doppler vibrometry) which points a 70MHz He-Ne laser beam on the vibrating surface. Finally, input and output signals are handled with National Instruments acquisition devices, which are controlled by a generic

laptop using a Matlab environment. More details of this experimental set-up are given elsewhere [5].

Indeed, some minor features have been enhanced for the measurements shown in this work. They are listed below:

- i. A new data acquisition device with a higher sample rate has been used in order to improve the signal resolution and to obtain a more accurate estimation of the material damping within a short portion of the signal (in which the stress is considered constant). In particular, we have used a National Instruments USB-6289 (mass term), which is able to measure 625kS/s.
- ii. The Hilbert transform has been implemented in the software in order to obtain the instantaneous amplitude of the time response of the specimen, i.e., its envelope. Using this method instead of the less sophisticated one, which was based on peak detection, we have increased the accuracy of the experimental system, especially regarding damping measurements.

Next, the results about the ΔE - and $\Delta \Psi$ -effects in pure iron and nickel will be shown and discussed, always taking into account the eventual influence of stress on them.

3 Experimental results

3.1 ΔE -effect

Although it is known that elastic modulus can be stress-dependent in ferromagnetic materials due to its inherent magnetomechanical coupling [4], the definition of the ΔE -effect stated in section 1 did not include any reference to such stress-dependence effects. This fact is due to the reduced level of stresses that is induced to the ferromagnetic specimen during our tests, always lower than 1.0MPa.

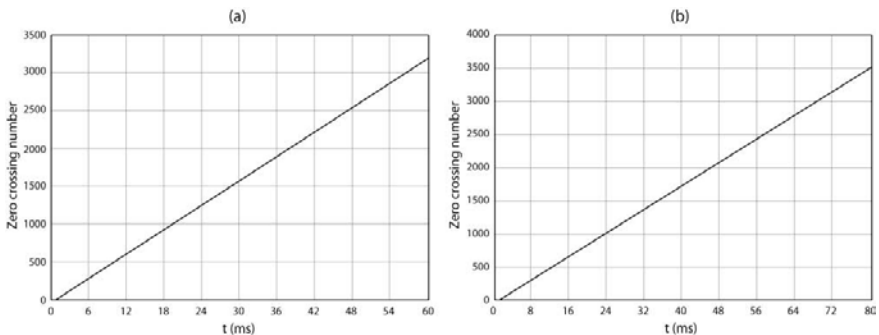


Figure 2: Zero crossing number vs. time for the time responses of iron (a) and nickel (b) (solid line: experimental results; dashed line: fitted curve).



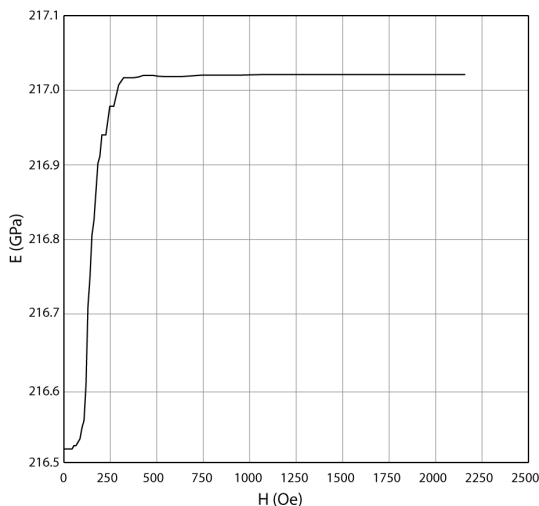


Figure 3: ΔE -effect in pure iron.

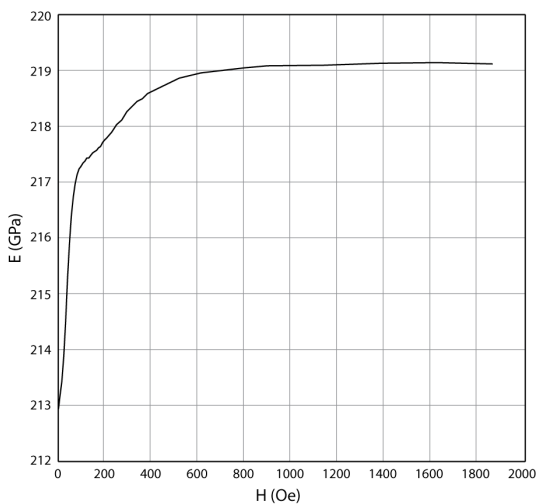


Figure 4: ΔE -effect in pure nickel.

Anyway, such hypothesis can be demonstrated by looking at fig. 2, which shows the zero crossing number distribution along the time, i.e., how frequent the time response of the vibration crosses zero. If the trend of the zero crossing number is linear, it means that the frequency of vibration is not dependent of the strain and therefore neither is the Young's modulus. In fig. 2 we can see that the linear fitting curve is perfectly superimposed to the experimental zero crossing number for the time responses in iron and nickel. The factor R^2 , which measures the goodness of the fitting process, is on the order of 0.999999 in both cases, i.e., practically the unit.



Next, figs. 3 and 4 show the ΔE -effect in iron and nickel, respectively. In both cases, two zones can be detected: an initial stage of rapid growth that belongs to the low magnetic field range (less than 250Oe in iron and 150Oe in nickel), and the second stage of slow growth until saturation. These results agree with the magnetic domain theory. Low magnetic fields lead to easy displacements of domain walls, whereas high ones imply the saturation of the sample in a single magnetic domain and the appearance of an upper limit that corresponds to the value of the Young's modulus if the material were nonmagnetic [6].

Table 2 shows the more significant numerical results regarding the ΔE -effect. It is clear that higher variations in elastic modulus via application of magnetic field are achieved in nickel.

Table 2: ΔE -effect results for pure iron and nickel.

Material	ΔE (GPa)	ΔE (%)
Iron	0.50	0.23
Nickel	6.21	2.93

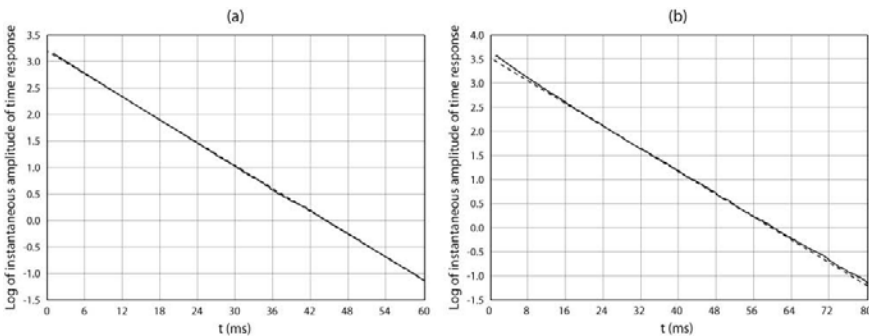


Figure 5: Logarithm of instantaneous amplitude vs. time of iron (a) and nickel (b) (solid line: experimental curve; dashed line: fitted curve).

3.2 $\Delta\Psi$ - effect

Unlike in the case of the ΔE -effect, the $\Delta\Psi$ -effect is highly dependent on stress. So, while measuring damping in ferromagnetic materials, this effect must be taken into account. In particular, the specific damping capacity of the material was measured within short portions of the time response where the stress or strain could be assumed constant ($\pm 10\%$ of variation). This procedure is detailed in Morales' recent work [5], although the initial idea is due to Atalay and Squire in their work [7].

Similarly to fig. 2, fig. 5 tries to demonstrate the influence of stress on the material damping. In this case we plot the natural logarithm of the instantaneous amplitude of the time response along the time, which is directly related to the



logarithmic decrement simply by dividing the slope of the curve by the oscillation frequency of the signal. So, if the material damping is dependent on the strain of the time response, the curve must not fit properly to a line. In fig. 5 we can see that the linear fitting curve is not as exact as in the case of the elastic modulus. In particular, the factor R^2 , which measures the goodness of the fitting process, is now on the order of 0.9999 and 0.999 in iron and nickel respectively. This fact demonstrates the stress-dependence of the specific damping capacity, but such influence is expected to be minute in our range of stress.

Next, figs. 6 and 7 show the $\Delta\Psi$ -effect in iron and nickel, respectively. Again one observes two different zones in the specific damping capacity curve: an initial rising stage that corresponds to the low applied magnetic field range (less than 250Oe in iron and 150Oe in nickel), and the second declining stage until saturation. This special trend can be again explained thanks to the magnetic domain structure of ferromagnetic materials. In the first stage of magnetization the damping increases as domain boundaries move irreversibly, whereas the second declining stage starts when the applied field is strong enough to suppress domain walls (by means of domain rotations) and make the specimen behave like a non-magnetic material [6].

Table 3 shows the more significant numerical results regarding the $\Delta\Psi$ -effect. It is clear that higher variations in specific damping capacity are achieved in nickel.

Another way of studying the influence of stress on the $\Delta\Psi$ -effect consists of estimating the exponent n of the Lazan's expression for mechanical losses [8]:

$$\Delta W = J\sigma^n \quad (3)$$

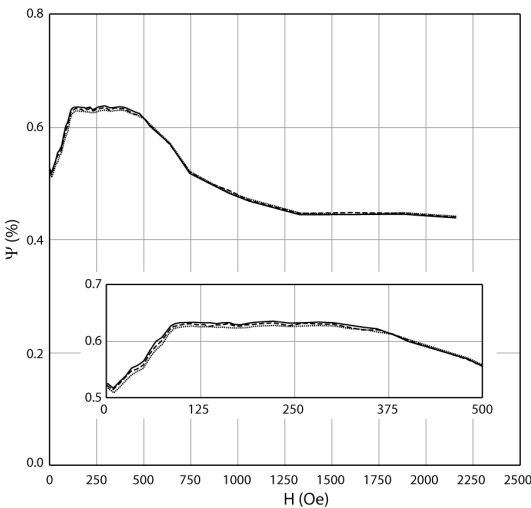


Figure 6: $\Delta\Psi$ -effect in pure iron (solid line: 0.75MPa; dashed line: 0.50MPa; dotted line: 0.25MPa).



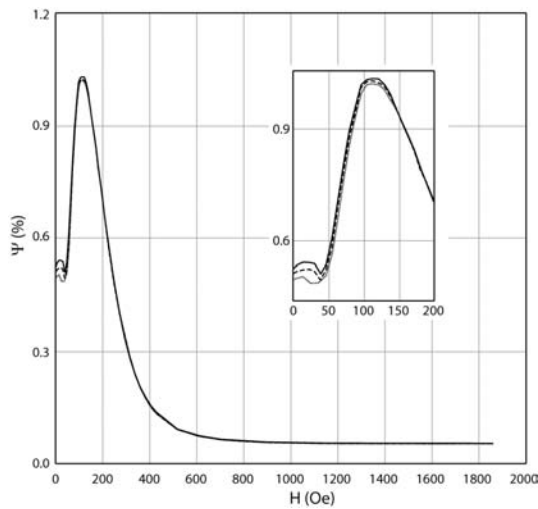


Figure 7: $\Delta\Psi$ -effect in pure nickel (solid line: 0.75MPa; dashed line: 0.50MPa; dotted line: 0.25MPa).

Table 3: $\Delta\Psi$ -effect results for pure iron and nickel.

Material	$\Delta\Psi$ (%) (increasing stage)	$\Delta\Psi$ (%) (decreasing stage)	$\Delta\Psi$ (%) (total)
Iron	0.109	-0.201	-0.092
Nickel	0.507	-0.976	-0.469

When ferromagnetic materials are considered, parameters J and n are not constant but they depend on both stress and magnetic field [9, 10]. Indeed:

$$\Psi_{H,\sigma} = \frac{\Delta W_{H,\sigma}}{W_{H,\sigma}} = \frac{J_{H,\sigma} \sigma^{n_{H,\sigma}}}{\sigma^2} = 2E_H J_{H,\sigma} \sigma^{n_{H,\sigma}-2} \quad (4)$$

This expression means that the specific damping capacity of the material becomes independent of stress when the exponent n is equal to 2.

The evolution of the exponent n of Lazan's expression for iron and nickel can be seen in fig. 8. Regarding iron, such exponent stays almost constant in a value of 2, which means that the specific damping capacity is the same for the three tested stresses and any variation is mainly due to measurement uncertainties. Regarding nickel, the exponent n seems to be slightly higher than 2, which means that little differences exist between the specific damping capacities of the three cases considered. In any case, the higher the applied magnetic field is, the smaller the dependence on stress is, because high magnetic fields make the sample saturate and behave like a non-magnetic material [6].



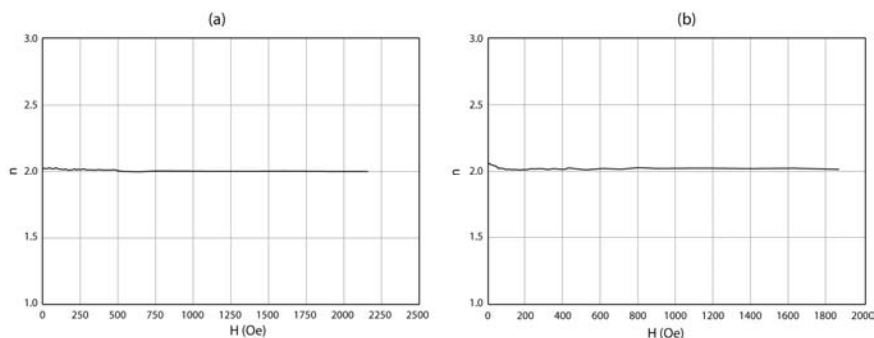


Figure 8: Field-dependence of exponent n for iron (a) and nickel (b).

4 Conclusions

In conclusion, the results shown have been obtained via a new experimental system which offers significant capabilities such as lack of interaction with the sample, non-destructive automatic and fast characterization, high accuracy and resolution in magnetic field, and the possibility of including stress-dependence studies.

In particular, qualitative and quantitative results show better magnetoelastic behaviour of nickel in comparison to iron since they offer higher ΔE - and $\Delta\Psi$ -effects. Furthermore, all results are in good agreement with magnetic domain theory.

Finally, the influence of stress on magnetoelastic results have been studied for three different values: 0.25MPa, 0.50MPa and 0.75MPa. Regarding ΔE -effect, results support the hypothesis of considering the elastic modulus independent of stress within our range of work. Regarding $\Delta\Psi$ -effect, results agree with the predicted stress-dependence but the stresses studied are so close that differences result minute.

Acknowledgement

This work was supported by the Consejería de Educación y Ciencia (Junta de Comunidades de Castilla-La Mancha, Spain) under Project PCI08-0082 "Análisis y diseño de elementos activos para el control de vibraciones".

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Experimental determination of representative elementary volume of sands using X-ray computed tomography

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Abstract

The concept of a representative elementary volume (REV) provides an effective means of developing macroscopic measures in the description of granular materials. However, due to the difficulties associated with the measurement and characterization of granular microstructure the existence and size of an REV has remained largely conjectural. This study presents a systematic method to examine the characteristics of the REV using X-ray computed tomography images. The 3-D images of Silica sand, and Ottawa sand have been characterized using advanced image processing techniques. The porosity variation of Silica sand and Ottawa sand showed three characteristic regions: an initial fluctuation region due to microscopic variations, a constant plateau region, and a region with a monotonic increase/decrease due to heterogeneity. The results show that for Silica sand composed mainly of elongated particles the REV is between 5 to 11 times of D50 and for Ottawa sand composed mainly of subrounded particles is between 9 to 16 times of D50.

Keywords: representative elementary volume (REV), porosity, X-ray computed tomography (X-ray CT), 3D image processing.

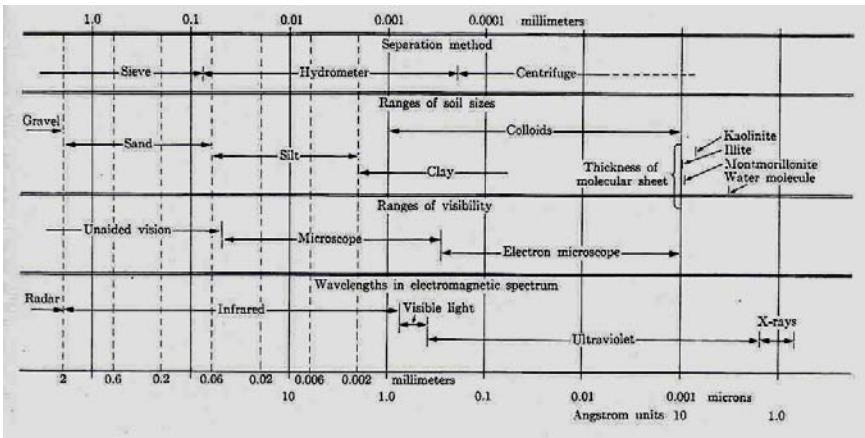
1 Introduction

The methods of continuum mechanics have provided an effective means of predicting the behavior of the collection of a large number of elements. The



fundamental continuum hypothesis is that the behavior of many physical elements is essentially the same as if they were perfectly continuous. Physical quantities such as mass and density, associated with individual elements contained within a representative elementary volume (REV) are regarded as being spread over the volume instead of being concentrated on each particle or element. Macroscopic variables are defined typically as averages of microscopic variables over a REV. Literature is jamming of many recent treatises used the above argument [1–6], however, the difficulties associated with the measurement and the characterization of granular microstructure had prevented the identification of the size of REV in real media. In the absence of experimental measurements, the minimum dimensions of the REV are set by the grain size with the best guess being the REV is between 100 to 1000 grain diameters. For sandy soils, a REV with a radius of 10 to 20 grain diameters appears to have been adequate for obtaining well defined average for applications in ground water flow [7]. Customarily, the grain diameter of sand is measured using sieve analysis. The classifications of grain size measurement in sand in relation to other physical measurement are shown in table 1 [8].

Table 1: Classification of soil size in relation to other physical measurements [13].



This study makes use of the current advances in microstructure characterization to accurately quantify the characteristics of REV of sands. High resolution X-ray computed tomography is used to obtain 3D images. These images are post processed using robust algorithms, and the variation of the porosity within a spherical volume element is studied.

1.1 X-ray computed tomography

X-ray computed tomography (X-ray CT) is a nondestructive technique that provides 3-D images of density distribution of specimens. Figure 1 shows the different parts of an industrial X-Ray CT system. Its main components include a



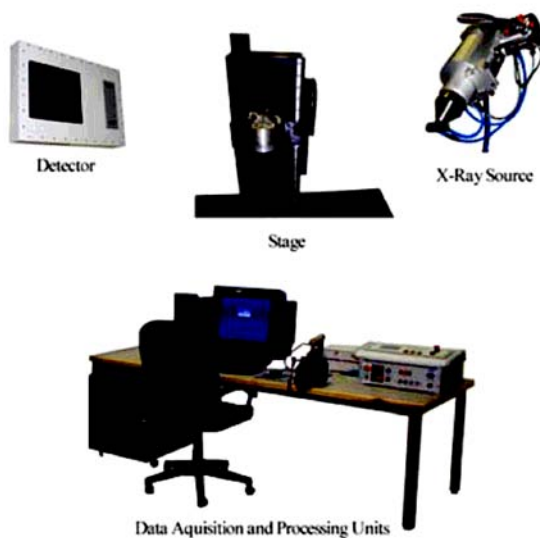


Figure 1: Main components of an industrial X-ray CT system.

radiation source of X-ray, a sensitive detector to X-ray, a precision rotary stage, a data acquisition unit, and a processing unit. The specimen is placed on the rotary stage between the X-ray source and detector. The stage rotates in several small steps to complete a full circle of rotation. The intensity of the X-ray on the detector or the projected image of the specimen on the detector at each step is saved as a digital image or a digital radiograph. The CT image slices are reconstructed from the digital radiographs [9]. The density distribution across the cross section of slices are reconstructed from the set of projection images (radiographs) using Radon transformation. This transformation is fundamental to X-ray CT reconstruction algorithms [9]. Spatial resolution, a measure of the ability of the X-ray CT system to separate and distinguish the minute details, depends on many factors such as the X-ray tube type and detector resolution. A CT image is the representation of the distribution of the point-by-point linear attenuation coefficients within the slice. These coefficients depend on the physical density of the material, its effective atomic number, and the X-ray beam energy. X-ray CT image is highly sensitive to differences in density; a difference of less than 1% in density is sufficient to separate objects. Voxels, the box-shaped volumes defined by the area of the pixel and the height of the slice thickness, form the 3-D CT image [10].

CT slices are stacked at equal distances on top of each other and the voxel value of the space between two successive reconstructed slices is linearly interpolated. The X-ray CT images are gray scale images in which normally white and black colors correspond to the highest and lowest densities, respectively. Figure 2(a) shows a two-dimensional CT slice of silica sand and

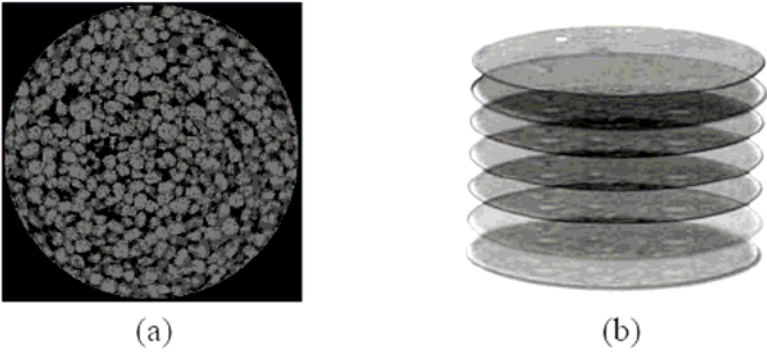


Figure 2: (a) A 2-D CT slice of silica sand; (b) A pile of 2-D CT slices to generate a 3-D CT image.

Fig. 2(b) shows how a three-dimensional CT images is generated by a pile of two-dimensional CT slices.

The CT scans for this study were done at the Washington State University high resolution X-ray computed tomography laboratory (www.waxct.wsu.edu). The facility consists of a flat panel amorphous silicon high-resolution computed tomography or FlashCT. FlashCT at WSU is a hybrid system with two different X-ray sources, 420 keV, and 225 keV micro-focus housed within a single chamber. Micro-focus X-ray source takes advantage of an electromagnetic field and a vacuum pump around the X-ray outlet to reduce the focal spot size. Minimum focal spot size of this source is 5 μm at 60 watts, which provides a spatial resolution down to 5 μm , and maximum operating energy of this tube is 225 keV. The micro-focus source was used for this study to obtain the highest possible resolution.

2 Materials and methods

Specimens were prepared from Ottawa and silica sands. The shape of the particles of Ottawa sand is composed mainly of subrounded particles, and that of silica sand is composed mainly of elongated particles. Specific gravity of Ottawa and silica sands are 2.65 and 2.7 respectively.

Table 2: Scan parameters of the specimens.

Specimen	<i>E, keV</i>	<i>I, mA</i>	Image Resolution, $\mu\text{m}/\text{pixel}$	Image Size, <i>voxel</i>
SS-1	160	0.284	40.0	675×671×672
SS-2	160	0.284	39.7	680×679×500
SS-3	160	0.284	39.8	675×678×500
OS-1	160	0.284	39.5	683×679×500
OS-3	160	0.284	39.5	679×683×500
OS-4	160	0.284	39.6	682×682×500

Six cylindrical specimens of both dry silica sand (SS-1 to SS-3) and Ottawa sand (OS-1 to OS-3) with different porosities were prepared in the laboratory. They were compacted in five layers by tamping on the sides of the plastic mold. All of the specimens were scanned using X-Ray CT following [11], ASTM E 1441-00, and their 3D images obtained. Table 2 shows the CT scan parameters, image resolution, and number of voxels for each specimen in the study.

3 REV and image characterization

An interactive computer program, M-REV, was developed in MATLAB environment to perform the analyses on the 3D CT images. First, the 3D CT image is read and stored as a 3D array so that the reconstructed CT slices show the top view of the specimen. If necessary the gray scale values of the voxels can be rescaled to spread the histogram of the gray scale values between 0 and 255. This is called histogram equalization for intensity adjustment. In most cases, CT slices contain some noise on the image background, which tends to propagate a significant error in processing. User can specify the outer boundaries of the specimen in the program to remove background noise.

In the next step, the image is converted to a logical image (black and white image or BW image) using a threshold value. In this study, the method proposed by [12], which chooses the threshold to minimize the interclass variance of the black and white pixels, was applied to find the best threshold to convert the image to a logical image. It is noted, however, that the user can manually choose a desired threshold between 0 and 255 to separate the features by looking at the image histogram and visual inspection. However, the use of a threshold alone does not separate the grain boundaries very well. Therefore, another advanced image processing technique called watershed transform [12, 13] with gradient is applied to segment or separate the contact points of particles. The watershed transform applies the same idea as in geography for segmentation of the gray scale images. Watershed ridgeline is the line, which separates the two connected objects. In order to apply watershed transformation to binary images, first a transformation of the distance from every pixel to the nearest nonzero valued pixel is calculated. Once the distance transformation of the image is determined, then watershed transformation is applied. In some cases, even with the use of watershed transform the boundaries of the particles may not be clear. For such cases, application of a gradient prior to using the watershed transformation is recommended. In the gradient method, the image is filtered by a 3x3 Sobel mask, which approximates vertical or horizontal gradients of the image [13]. In case of over-segmentation due to watershed transform in which many grains have been segmented around the boundaries and inside, the method of regional minima is applied to remove the unnecessary segmentation within the grains [13].

The REV program chooses a spherical volume element whose center can be fixed anywhere within the specimen (fig. 3). Once the location of the center is fixed, the radius of the sphere is increased from zero to its maximum limited by the specimen boundary. The variation of porosity with the radius of volume element is plotted for each incremental step of the spherical radius.



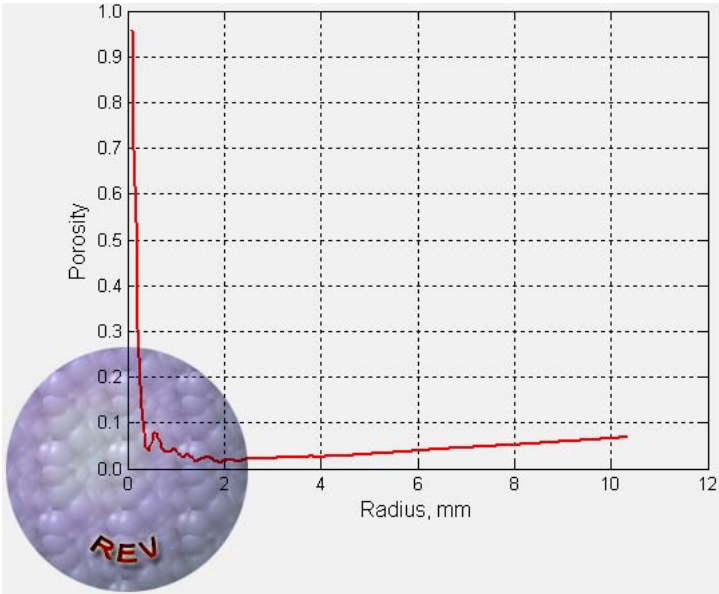


Figure 3: A sample plot of variations of porosity versus the radius of the spherical volume element.

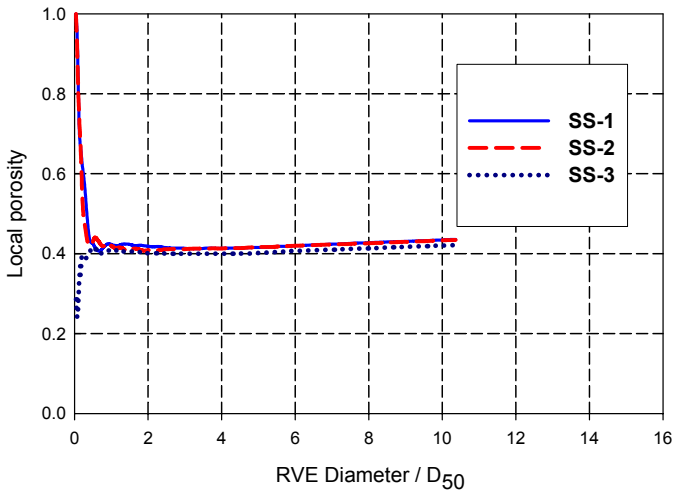


Figure 4: Normalized REV range to D_{50} for silica sand specimens.

In REV program, the user can examine the images from three different viewpoints; top, front, and right. The user can zoom (in or out) the images, find the location of each plane, the gray scale value of any voxel, and distance



between different objects on images. The output results are saved in MATLAB, and can also be exported to spreadsheet.

4 Results and discussion

The variation of porosity, $n=V_v/V_T$ where V_v the volume of voids and V_T the total volume, versus the normalized radius of the spherical volume element with respect to main grain diameter, D_{50} , for the three silica sand specimens is shown in Fig. 4. It can be seen that the variation of the porosity of all three specimens show three distinct regions; a segment with fluctuation part at the beginning, a constant segment in the middle and a monotonically increasing segment at the end. It is also evident that the boundaries of the region are nearly the same in all of the specimens. The same trend is evident in the case of Ottawa sand (Fig. 5) although the region III in these two materials has both an increase and a decreasing trend.

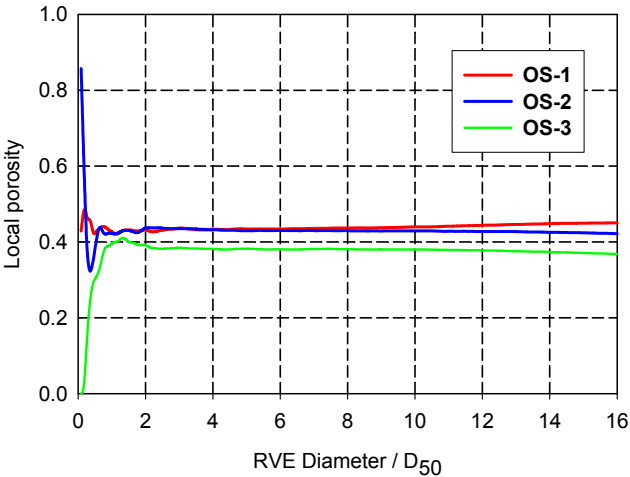


Figure 5: Normalized REV range to D_{50} for Ottawa sand specimens.

Figure 6 shows the plot of variation of porosity respect to the normalized radius of the spherical volume element for two selected specimens of silica sand (SS-3) and Ottawa sand OS-1). It can be seen that the REV radius for Ottawa sand is formed with more grains with a diameter of D_{50} . The ranges of representative elementary volume radius for all specimens are summarized in table 3. Comparison those ranges with D_{50} of sand specimens show that the ratio of the REV radius to D_{50} is about 5 to 11 times of for silica sand, and 9 to 16 times for Ottawa sand.

The last column of table 3 shows the comparison of the porosity obtained from image processing (n_{ip}) and the laboratory measured values (n_{lab}). The values compare very well. It is noted, however, that the relative error is much



higher in Ottawa sand. This sand had finer grains and although the size of the finest grains of Ottawa sand specimen was more than the resolution of CT image less number of pixels is used to form the image in sands with finer grains for a given magnification. This problem tends to propagate the error in processing the images and results in a higher relative error. Smaller specimens with higher magnification will reduce such error but the processing is limited by available memory.

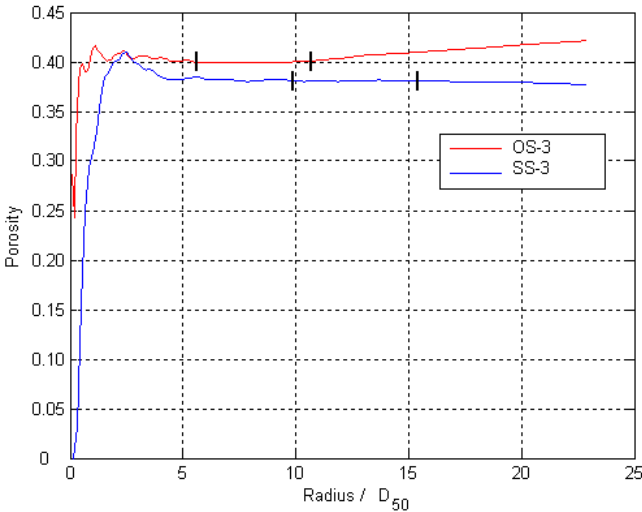


Figure 6: Normalized REV range to D_{50} for (SS-3) and (OS-1).

Table 3: REV radius and relative errors.

Type	Specimen	R_{REV} Range, mm	R_{REV}/D_{50} Range	n_{ip}	n_{lab}	% Error
Silica Sand	SS-1	[2.54, 3.34]	[5.6, 7.4]	0.454	0.462	1.73
	SS-2	[3.04, 4.66]	[6.7, 10.3]	0.412	0.405	-1.73
	SS-3	[2.54, 4.83]	[5.6, 10.7]	0.401	0.401	0.00
Ottawa Sand	OS-1	[2.63, 3.80]	[9.9, 15.4]	0.379	0.419	9.55
	OS-2	[2.44, 3.64]	[9.9, 14.8]	0.429	0.412	-4.13
	OS-3	[2.23, 2.73]	[9.1, 11.1]	0.435	0.451	3.55

5 Conclusions

This study presents a systematic technique to determine the size RVE of granular materials. It makes use of the X-ray computed tomography imaging techniques to determine the RVE for almost any granular material. 3-D CT images of Silica and Ottawa sands specimens, compacted in small cylindrical molds, were obtained. A 3-D interactive image processing program was developed to process the 3-D CT images to determine the local porosity variation. Comparing the



local porosity variation obtained from the X-ray computed tomography imaging techniques with an average porosity of the sample obtained in the conventional laboratory tests enable us to determine the RVE. The REV radius for silica sand composed mainly of elongated particles is between 5 to 11 times of D_{50} , and for Ottawa sand composed mainly of subrounded particles is between 9 to 16 times of D_{50} .

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Short-time test for evaluating the machinability of alloys

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Abstract

Machinability is an important property of materials, especially because it affects the manufacturing cost of products. Since there is no accepted definition of machinability, there is no accepted test for measuring it. Researchers have studied two dimensional cutting forces, chip thickness, using orthogonal cutting models, others have concentrated on comparing three dimensional cutting forces, surface roughness and power consumption in oblique cutting. All these tests converge in the necessity of determining which material has better machinability. In this paper machinability tests by other authors are reproduced, proper modifications are made, to visualize which test should be considered and which to discard in the measurement of machinability.

Keywords: cutting force, thrust force, surface roughness, cutting temperature, orthogonal cutting, emissivity, chip morphology, dynamometer.

1 Introduction

Machinability is a measure of ease with which a work material can satisfactorily be machined. The machinability aspect is of considerable importance for production engineers so that processing can be planned in an efficient manner [1]. The expenses for removing material from a workpiece during a manufacturing process reach more than US\$100 billion yearly in the United States and only four machining processes are responsible for 75% of this value



which are turning, drilling, milling and grinding [2]. Since there is no universally accepted methodology for evaluating machinability and numerous new materials enter the market every year, many manufacturers are encountering difficulties in selecting the most appropriate material for their products [1].

Machinability takes into account many variables, such as tool life, cutting forces, specific power consumption, surface finish, temperature generated, noise and chip characteristics. Tool life has been the classical machinability test for many years. This article presents a different approach.

2 Literature review

Some investigators developed orthogonal tests for measuring machinability, chip thickness, shear planes, two dimensional cutting forces, Merchant circle, tool life and tool wear analysis are made using cylindrical samples. Özel and Kapart [3] propose finite element methods to predict cutting forces, stresses and cutting temperature based on orthogonal cutting data and a work material constitutive model. The results are close to the experimental data in different cases which shows a powerful tool for two-dimensional machining predictions. Unfortunately just a few industrial processes are orthogonal major machining process are oblique.

Thiele et al. [4] presented ASTM E618 test accelerated with harder tools, to compare machinability of brass, aluminium and steel. Dabade and Joshi [5] measured undeformed chip thickness and chip thickness and uses shear plane relation to establish the differences in Al/Si composites with different particle size. Vilarinho et al. [6] perform three dimensional force measurement under one cutting condition, 27 different brass alloys are tested relations between hardness, roughness, cutting forces and chemical compositions are shown.

Dasch et al. [7] realized drilling test on aluminium with lead, bismuth, tin, and indium as alloying elements, in this research spindle power is measured, also cutting temperature is recorded by a thermographic camera. Pereira et al. [2] show a tool wear analysis for evaluate the effect of sulphur in gray cast iron, tool life criteria is 0.3 mm of flank wear, this work compares the tool wear vs. cutting time, for three gray cast iron alloys with different sulphur content, cylindrical samples were used.

Fang and Wu [8] compared two dimensional cutting forces in high speed machining of T6Al4V and Inconel 718 experiment consist in five cutting speeds and four feed rates. The results compare these two alloys under same cutting conditions and set-up, a total of twelve empirical regressions relations between cutting forces, feed forces and force ratio are presented. Arrazola et al. [9] analyzed Ti555.3 and Ti6Al4V under tool wear criteria for machinability, tool wear vs. cutting velocity is shown, the feed rate and depth of cut is constant varying cutting speed from 40 m/min to 90 m/min. Tool life criteria is based on 0.3 mm of flank wear. Chip morphology is visualized under microscope finding adiabatic shear bands in the chips. Ebrahimi and Moshksar [10] compares the machinability of microalloyed steels (30MnVS6) and quenched-tempered (QT) steels (AISI 1045 and AISI 5140). A turning test was made over cylindrical



specimens two-dimensional cutting forces are measured; chip analysis and chip/contact length is calculated.

Lopez [13] performed a temperature analysis in aluminium 6063 alloy during milling, an infrared thermometer is used, and data is recorded and exponential fit is obtained from the lectures.

3 Experimental procedure

The experimental plan and setup is presented for each test; the purpose is to try the most of the tests included in the literature by others researchers, to demonstrate which are more significant for machinability measurement. We intended to compare the experiments developed by others researches instead of comparing their results. All the samples were melted in a medium frequency induction furnace, a tilt casting process using copper-nickel permanent mold with graphite coating was used for obtaining the solid bar samples, 150 mm long and 30 mm diameter, samples consist in the same base alloy CuZn38 just varying 1% of composition with alloying elements, samples are denominated A1, B2, C3, D4. Samples chemical composition is been review for patent possibility, so no composition is presented. For the objective of this study no composition is needed just know that samples are distinguishable.

3.1 Roughness test

The experimental plan for surface roughness was laboured in a HAAS SL-10 CNC Lathe, since feed is the most relevant factor a first experiment for 8 levels of feeds are developed at two cutting speeds over a 60 mm cutting length, with 3 replicas for each cutting condition is realized. In this experiment feed speed (mm/seg) as primary variable instead of feed rate (mm/rev) because feed speed

Table 1: Roughness experimental plan.

Experiment #1			Experiment #2	
Feed velocity (mm/seg)	Cutting velocity 1 (m/min)	Cutting velocity 2 (m/min)	Feed rate (mm/rev)	Cutting velocity (m/min)
2	59	94.5	0.1172	94.5
2.5	59	94.5	0.1406	94.5
3	59	94.5	0.1641	94.5
3.5	59	94.5	0.1875	94.5
4	59	94.5	0.2109	94.5
4.5	59	94.5	0.2625	59
5	59	94.5	0.2667	66
5.5	59	94.5	0.27	73.8
			0.3	59
			0.3375	59



compare the surface roughness with the machining time, for industrial processes this parameter affects the production rate and is never included in machining tests. The second experiment compares the feed rate with the R_a . In this experiment lubricant is used because thermal energy released from the cut modifies the surface characteristics. The tool used for this experiment was a cemented carbide insert DNMG 150408 NN grade LT-10. The arithmetic value of roughness R_a is measured with a Mitutoyo profilometer, model 178-293-2A, series 500153, the measure temperature is 19°C - 21°C, the relative humidity 40%-60%, the standard used is JIS'94, the cut-off is 0.8 mm x 5, the evaluation length is 4 mm.

3.2 Chip morphology test

During the roughness test chips from different conditions were collected. The chips collected are dried, cold mounted in acrylic resin, polished and chemical attacked to reveal microstructure using an optical microscope qualitative characteristics are observed. For slow feeds semi-long curl chips are formed, and for high feeds segmented toothed chips were formed. Because it is not an orthogonal cut we are not interested in measure chip thickness and made relations. Optical micrographs are taken, and important characteristics are measured using an image analyzer.

3.3 Power consumption test

Power turning test was improved in a conventional lathe by measuring the current increment in one phase of the lathe motor at one fixed cutting condition. The current was read exactly before the cut starts and during the middle of the cut. The lathe used was an Emco Maximat V13, with a 220 VAC motor, 60 Hz, 9 amps and 0.83 of power factor. The fixed parameters of cut were 1180 RPM, 0.225 mm/rev, depth of cut 2.7 mm and the length of cut was 66.3 mm, no lubricant was used, balanced phases of the motor are assumed.

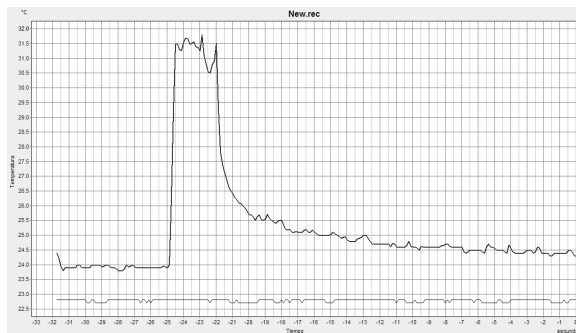


Figure 1: Temperature measured for 80 m/min, 0.3 mm/rev, 2 sec cutting time on D4 sample.



3.4 Surface temperature test

The surface temperature is measured by an infrared non-contact thermometer Fluke 574, with RS232 data recording capability, the emissivity of the surface was calibrated by measuring the sample surface temperature and with type K thermocouple, taking readings until they match. This test is realized together with the cutting forces measurement on D4 sample so that temperature generated and cutting forces could be related. The temperature is measured 0.125 ms the resultant data is then exported to a file for analysis.

3.5 Three dimensional cutting forces test

In the cutting forces experiment solid bars are machined in a CNC lathe Milltronics ML14 with 9 kW spindle power and a maximum of 4500 rpm, the tool insert used is a cemented carbide insert DNMG 150408, 0.8 mm corner radius, 4.76 mm thickness 0° clearance angle and 15 mm of cutting length. The experimental design for the test is a two factors and three level central composite design with one center point and an alpha value of one.

A total of 9 runs, three cutting velocities and three feed rates, and three replicas are done. The cutting force F_z , the feed force F_x and the radial force F_y are measured by using a three component dynamometer Kistler 9257B, a Kistler 5814B1 multichannel charge amplifier and a Tektronix oscilloscope. First we place the zero on the oscilloscope interface then the forces are recorded in the oscilloscope, and data is exported to file. With the oscilloscope cursors we measure the increments in voltage and convert with the amplifier gain into mechanical units. We confirm the measure by plotting the voltage vs. time obtained in the exported files.

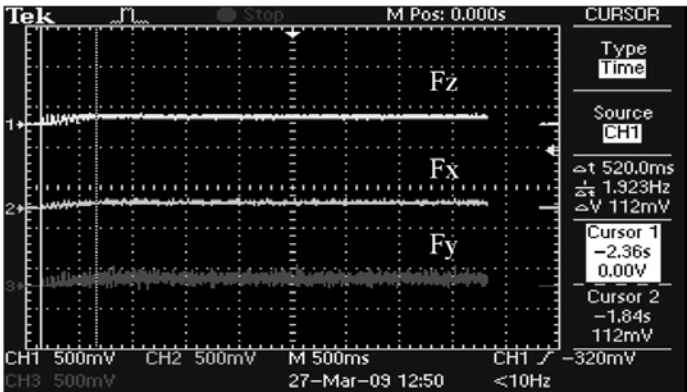


Figure 2: Oscilloscope interface with the three component forces from the dynamometer.



4 Experimental results

4.1 Roughness results

The common values reported in the measure of roughness is R_a arithmetic mean value defined by eqn (1), but there are other measures of roughness that are critical depending on the application, so we complement the measurement by calculating R_z ten point height eqn (2) and R_y maximum peak-to-valley.

$$R_a = \frac{1}{n} \cdot \sum_{i=1}^n |f(x_i)| \quad (1)$$

$$R_z = \frac{(R_1 + R_3 + R_5 + R_7 + R_9) + (R_2 + R_4 + R_6 + R_8 + R_{10})}{5} \quad (2)$$

For the first experiment fig. 3 shows the difference in arithmetic roughness changing the cutting velocity, but it is because of the inherent decrease in feed rate. So even though the cutting velocity has an impact in roughness considering feed velocity in the “x” axis, feed rate is still the most predominant factor in the R_a , R_y and R_z measure. No significantly differences were found between R_a , R_z and R_y of B2 and C3 samples in the first experiment. However, the second experiment shown in fig. 4 results in differences between A1, B2 and C3 samples. A polynomial quadratic fit is obtained for each sample. Eqns (3), (4) and (5) show the R_a as a function of the feed “f”. The R^2 values for the equations are 0.9269 for A1, 0.9723 for B2, and 0.9963 for C3.

$$A1R_a(f) = -35.508f^2 + 23.205f - 1.0463 \quad (3)$$

$$B2R_a(f) = 32.495f^2 - 0.4726f + 0.8789 \quad (4)$$

$$C3R_a(f) = 38288f^2 - 1.3513f + 0.6059 \quad (5)$$

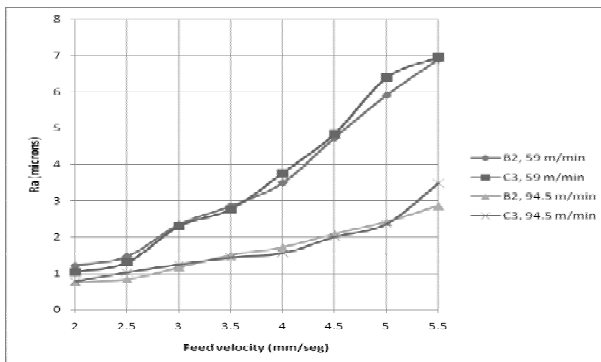


Figure 3: First experiment; B2 and C3 samples are compared under same conditions. No differences are obtained graphing feed velocity.



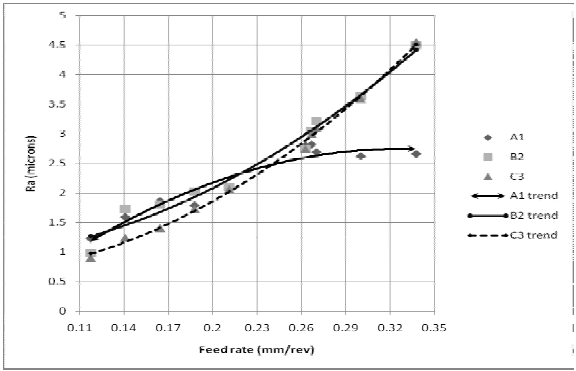


Figure 4: Second experiment; Differences between the R_a of the samples is clearly shown, a quadratic fit is obtained from this test.

4.2 Power consumption results

The specific power is the power required to remove a unit volume per unit time. The specific and total power is related by eqn. (6), according to [12] the specific power consumption can also be calculated by eqn. (7), where it is related to the cutting force, the cutting velocity and the material removal rate,.

$$\Delta P = P_s \cdot MRR \tag{6}$$

So we proceed to measure the current increments in the conventional lathe motor. They were 6 replicas for each experiment; the standard deviation is taken as the variation. The MMR or material removal rate was 31,472 mm³/min. The values in table 2 are not far from what [12] has shown of others experiments.

Table 2: Results of the power consumption test.

Sample	Current increment (amps)	Power increments (watts)	Specific cutting power (kW/mm ³ /min)	Variation
A1	0.875	333.38	1.06 x 10 ⁻⁵	9%
B2	0.7891	300.65	0.955 x 10 ⁻⁵	20.8%
C3	0.7783	296.54	0.942 x 10 ⁻⁵	7%
D4	0.9033	344.16	1.09 x 10 ⁻⁵	11.3%

4.3 Chip morphology

The chips in this analysis were collected from the roughness experiment. The chip morphology qualitative analysis reveals certain characteristics occurring in chips. In fig. 5 chip sample of B2 at 0.1172 mm/rev, 94.5 m/min and 2 mm and sample of B2 at 0.3 mm/rev, 59 m/min and 2 mm of depth of cut. Notice the difference in the same alloy under different cutting conditions, this shows us that different phenomenon is happening during cutting.



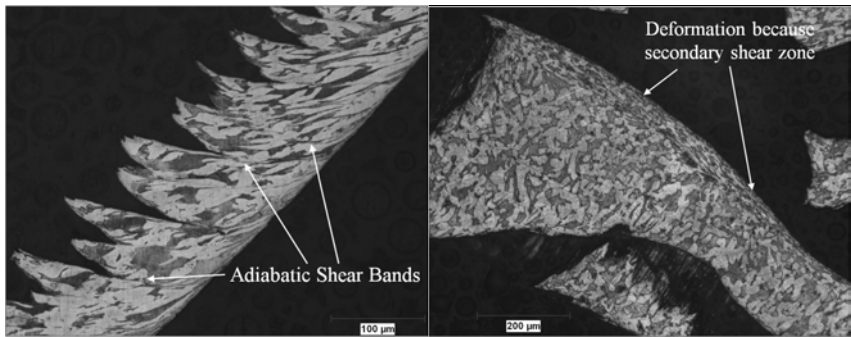


Figure 5: The chip showing different characteristics according to its cutting conditions.

Table 3: Results of the surface temperature experiment.

Cutting velocity (m/min)	Feed rate (mm/rev)	Cutting force (N)	Ambient temperature (°C)	Surface Temperature (°C)
40	0.1	80	24	30
40	0.2	144	23.5	28.5
40	0.3	180	22.5	26.5
60	0.1	72	24	35
60	0.2	160	23.5	28.5
60	0.3	224	23.4	30.9
80	0.1	64	23	33
80	0.2	112	24	32.5
80	0.3	216	24	31.6

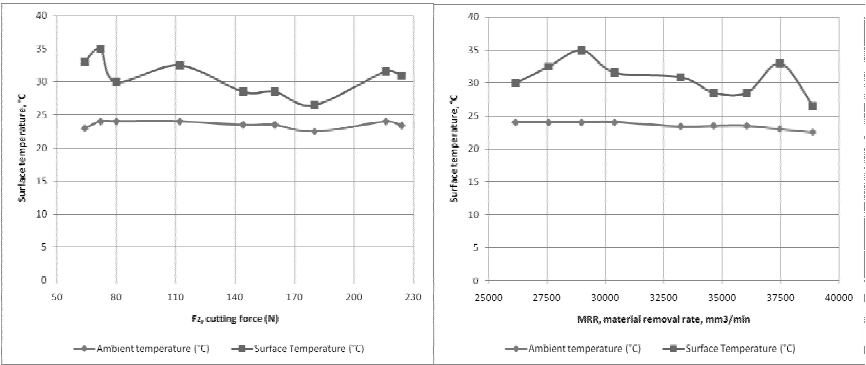


Figure 6: The results show no relation between the cutting forces and surface measure, and no relation between MRR and surface temperature.



4.4 Surface temperature

The emissivity of C3 sample is 0.6 under this parameter the corresponding temperatures are measured. Because the infrared spectrum cover a wide range of wavelengths (0.78 to 500 microns) of the thermal radiation is useful in the measurement of surface temperature. The results show no relation in surface temperature and cutting velocity, surface temperature and cutting force, and surface temperature and material removal rate. It has to be clear that surface temperature differs from average tool/chip contact temperature.

4.5 Cutting forces

The voltage increment measured were transformed to mechanical units, the conversion were 1000 MU/volt so a direct conversion to newtons 112 mV represents 112 N. The data obtained in this test is subject to multiple regression analysis, and to pareto regression coefficients to determine which variable has a major influence on each cutting force. The multiple regression analysis shows eqns. (7), (8), (9) and a value of R^2 of 0.7212, 0.6170 and 0.9447 respectively.

$$F_x = 110.74 - 0.777V_c + 30.778f + 6.5V_c f \quad (7)$$

$$F_y = 221.04 - 1.778V_c + 76.667f + 29.33V_c f \quad (8)$$

$$F_z = 136.41 - 6.611V_c + 65.33f + 9V_c f \quad (9)$$

Table 4: Results of the cutting forces experiment.

Cutting velocity (m/min)	Feed rate (mm/rev)	F _x	F _y	F _z	Resultant force	F _z /F _x
40	0.1	88	169.33	77.33	205.90	0.878
40	0.2	106.66	253.33	155.66	315.88	1.459
40	0.3	141.33	246.66	188	340.82	1.330
60	0.1	78.66	113.33	68	153.80	0.864
60	0.2	120	246.66	154.66	314.89	1.288
60	0.3	130.66	301.33	202.66	385	1.551
80	0.1	71.33	120	58.66	151.42	0.822
80	0.2	109.33	314.66	117.33	353.17	1.073
80	0.3	150.66	314.66	205.33	404.80	1.362

5 Conclusions

We draw the following conclusions:

- In the roughness test most important factor is feed rate, instead of feed velocity, but machining time is important because it affects the production rates. Differences are appreciable in fig. 4.
- Also for this same experiment we could obtain a quadratic polynomial fit which is necessary for predict roughness. Roughness test should be considered in any machining test.



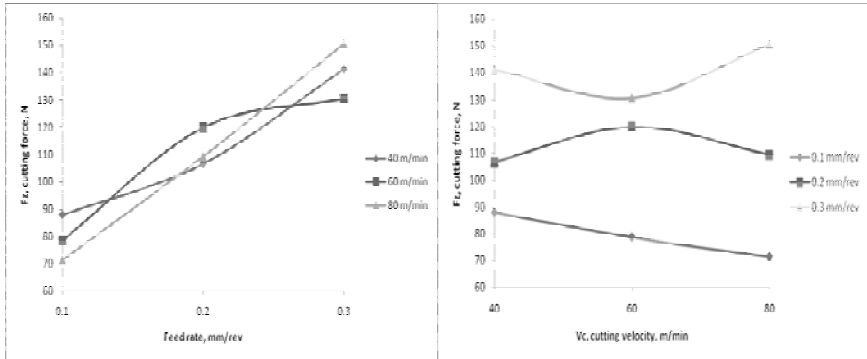


Figure 7: Relations between feed rate and cutting force, and relation between cutting velocity and cutting force.

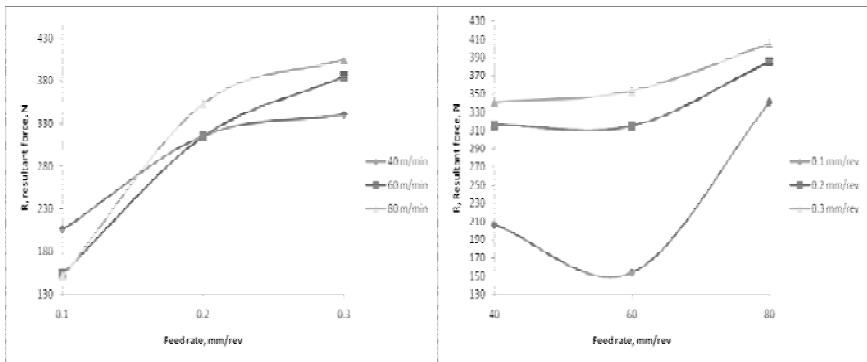


Figure 8: Relationship between the feed rate and the resultant force, and relationship between cutting velocity and resultant force.

- Power consumption test is easy and fast, although results are good in accordance to data presented in [12], the variation presented in samples B2 and D4 demonstrate the necessity of explore more cutting conditions and/or more replicas.
- Chip morphology is a successful and important test that should be considered in every machining test. Although experience is necessary to interpret the corresponding micrographs, but it can show to us the characteristic phenomenon occurring at different conditions.
- Surface temperature has no relation with cutting velocity, or cutting force, or material removal rate, so a surface temperature test by a radiation method with an infrared thermometer may not be as relevant as one could expect. Thermographic methods could be more efficient as Dasch [7] presented.
- Cutting forces test, in three dimensions is a very liable test, capable of analyze and predict different conditions; effectiveness of these methods relies in the experimental design and the number of replicas.



The proposal is an integrated experiment, which includes the measure of R_a , R_y and R_z , three-dimensional cutting forces, and chip morphology analysis. The validity of the data relies in the robustness of the experimental design and not in the collecting method. It is necessary to record machining time and material removal rate for each cutting condition. The surface temperature and power consumption is optional; orthogonal cutting experiment could be helpful in the obtaining of cutting models and comparison with oblique cutting is interesting.

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Dynamic shear stress in a double lap bonded assembly

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Abstract

This work consists of investigating the dynamic shear behaviour of adhesively bonded assemblies at high rates of loading. A double lap joint sample was adopted, such as the compressive wave, and transformed to a shear loading within the adhesive layer. The tool used for this target is the Split Hopkinson Pressure Bar (SHPB). A temperature of 20°C and hygrometry of 50% are the ambience conditions used in the sample in order to avoid temperature and humidity effects. The adhesive material is the cyanoacrylate, while the adherent material is steel. The influence of high rates is remarkable on these bonded assemblies.

Keywords: Hopkinson bar, adhesively bonded assembly, shear, in-plane load, high strain rate.

1 Introduction

Bonded assemblies are becoming used very frequently and are widespread in industry, mainly in aircraft, automotive and electrical fabrications. Contrary to other ways of assembling, bonding has low costs, simplicity of manipulation and also ensures the uniformity of stress repartition on the bonded surfaces. In these applications, the adhesive joints can subdue impact loads as well as quasi-static loadings. However, the main goal of many researchers is to study the influence of the loading rate on the mechanical behaviour of adhesively bonded



assemblies. Multiple quasi-static tests are specified in the ASTM standards [1]. Only a few investigations were carried out on the impact response of these assemblies. Kinloch and Kodokian [2] used the three-point bending specimen to study the fracture energy, while Sato [3] studied the absorbed energy in a CFRP-aluminium alloy beam. Roy and Reddy [4] investigated the dependence of the resonance frequencies and loss factor on the adhesive shear modulus, lap ratio and strap thicknesses. Lawrence Wu et al. [5] measured the absorption energy in electronic adhesive joints using the Hopkinson bar technique. However, the investigation of adhesive joint strength did not constitute the topic of any of these studies.

Kaya [6] used the finite element method to investigate dynamic characteristics in an adhesively single lap joint under dynamic forces. Owen et al. [7] investigated the influence of surface roughness on shear joints. Harris et al. [8] measured the shear strength in a single-lap joint under an impact load. However, only a low-impact velocity of 1.34 m/s is reached. Lataillade et al. succeeded in achieving higher impact velocities by using the Hopkinson bar technique (Lataillade et al. [9], Keisler and Lataillade [10]) and a tensile technique with an inertial wheel [11]. In line with [9], Yokoyama and Shimizu [12, 13] investigated the impact shear strength using a modified split Hopkinson bar by proposing a new geometry of the sample: a pin-and-collar specimen. While Srivastava et al. [14] did a similar study with another new sample geometry: a double-L specimen. The impact velocity can reach 20m/s in these techniques. Different loading configurations were also investigated. For instance, the tensile strength of adhesive joints was investigated [15–19]. Moreover, the combined tension-torsion load was investigated by Sato and Ikegami [20,21] using the Hopkinson bar technique.

In this paper, we are using the Hopkinson bar technique to determine the shear strength in the adhesively bonded joints. This technique takes into consideration the wave propagation in the experimental set-up. Since the specimen geometries proposed in the literature yield to an impedance mismatch with the bar, a new M-shaped specimen is proposed. It consists of a double lap adhesive joint.

The impedance mismatch has highly negative effects on the input and output force measurements: the incident wave, induced in the input bar by the strike of the projectile, reflects in this bar before reaching the adhesive joints. In the same way, the transmitted wave, through the adhesive joint, reflects before reaching the strain gauge cemented on the output bar.

2 Theoretical study

2.1 Description of the Hopkinson bar apparatus

Two elastic bars are the main components of the conventional Hopkinson bar apparatus [22], the first is the incident bar and the second is the transmitted bar; they are also known as input and output bars respectively (Fig. 1). A striker bar, whose length is less than the half that of the input bar, will move horizontally



under N_2 pressure of an air gun to hurt the first extremity of the input bar and thus to generate a compressive wave in this bar. This incident wave moves through the input bar until it reaches the bar-specimen interface. At this interface, the first part of the wave is reflected back into the input bar as a tensile wave and the second part is transmitted through the specimen into the output bar as a compressive wave. In order to measure the bars deformations, one gauge station is cemented on each bar. The input gauge station measures the incident and reflected waves while the output gauge records the transmitted wave. The input gauge is cemented in the middle of the input bar while the output gauge is positioned nearer to the specimen-output bar interface. In this case, the incident and the reflected waves are recorded separately with the input gauge. Assuming one-dimensional wave propagation, the forces applied by the bars on the specimen are given by:

$$F_{in}(t) = A_{in} E_{in} (\varepsilon_{inc}(t) + \varepsilon_{ref}(t)) \quad (1a)$$

$$F_{out}(t) = A_{out} E_{out} \varepsilon_{tra}(t) \quad (1b)$$

where the subscripts *in*, *out*, *inc*, *ref* and *tra* mean input bar, output bar, incident wave, reflected wave and transmitted wave, respectively, and A is the cross-section area, E the Young's modulus, ε is the wave's strain.

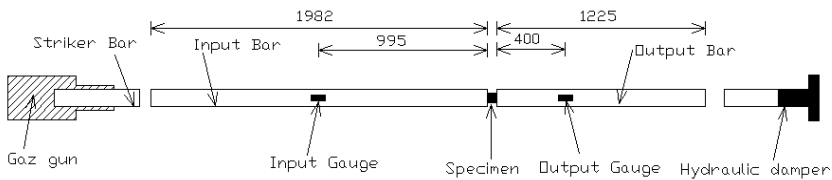


Figure 1: Simplified scheme of the Hopkinson bar apparatus.

2.2 Specimen geometry

The M-shaped specimen involves three adherent plates bonded by two adhesive layers (Fig. 2). The middle adherent plate is shifted from the other two. This gap will be useful to convert the compression loading into shear loading inside the adhesive layer. It is aligned with the output bar end while the lower and the upper plates will be aligned with the input bar end. The geometry of the specimen allows one to carry out all of the experiments on a classical Hopkinson Bar technique without any modification and thus avoiding any added impedance mismatch to the system. The mechanical impedance of each adherent plate is constant so as not to induce any undesired reflection of the waves. The in-plane movement of the bars is transformed by the geometry of the specimen to a shear loading on the adhesive layers. Assuming dynamic equilibrium in the specimen, the shear stress is calculated in the function of the input and output forces and the area of a single lap joint (A_{adh}) as follows:



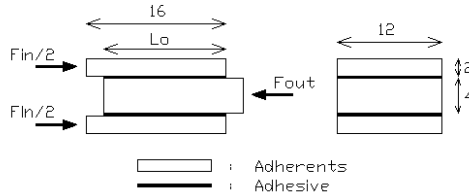


Figure 2: Specimen geometry: (a) side sight (b) rear sight.

$$\tau(t) = \frac{F_{in}(t) + F_{out}(t)}{4A_{adh}} \quad (2)$$

2.3 Bonding steps

To ensure the good alignment of the specimen a special mounting device is developed (Fig. 3). To prepare the specimen, the following steps are followed:

1. The lower and middle adherent plates are wiped with dry paper.
2. The thickness of each plate is measured using a micrometer.
3. The mounting device is cleaned with acetone, while both plates are immersed in acetone to be treated by ultrasound waves for one minute.
4. A hairdryer is used to dry the plates.
5. The adhesive is spread on the upper face of the lower plate, this plate is then fixed by a screw in the mounting device as shown in Fig. 3a.
6. The adhesive is spread on the lower face of the middle plate, this plate is then fixed by a screw in the mounting device on the opposite side to the first screw to create the gap between the two plates, and then both plates are fixed by a vertical screw to keep constant pressure as shown in Fig. 3b.
7. The assembly is kept at room conditions for 5-6 hours.
8. The upper plate is treated similarly to the previous plates as mentioned above.
9. The vertical screw is unscrewed, the adhesive is spread on the upper face of the middle plate and on the lower face of the upper plate and this plate is fixed by a screw in the mounting device on the same side as the first screw, as shown in Fig. 3c.
10. The whole specimen is then fixed in the mounting device by a vertical pressure screw to keep a constant pressure and ensure a convenient adhesion between the three plates, as shown in Fig. 3d.
11. The specimen is cured at room temperature for 18 hours.
12. The specimen is kept in a conditioned room (local temperature 20°C, relative hygrometry 50%) for at least one week.
13. The specimen is tested at room temperature after no more than two hours from getting it out from the conditioned room.

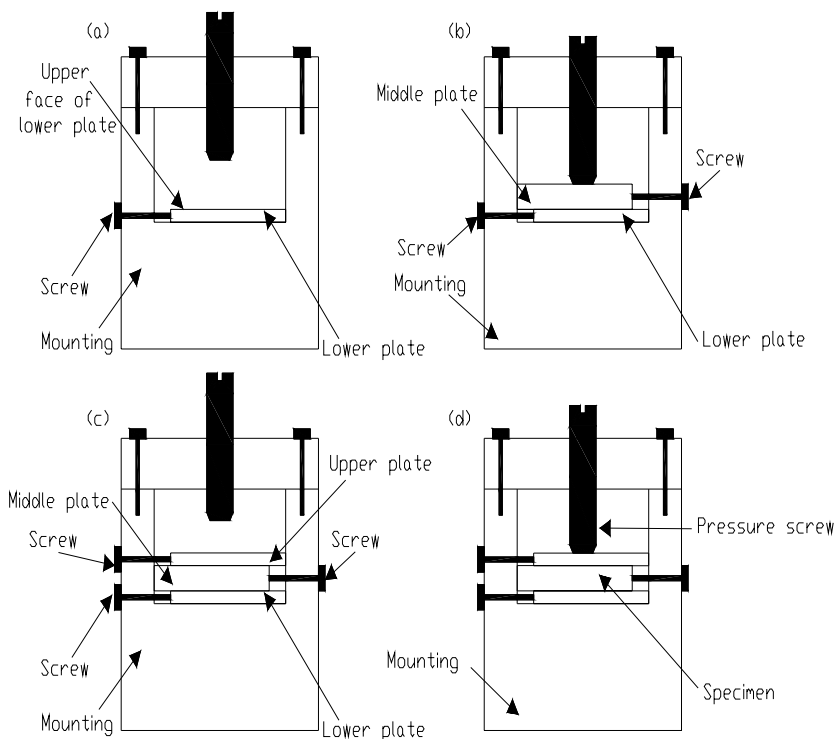


Figure 3: Specimen preparation, bonding steps.

3 Experimental study

The input and output Hopkinson bars are both made from steel material (Fig. 1). Their mechanical properties are suitable for high rates of loading. We present in the following all the engineering properties in the experiments:

- The bars' diameter is 16mm.
- The bars' Young's modulus is 190GPa.
- The bars' elastic limit is 1400MPa.
- The specimen's adherent plates are made of steel (35NCD16).
- The three adherent plates are bonded with a cyanoacrylate based adhesive (2610).
- The adhesive layer thickness is $20\mu\text{m} \pm 8\mu\text{m}$.
- The strain measurements are recorded at a frequency rate of 10MHz.

The software DAVID [23], developed at the Ecole Polytechnique (France), is used to treat the deformations' signals recorded by the strain gauges and then to



compute the values of the forces at both interfaces specimen bars. Thus, the shear strength is deduced using Eq. (2).

On the other hand, comparison is carried out between the impact shear strength and a conventional quasi-static machine, where tests were applied to this M-shaped specimen. Fig. 4 shows the variation of the shear strength with the mean value of the shear rate. Since a bilinear behaviour is observed, the shear strength is found to be highly rate-sensitive. As the graph shows, at rates greater than $5 \cdot 10^5$ MPa s⁻¹, the gradient increases considerably. Two joint overlap lengths (l_j : see Fig. 2) are tested (9 and 14 mm). The results obtained with the short specimens confirm the bilinear behaviour.

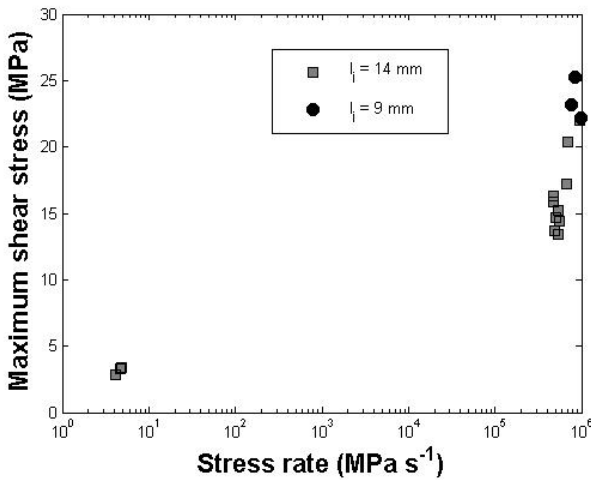


Figure 4: Variation of the shear strength with the loading rate.

4 Conclusion

A new sample geometry was presented in this paper. Its advantage is that it minimizes the impedance mismatch with the bar. The influence of the loading rate on the shear strength of double-lap adhesive joints was investigated using the Hopkinson bar technique. It was found high-rate sensitive: a bilinear behaviour is observed. Moreover, a mounting device is developed to ensure an accurate alignment between the specimen and the two bars.

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High velocity impact of carbon composite plates: perforation simulation

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Abstract

Aircraft structures are large and complex, generally constructed from thin sheet metal or composite materials. As a result, analysis and prediction of the behaviour of such structures when subjected to high-energy impacts is very complex. Computational design analysis techniques have the potential to provide a deeper understanding of the problem and hence enable the design of safer and more efficient airframes. With this end in mind, it is important to develop and identify good modelling techniques to ensure accurate representation of real life situations.

The mechanism of damage initiation and growth in layered composites subjected to high-velocity impacts is simulated using a damage mesomodel approach. The implementation of the model into the commercial finite element code ABAQUS via use-defined FORTRAN subroutines is described. The implemented model involves damage in both the mesoscale layer and an interface between the layers. In this paper, the first experimental and numerical results of high-velocity impacts of composite plates are described and compared, the advantages and disadvantages of numerical methods used are discussed and future developments are announced.

Keywords: ballistic impact, composites, models.

1 Introduction

Composite material has various advantages (high specific elasticity and strength, lightness in weight etc.), so it has been considered as the most prospective structural material in the aeronautic field for a long time. The topic of impact



damage in laminated composite materials has been studied mostly for the low-velocity impact caused by dropped tools or runway debris. Other studies deal with ballistic impacts caused by missiles or shell fragments with a velocity of less than 1000m/s. This paper focuses on the ballistic impacts, ranging from 1000m/s to 3500m/s, of thin carbon/epoxy laminated composite plates. Recent progress in materials modelling and numerical simulation of the impact response of fibre-reinforced composite plates are described. This paper makes use of continuum damage mechanics as developed by Ladevèze [1], as a framework within which in-ply and delamination failure may be modelled. The mesomodel of Ladevèze was developed originally for quasi-static loads, but it can be used because of the assumption that the damage mechanisms of laminated composites in dynamic are the same in static.

An important requirement for operational utilization is to develop numerical methods for the simulation of ballistic impacts on composites plates, thus the composite materials models need to be implemented and validated in finite element codes. Emphasis is placed in this paper on the implementation of the ply damage model and delamination models into the commercial explicit code Abaqus/Explicit and on the numerical difficulties of penetration phenomena.

2 Damage mechanics and mesomodelling of laminates

When dealing with composites, the key issue is the scale on which the model is constructed. This is also the scale on which the calculations have to be performed. On the one hand, the use of the microscale, besides numerous other difficulties, would raise the computing costs beyond reasonable limits. On the other hand, the use of macroscale would not enable a proper representation of the basic features of the laminate and of its deterioration mechanism. Moreover, for severe dynamic loading, the concept of homogenized material is meaningless. Therefore, it is necessary to define a scale on which the material can be described properly without going into excessive detail. A pragmatic approach consists of determining a characteristic length of the main damage mechanisms. For laminated composites, between the macroscale of the structure and the microscale of the single fibre, there is an intermediate modelling scale called the mesoscale. This scale is associated with the thickness of the layer and the thicknesses of the different interlaminar interfaces. On this scale, the main

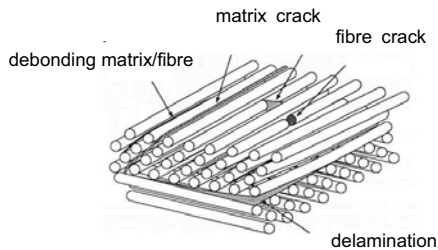


Figure 1: Main damage mechanisms.

damage mechanisms (delamination, matrix microcracking, fibre/matrix debonding and matrix breakage (Fig. 1)) appear nearly uniform throughout the thickness of each mesoconstituent, at least under quasi-static loading. Thus, they can be described in a relatively simple way.

In our method, we conjecture that due to the smallness of the mesoscale (one-tenth of a mm) a static description of the damage mechanisms should remain valid even for high loading rates. Therefore, we proposing to adapt a mesomodel previously defined for static loading [1–5] to the dynamic case. This mesomodel is initially defined by means of two constituents:

- a single layer which is assumed to be homogeneous and orthotropic,
- an interface, which is a mechanical surface connecting two adjacent layers and which depends on the relative orientation of their fibres (Fig. 1)

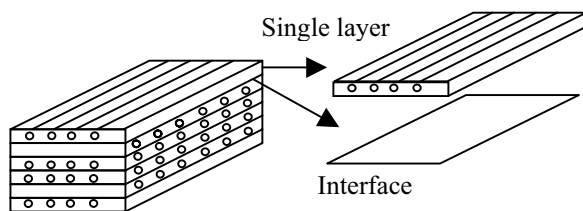


Figure 2: Mesomodel of a laminate.

The damage mechanisms are taken into account by means of internal damage variables. Then, a mesomodel is defined by adding another property, which consists of prescribing a uniform damage state throughout the thickness of the elementary ply.

2.1 The single-layer model

The ply is modelled as a homogeneous orthotropic elastic-plastic damaging material whose properties are degraded on loading by microcracking prior to ultimate failure. The first expression used of the strain energy density of damage elementary layer was:

$$\begin{aligned}
 E_D = \frac{1}{2} & \left[\frac{\langle \sigma_{11} \rangle_+^2}{E_1^0(1-d_1)} + \frac{\langle -\sigma_{11} \rangle_+^2}{E_1^0} - 2 \frac{\nu_{12}^0}{E_1^0} \sigma_{11} \sigma_{22} - 2 \frac{\nu_{13}^0}{E_1^0} \sigma_{11} \sigma_{33} \right. \\
 & + \frac{\langle \sigma_{22} \rangle_+^2}{E_2^0(1-d_2)} + \frac{\langle -\sigma_{22} \rangle_+^2}{E_2^0} - 2 \frac{\nu_{23}^0}{E_2^0} \sigma_{22} \sigma_{33} \\
 & \left. + \frac{\sigma_{33}^2}{E_3^0} + \frac{\sigma_{12}^2}{G_{12}^0(1-d_{12})} + \frac{\sigma_{13}^2}{G_{13}^0} + \frac{\sigma_{23}^2}{G_{23}^0} \right]
 \end{aligned} \tag{1}$$

where $\langle \cdot \rangle_+$ designates the positive part.

This expression enables us to distinguish between tension and compression depending on whether the cracks are closed or open. The rates of release of damage energy associated with d_1 , d_2 and d_{12} are expressed as follows:

$$\begin{cases} Y_1 = \frac{\partial \langle E_D \rangle}{\partial d_1} \Big|_{\sigma} = \frac{\langle \langle \sigma_{11} \rangle_+^2 \rangle}{2E_1^0(1-d_1)^2} \\ Y_2 = \frac{\partial \langle E_D \rangle}{\partial d_2} \Big|_{\sigma} = \frac{\langle \langle \sigma_{22} \rangle_+^2 \rangle}{2E_2^0(1-d_2)^2} \\ Y_{12} = \frac{\partial \langle E_D \rangle}{\partial d_{12}} \Big|_{\sigma} = \frac{\langle \langle \sigma_{12} \rangle_+^2 \rangle}{2G_{12}^0(1-d_{12})^2} \end{cases} \quad (2)$$

where $\langle \langle \cdot \rangle \rangle$ designates the mean value through the thickness.

For the sake of simplicity, the behaviour in the fibre's direction is assumed to be independent on the transverse and shear behaviour. Moreover, through the material parameter b , the model introduces a coupling between the evolution of d_2 and that of d_{12} , which, on average, are both associated with the same types of cracks. Then the damage evolution is given by:

$$\begin{cases} d_1 = f_1(\sqrt{Y_1}) & \text{If } d_1 < 1, d_1 = 1 \text{ otherwise} \\ d_2 = f_2(\sqrt{Y_{12} + bY_2}) & \text{If } d_2 < 1, d_2 = 1 \text{ otherwise} \\ d_{12} = f_{12}(\sqrt{Y_{12} + bY_2}) & \text{If } d_{12} < 1, d_{12} = 1 \text{ otherwise} \end{cases} \quad (3)$$

where $\underline{Y} = \sup_{\tau < t} Y|_{\tau}$ for each quantity Y .

The static identification of these evolution laws is carried out by macrotest intension-compression on different stacking sequences of laminate.

Then, in order to model the inelastic strains induced by damage, a plasticity model was built. The elastic domain is defined by the function f such that:

$$f = \sqrt{\tilde{\sigma}_{11}^2 + a^2 \tilde{\sigma}_{22}^2} - R(p) - R_0 \quad (4)$$

where the threshold R is a function of the accumulated plastic strain p ; $p \rightarrow R(p)$ is a material characteristic function, and a^2 is a material characteristic constant.



With $\tilde{\sigma}$, the effective stress:

$$\tilde{\sigma} = \left[\begin{array}{c} \sigma_{11} \\ \frac{\langle \sigma_{22} \rangle_+ + \langle \sigma_{22} \rangle_-}{1 - d_2} \\ \frac{\sqrt{2} \sigma_{12}}{1 - d_{12}} \end{array} \right] \quad (5)$$

The model assumes that no plastic yield exists in the fibre direction.

2.2 Interface model

The interface is simulated as a user contact law between the layer's elements.

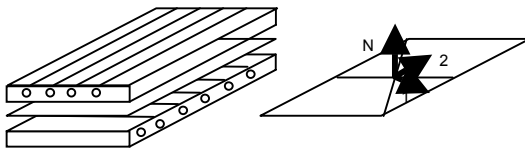


Figure 3: The orthotropic directions of the interface.

This contact law is defined such that:

$$\begin{aligned} \sigma_n &= K_n \left[(1 - D_n) (U_n^r)^+ + (U_n^r)^- \right] \\ \sigma_{cis1} &= K_{cis} (1 - D_{cis}) U_{cis1}^r \\ \sigma_{cis2} &= K_{cis} (1 - D_{cis}) U_{cis2}^r \end{aligned} \quad (6)$$

with U^r being the relative displacement.

For the interface, the damage evolution is given by

$$\begin{aligned} D_n &= f(U_n^r) \\ D_{cis} &= f\left(\sqrt{(U_{cis1}^r)^2 + (U_{cis2}^r)^2}\right) \\ D_n &= \max(D_n, D_{cis}) \\ D_{cis} &= \max(D_n, D_{cis}) \end{aligned} \quad (7)$$

3 Simulation of impact

In order to perform the simulation, the constitutive damage mesomodel was implemented into the explicit finite element code Abaqus/Explicit. To enable the penetration, when d_2 or $d_{12} \geq 1$, the mesh is eroded.



3.1 Delay effect

A first difficulty with the erosion is the mesh dependency. The following calculation (Figs. 4 and 5.) was performed on a perforating impact of carbon/epoxy layer by a spherical rigid projectile. The problem is solved with the adding of delay effect on damage evolution.

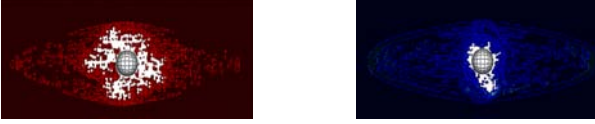


Figure 4: Without delay effect.



Figure 5: With delay effect.

3.2 Failure criterion

With the presented model, calculation didn't be completed because of lot numerical errors, like excessive distortion or time increment fall... To solve these errors, the deformation energy and the erosion criterion were changed. The new deformation energy is:

$$E_D = \frac{1}{2} \left[\frac{1}{(1-d_1)} \left(\frac{\langle \sigma_{11} \rangle_+^2}{E_1^0(1-d_1)} - 2 \frac{\nu_{12}^0}{E_1^0} \sigma_{11} \sigma_{22} - 2 \frac{\nu_{13}^0}{E_1^0} \sigma_{11} \sigma_{33} \right) + \frac{\langle -\sigma_{11} \rangle_+^2}{E_1^0} + \frac{\langle \sigma_{22} \rangle_+^2}{E_2^0(1-d_2)} + \frac{\langle -\sigma_{22} \rangle_+^2}{E_2^0} \right. \\ \left. - 2 \frac{\nu_{23}^0}{E_2^0} \sigma_{22} \sigma_{33} + \frac{\sigma_{33}^2}{E_3^0(1-d_2)} + \frac{\sigma_{12}^2}{G_{12}^0(1-d_{12})} + \frac{\sigma_{13}^2}{G_{13}^0(1-d_{13})} + \frac{\sigma_{23}^2}{G_{23}^0(1-d_{23})} \right]$$

With the propagation of the fibre's direction damage to the normal direction, the time increment which is driven by the normal direction increase during the calculation.

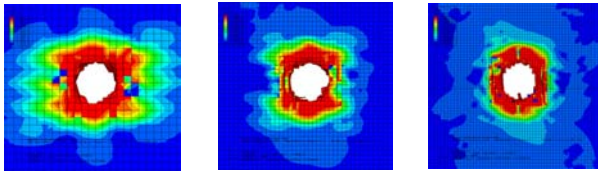


Figure 6: Erosion criterion in the fibre's direction.

In order to be more consistent and have not numerical difficulties with fibre-stocked energy, the failure criterion has been changed. Mesh was eroding only when $d_1 \geq 1$. A delay effect is introduced for every damage variable.

The new erosion criterion and damage evolution law in the fibre's direction enable to have consistent results in a consistent time with one or more layers.

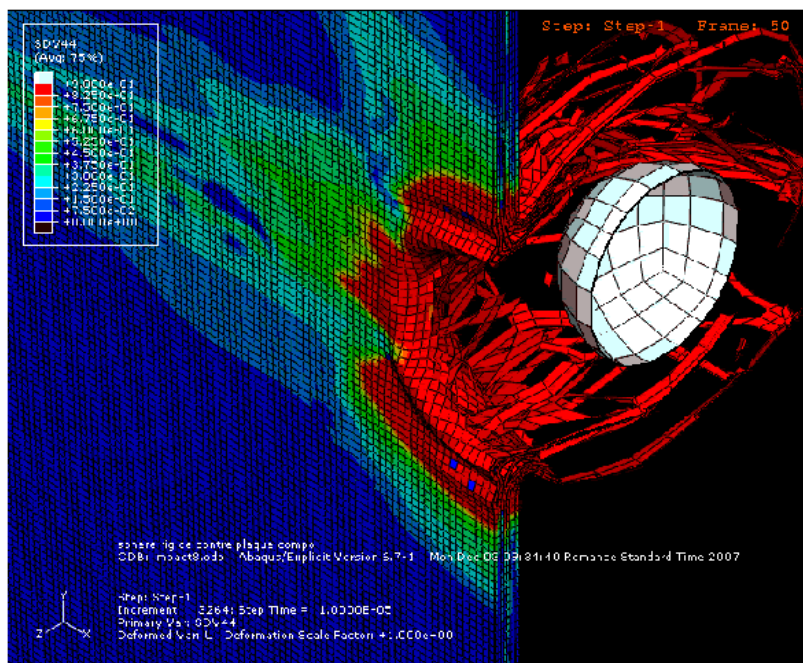


Figure 7: Damage on laminate.

3.3 First results on laminates

Calculation mechanical description:

- rigid projectile 10g, 1500m/s
- 8 layers, 320 000 elements
- 7 contact surfaces of 40000 elements

Calculation numerical description:

- 4 processors
- 2gb of memory
- 4h calculation time



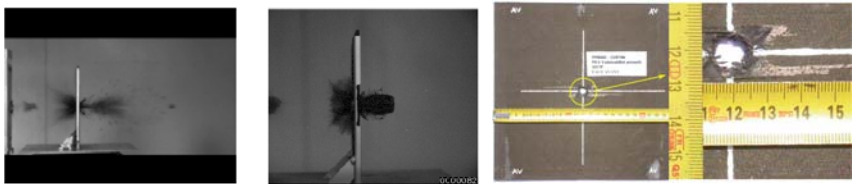


Figure 8: During and after 1500 m/s impact.

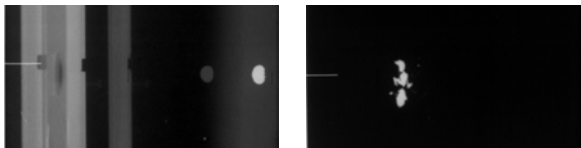


Figure 9: Projectile fragmentation at 3500 m/s.

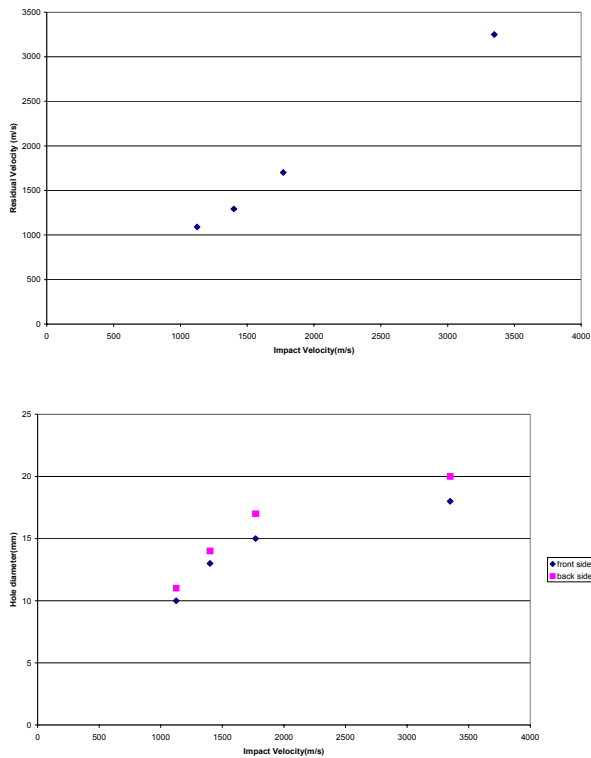


Figure 10: Residual velocity and hole diameter with impact velocity.



4 Experimental results

For velocity ranging from 1000 to 2000m/s the impact tests have been conducted using a powder gun and for velocity ranging 2000 to 3500m/s they have been conducted using the double stage gun Athena in operation at the CEG.

Four tests are presented, for each one the diameter projectile is 10mm and the target is thin carbon/epoxy plate.

4.1 Results

4.1.1 Analysis

The first calculation results are about the same, but CND of plates are waited to have more interested information. We just know at the moment there is non-deceleration of the projectile; the hole's diameter is about the same as the projectile's diameter for 1000 m/s and increase with the velocity. An interesting observation is the projectile fragmentation for 3500m/s impact, so we can assume that the physic change between 2000 and 3500 m/s.

5 Conclusion and perspective

In this paper a static mesomodel was adapted to dynamic and penetrating impact. The model presented enable having consistent result in a consistent time. Future works concern a best coupling between different mode in the interface and a best interaction between interface and layer.

Other experimental tests and analysis are pending to validate the numerical results.



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The effect of bent-up tab shear transfer enhancement shapes, angles and sizes in precast cold-formed steel-concrete composite beams

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Abstract

This paper deals with the evaluation of the effect of shapes, angles and sizes of bent-up tab shear transfer enhancement in precast cold-formed steel-concrete composite beams. The study is performed through push-out testing on 14 specimens. The push-out test has been employed to assess the shear strength as well as the behaviour of the shear transfer enhancement. It is shown that specimens employed with shear transfer enhancements increase the shear capacities of the specimens as compared to those relying only on a natural bond between cold-formed steel and concrete. In the shear transfer enhancements investigated, a new proposed shear transfer enhancement called bent-up triangular tab shear transfer (BTTST) provided the best performance in terms of strength. Shear capacities of the shear transfer enhancement also increase when the angles and sizes of bent-up tabs shear transfer enhancement is increased. It is concluded that more efficient and feasible precast cold-formed steel-concrete composite beams can be obtained with this innovator proposed shear transfer enhancement.

Keywords: cold-formed steel, composite beams, precast beams, shear transfer mechanisms.



1 Introduction

The application of cold-formed steel composite concrete floor systems in small commercial and residential construction has gained popularity in recent years. The application of this system only uses cold-formed steel sheets. However, the use of cold-formed steel sections, such as C-section, as the composite floor joint in slab systems is still limited. The structural performance of cold-formed steel can be improved by using it in conjunction with other materials, such as concrete, to form the composite system. Common ways to do this are to use the cold-formed sections as composite beams in concrete slab systems [1]. However, a previous study showed that there is very little work and a lack of technical literature, such as codes of practice, regarding cold-formed steel-concrete composite beams [2]. The main problem for cold-formed steel-concrete composite beams is the welding of shear studs, due to the light gage and thickness of the sections for cold-formed steel being too small. From this viewpoint, this research is being carried out to study the possibility and performance of the use of back-to-back cold-formed steel lipped channels by bolted connection to form the I-beam. The top flange of the I-beam was modified by providing the new proposed shear transfer enhancement, named bent-up triangular tabs shear transfer (BTST) to be used in the composite concrete floor systems. The purpose of this research was to investigate experimentally the efficiency of the BTST in push-out testing and to determine the strength and behaviour of the shear transfer enhancement. Fourteen push-out specimens were constructed and tested to assist with evaluation.

2 Parametric study

Three parameters were identified as being of particular importance, as they affect the strength capacity of the shear transfer enhancement. These parameters are as follows.

2.1 Shapes of shear transfer enhancement

Two shapes of shear transfer enhancement were tested.

(i) Lakkavalli and Liu bent-up (LYLB) as shown in Figure 1 [3].

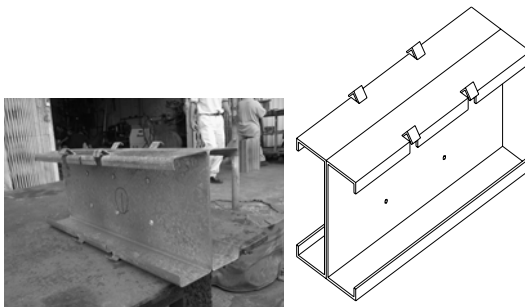


Figure 1: Lakkavalli and Liu bent-up tabs shear transfer (LYLB).



(ii) A newly proposed shape, named the bent-up triangular tab shear transfer (BTTST) as shown in Figure 2.

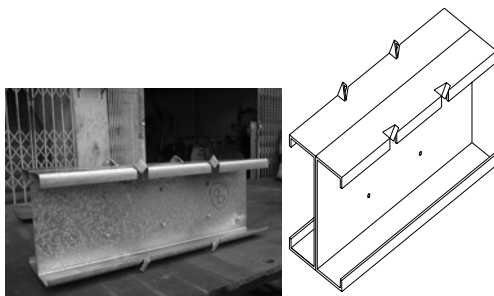


Figure 2: Bent-up triangular tab shear transfer (BTTST).

2.2 Angles of shear transfer enhancement

Three different angles θ were studied (Figure 3), i.e. 30° , 45° and 60° .

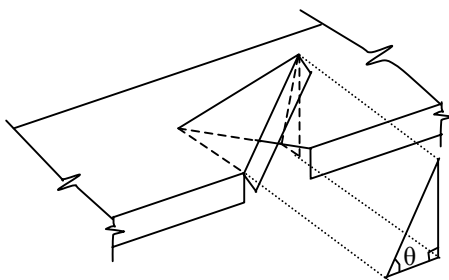


Figure 3: Angles, θ of the shear transfer enhancement.

2.3 Sizes of shear transfer enhancement

The dimensions of the tabs, (A x B) (Figure 4) are 20mm x 20mm, 25mm x 25mm and 30mm x 30mm.

3 Experimental program

3.1 Specimen

In this study, 14 push-out test specimens were tested to failure. Figure 5 shows the detail of the cross section of the push-out test specimen. A cold-formed steel I-section beam formed by a back-to-back lipped channel was used with the flanges cast into a 300mm wide x 90mm depth x 550mm height concrete slab. One layer of 100 mm square welded wire fabric steel reinforcements with a diameter of 8 mm was provided in the concrete slab. A recess of 50mm in height was provided

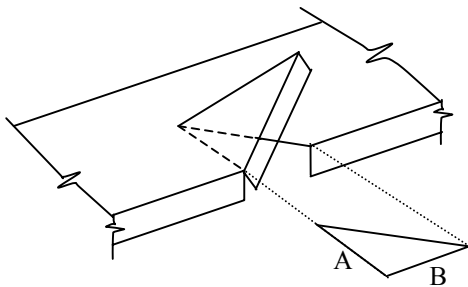


Figure 4: Calculated area ($A \times B$) of the shear transfer enhancement.

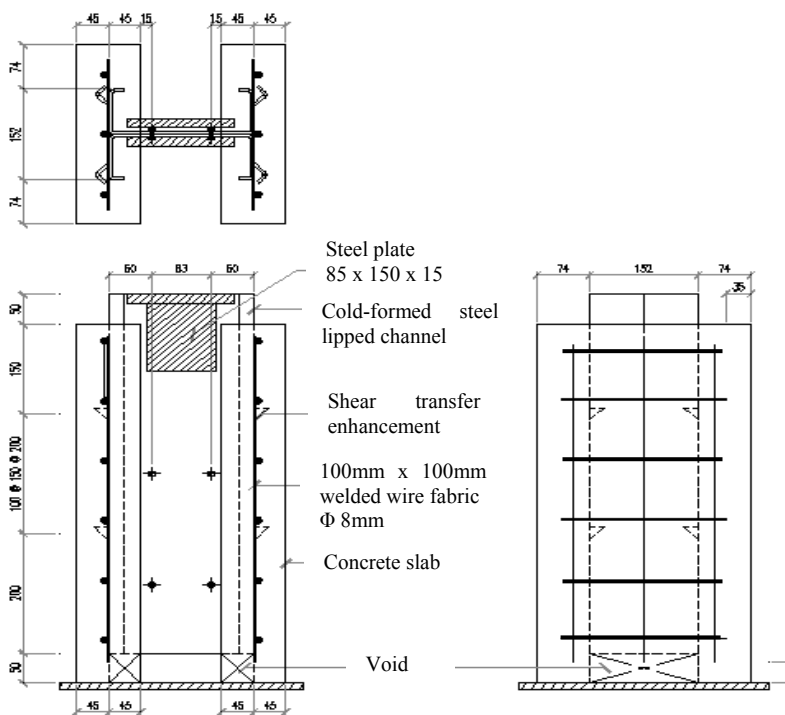


Figure 5: Layout for the push-out test specimen.

between the bottom of the concrete slab and the lower end of the cold-formed steel section to allow for slip during testing. Twelve specimens were provided with the shear transfer enhancement connectors in the spacing of 150 mm on the steel flange as shown in the figure. Meanwhile, two out of the fourteen specimens (S1 and S10) without the shear connector are used as the control



specimens. Both sides of the flange of the I-beam for each specimen were embedded in the concrete slab to form the composite system. The details of each specimen are summarized in Table 1.

Table 1: Specimen push-out test.

No	Shape of Enhancement	Dimension of Enhancement (mm x mm)	Angle of Enhancement (degree)	Channel Section Thickness (mm)	Concrete Strength (N/mm ²)
S1	Without shear transfer enhancement (control)	-	-	1.9	36.62
S2	LYLB	25 x 25	45	1.9	36.62
S3	BTTST	25 x 25	45	1.9	36.62
S4	BTTST	25 x 25	30	1.9	36.62
S5	BTTST	25 x 25	60	1.9	36.62
S6	BTTST	20 x 20	45	1.9	36.62
S7	BTTST	30 x30	45	1.9	36.62
S8	Without enhancement (control)	-	-	2.4	36.62
S9	LYLB	25 x 25	45	2.4	36.62
S10	BTTST	25 x 25	45	2.4	36.62
S11	BTTST	25 x 25	30	2.4	36.62
S12	BTTST	25 x 25	60	2.4	36.62
S13	BTTST	20 x 20	45	2.4	36.62
S14	BTTST	30 x30	45	2.4	36.62

3.2 Test setup and procedures

As shown in Figure 6, the specimen was placed vertically in the Universal Testing Machine (UTM IPC 1000). It was loaded by the 1000kN existing jack vertical load through a displacement-controlled method and monitored by the readings from calibrated load cells. The control speed of the displacement was set at 0.0095 mm/s. The test procedure was based on Eurocode 4 [4]. The load was applied up to 40% of the estimated failure load. The load will be cycled 25 times between 5% and 40% of the expected failure load. Testing was discontinued when the specimen failed to take the additional load or when a



significant load drop had occurred. After the test, the specimen was dismantled to investigate the condition of the shear transfer enhancement wherever possible. The vertical slips between the slab and the cold-formed steel beam were measured by two displacement transducers (LVDT). Transducers were placed vertically at both sides of the cold-formed steel web specimen. Thin plywood with 3mm thickness was placed beneath the slab and on to the upper part of the beam to level the surface. Steel plate of 30mm thickness was placed on the upper plywood to receive the jack. Steel plates were fastened to the loaded end of the cold-formed steel to prevent local buckling.

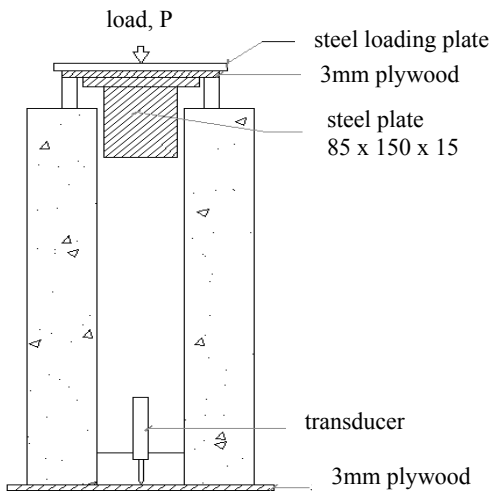


Figure 6: Push-out test arrangement.

4 Test results and discussions

Table 2 contains a summary of the test results at failure condition. More detailed observations of the mechanical behaviour of the tested specimens are presented in the following sections.

4.1 Effect of the shape of shear transfer enhancements

There will be two types of shear transfer enhancement discussed in this section named LYLb and BTTST in comparison with control specimen which no shear enhancement used and its covers both thickness of 1.9mm and 2.4mm. The test results indicate that a significant increment of loading achieved when bent-up tap shear enhancement used in both LYLb and BTTST for both thickness 1.9mm and 2.4mm. Referring to Figure 7, for 1.9mm thick cold-formed steel section, the loading increased more than 100% for BTTST and up to 80% for LYTB as compared to the control specimens, and for 2.4mm thickness, the result shows

Table 2: Result of push test.

Sp.	Ultimate Load, $P_{u(push)}$ (kN)	Percentage of P_u Compared with Specimen (100%)- (%)						Slip, δ_{push} (mm)
		Shape		Angle		Size		
S1	140.55	100	-	-	-	-	-	1.58
S2	253.19	180	100	-	-	-	-	0.88
S3	294.65	210	116	124	100	156.7	100	0.91
S4	237.50	-	-	100	-	-	-	2.22
S5	302.41	-	-	127.3	102.6	-	-	0.47
S6	188.05	-	-	-	-	100	-	0.62
S7	307.79	-	-	-	-	163.7	104.5	0.57
S8	163.81	100	-	-	-	-	-	2.40
S9	289.72	175	100	-	-	-	-	0.95
S10	321.14	196	112	108	100	136.7	100	1.25
S11	297.24	-	-	100	-	-	-	2.00
S12	352.00	-	-	118.4	109.6	-	-	2.56
S13	234.90	-	-	-	-	100	-	0.99
S14	358.35	-	-	-	-	152.5	111.6	1.31

the enhancement for LYLb and BTTST is increased up to 75% and 96% respectively. A comparison of the capacities of LYLb and BTTST indicates that the BTTST result in even higher capacities. The ultimate capacity of specimen S3 is 16% higher than that of specimen S2 and specimen S8, 12% higher than that of specimen S7. Figure 7 also shows that the specimens with shear enhancements demonstrate significantly reduced in term of slip at the interface as compared to the control specimen. Comparing between BTTST and LYLb, better performance demonstrates at ultimate load for both thicknesses by BTTST reflecting the effect plays by the concrete at upper part and lower part of the bent-up shear tab. These comparably more desirable results can be attributed to better interlocking at the cold-formed steel-to-concrete interface.

4.2 Effect of different BTTST angles

The other parameter which controls the capacity of the ultimate load is the angle of the bent-up tab. Referring to Table 2, with the same angle of bent-up tab, the ultimate loading capacity of the tested specimens with 2.4mm thickness is higher as compared with the specimens with 1.9mm thick. Its shows that the thicker the specimen there will be an increment in the stiffness hence increased the capacity of the ultimate loading. Referring to the specimens of 60° for both thicknesses, the specimen S12 gives the 16% higher compared to the specimen S5 but more significant result shows by the specimen S11 as compared to the specimen S4



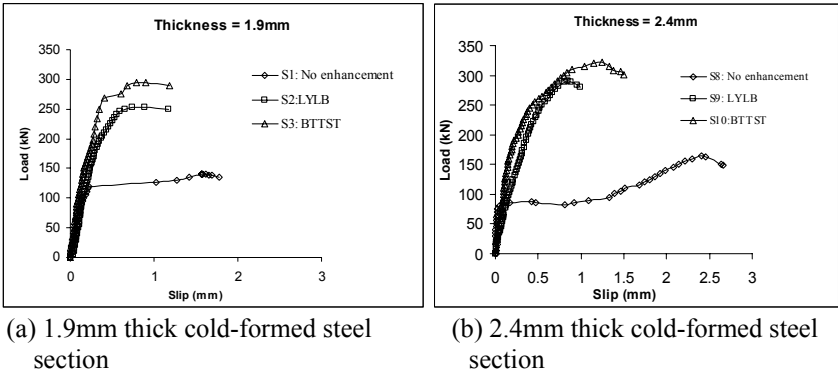


Figure 7: Shear transfer enhancement comparison load-slip curves.

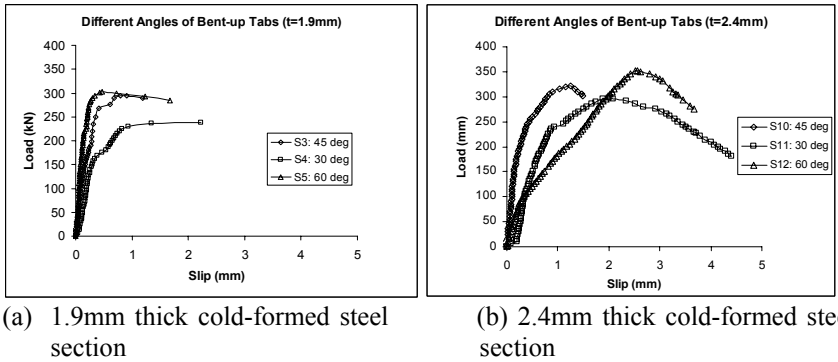


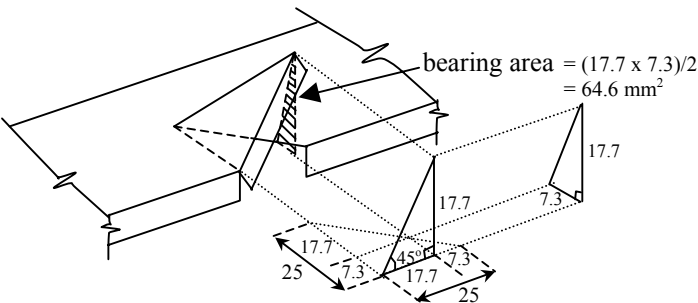
Figure 8: Effect of the BTTST of different angles on load-slip curves.

approximately 25%. Figure 8 shows the curves of the variation of ultimate load resulted from this parameter. The ultimate capacity of specimen S5 with angle 60° BTTST is higher than that of specimen S3 and S4 with angle 45° and 30° , respectively. It is 2.6% higher than specimen S3 and 27.3% than specimen S4. The ultimate capacity of specimen S3 is 24% higher than specimen S4. While from Figure 8(b), S12 with angle 60° BTTST shows a 9.6% increase in ultimate capacity over specimen S10 and 18.4% increase over specimen S11. Specimen S10 is higher by about 8% than specimen S11. By increase the angle of the bent-up tab, the bearing area of the tab will be increased hence the ultimate load of the push out test increased. Figure 9 shows the orientation of the tab with different bent-up tab angle. For angle 45° the bearing area measured was 64.6mm^2 and for angle of 60° the bearing area measured was 135mm^2 increased by up to 100%.

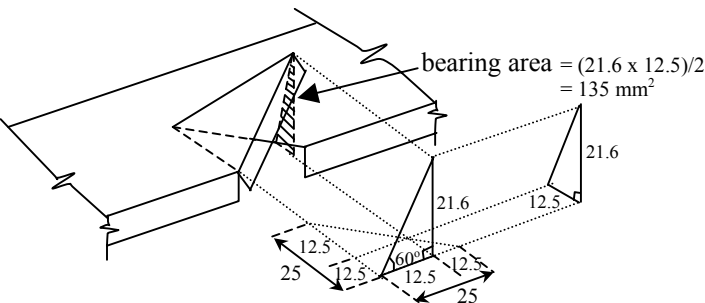
4.3 Effect of different BTTST sizes

Size of bent-up tab other than angle, also plays the important role to increase the bearing area hence the shear capacity of the tab. This study has been conducted





(a) Bearing area of BTTST with 45° angle



(b) Bearing area of BTTST with 60° angle

Figure 9: Bearing area of the BTTST.

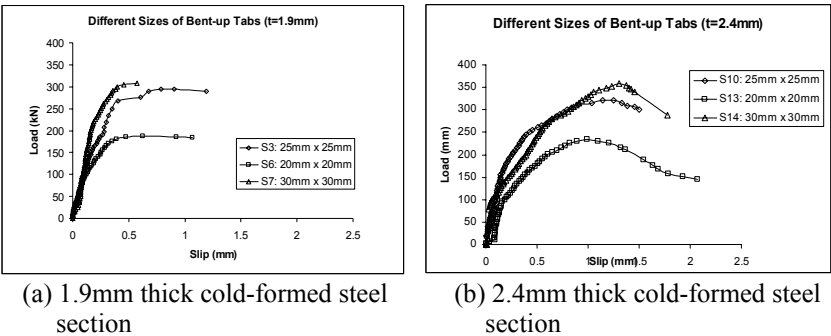


Figure 10: Effects of different sizes of BTTST on load-slip curves.

on different sizes of bent-up tab shows the significant increment of the ultimate load with the increment of the bent-up tab size. For three sizes, which are 20mmx20mm, 25mmx25mm and 30mmx30mm for both thickness of 1.9mm and 2.4mm, all specimens demonstrated the variation on their ultimate load. Referring to Figure 10, the higher area of a bent-up tab gives the higher the



ultimate capacity of the specimen. Specimen S7 and S14, 30mmx30mm tab area increase in ultimate loading significantly as compared to the specimen S3 and S10 with the 25mmx25mm tab area and S6 and S13 with the 20mm x20mm tab area. Referring to Table 2, specimen S14 (2.4mm thick) has an increment of 16% as compared with the specimen S7 (1.9mm thick) with the same shear area shows that the ultimate load was increased by increasing the thickness of the specimen. The same behaviour also showed by other tested specimens with different thicknesses. Figure 10 shows the increment of P_u when the size of BTTST is increased. Increased size of BTTST would increase the bearing area. As previously discussed, the increased of bearing area tends to increase the shear resistance. This can increase the load capacity on to the cold-formed steel until the concrete achieves the ultimate load and then cracks.

5 Conclusions

In this paper, the problems for cold-formed steel-concrete composite beam are discussed and the enabling solution for overcome the problem are described. Previous study showed that there is very little work and lack of technical literature such as codes of practice in cold-formed steel-concrete composite beams. From this viewpoint, this research is to be carried out to study the possibility and performance of the use of a new shape of shear transfer enhancement called bent-up triangular tabs shear transfer enhancement (BTTST). BTTST enhancement was employed on the surface of the flange embedded in the concrete to provide shear transfer capacity. Fourteen companion push-out specimens were tested to evaluate the strength and behaviour of a bent-up tabs shear transfer enhancement. The results show that specimens employed with shear transfer enhancements increase the shear capacities of the specimens as compared to those relying only on a natural bond between cold-formed steel and concrete. As these two types of shear transfer enhancements investigated, BTTST provided the best performance in terms of strength. Shear capacities of the shear transfer enhancement also increase when angles and sizes of bent-up tabs shear transfer enhancement is increase. It is concluded that the proposed shear transfer enhancement has sufficient strength and it is feasible.

Acknowledgements

The authors would like to thank the Ministry of Higher Education, Malaysia, Universiti Tun Hussein Onn Malaysia and Universiti Teknologi MARA for sponsoring this research.

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Material phase transformations due to shock wave loading in contact geometry

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Abstract

When an explosive is detonated, it generates a transient shock wave in the medium. The shock wave energy turns out to be invigorating with insuperable power when used in a more convenient, advantageous and efficacious manner. This shock wave, when it propagates through the material, produces new phases/transformations. The monolithic materials thus formed have important technological applications. This paper describes the experimental technique used to synthesize the newer materials under shock wave loading and the characterization of post shock compacts by means of spectroscopic and other methods. Hexagonal boron nitride powder has been transformed into its cubic structure by loading the material by shock waves. X-ray analysis of the recovered samples with $I/I_0 = 8$ at $d = 1.808$ (angle $2\theta = 50.4^\circ$) has indicated complete conversion of h-BN to c-BN. Super alloy powders of IN 718 and EP 741 NP of various chemical compositions and unique physical properties have been shock compressed. In EP 741 NP, the dendritic structure has been clearly observed in the centre with dendrites oriented in the radial direction, which happens to be the direction of heat flow. The structure needed for best results has been obtained. In IN 718, the dendritic structure within the particle is intact. The structure in the outer portion is better with satisfactory microstructure since the grain boundary has undergone solidification. Explosive compaction of a mechanical mixture of 80Ni-15Fe-5Co of grain size of about 30 nanometres has also been carried out for magnetic applications to study the effect of particle morphology. SEM analysis has indicated that the crystalline structure is intact in the shock-compressed specimens.

Keywords: dendritic structure, IN 718, EP 741 NP, 80Ni-15Fe-5Co, particle morphology, SEM analysis, X-ray analysis, diffractogram, mechanical mixture, microstructure.



1 Introduction

The shock wave, when it propagates through materials, produces sudden changes of pressure and temperature, which ultimately result in the production of new phases/transformations. The compaction achieved by shock wave technology has contributed to the progress of material science by providing a way to study the shock induced phase transformations. The dynamic changes observed in the materials after the passage of shock waves have been the object of scientific curiosity all over the world. The transformations brought about by the shock waves are permanently retained in the materials after the passage of the shock pulse. The newer materials are produced by sudden densification/compaction of the powder by the shock wave pressure and heat. Densification of powders is due to the extremely rapid and intense deposition of energy over the grain boundaries. Solidification mainly occurs due to the transient pressure of the shock wave. Because of the short duration of the shock wave pulse, new monoliths are produced without changing the unique inherent material properties with limited grain growth.

In the literature, a number of scientists have reported shock consolidation of several rapidly solidifying powders to produce super hard materials, but still a number of problems remain to be investigated. A few of them are remaining cracks, weak inter particle bonding, inhomogeneities of consolidated material, clarity gradient and porosity at the core. Preparation and characterization of newer materials have attracted a wide range of fundamental and practical interest because of their interesting applications. Phase change due to the passage of shock wave, size reduction, morphology and compositions are the main concerns in applied material science. The selection of a technological material depends upon its cost, size, morphology, homogeneity and stoichiometry of the composition. There are also other applied aspects like increase of magnetic storage capacity with improved coercivity, retentivity and saturation magnetization, increased density with higher sharpness and hardness, the reduction of particle/grain size of the metal powder with potential utility for pyrophoric coatings and thin film deposition. Further investigations are needed to optimize the material applications in various devices such as memories, detectors, sensors, tuneable devices, switches etc. The optical band gap, refractive index, and the extinction coefficient are the most significant parameters.

The monolithic materials synthesized by the shock compression technique like cubic boron nitride, nickel based super alloys i.e. IN 718, EP 741 NP and Ni-Fe-Co have numerous industrial applications. C-BN is a very hard material with hardness ranking almost equal to diamond on Mohr's scale. This material is mostly used in cutting tool applications. Alloy Ni-Fe-Co is mainly used for ferromagnetic applications. The work reported in this paper is a part of the well-defined experimental programme coupled with computer simulation studies to fabricate the aforesaid materials including refractory compounds, cermets and ceramic-metal composites. This technique is being further used as a pre-densification step before sintering.



2 Theoretical discussion

Dynamic compaction by a shock wave is accompanied by high pressure acting on the material for a very short duration as compared to static compaction. The various physicochemical changes brought about by shock waves in the materials to synthesize the newer ones with unique properties and a number of industrial applications are difficult to achieve by static methods.

When an explosive is detonated, an axisymmetrical detonation wave propagates along the longitudinal direction of the undetonated part. Shock wave converges towards the axis and pressure grows steadily. The pressure generated accelerates the wall of the tube. This phenomenon has been depicted in fig. 1.

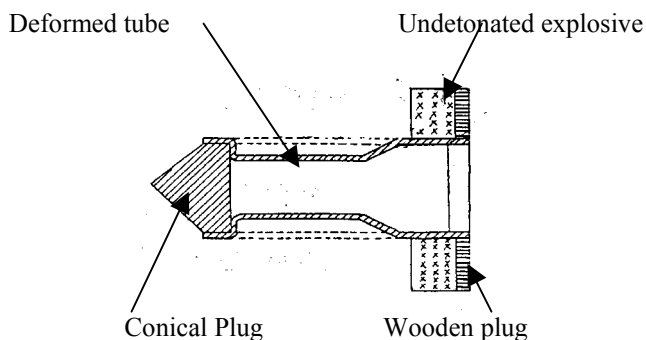


Figure 1: Shock compaction of metallic cylinder.

The propagation of shock waves in the powder takes place at a speed that is much smaller than the shock wave velocity in the corresponding solid cylinder. Therefore in the cylindrical arrangement of explosive compaction of the powder, oblique shock wave interaction is likely to occur. During propagation of shock wave in the cylindrical geometry, two opposing effects are decisive. The first one is the shock wave interaction of converging nature where the intensity increases towards the centre of the sample and the second one is the work performed on the powder primarily by plastic deformation of cutting or crushing of particles. Both effects in ideal cases are counterbalanced and uniform compaction over the cross section of the sample is achieved. Otherwise under or over compaction of the sample will result as reported by other workers [1, 2].

The densification and inter particle bonding mechanism which occur on a particulate scale during the dynamic/explosive compaction are extremely complex processes. In a transition from the powder state to a fully dense state during the passage of compaction wave, the particles must rapidly deform and flow to eliminate the void space and form stray inter particle bonds. It depends upon the generation of frictional and deformational heat, which softens the particle surface during the relative movement of the particles.

The explosive compaction zone is composed of a shock front followed by a zone of significant width in which powdered structure is transformed into a solid under the action of dynamic pressure generated by the explosive energy source.



The shock wave energy is consumed in absorption and transition processes. The word absorption means the energy consumed by the particles and the transition means the energy consumed while imparting velocity to the particles. Greater the energy is absorbed the lesser is the energy transmitted to the subsequent neighbours.

A shock wave is a region of high pressure and temperature. The matter compressed by the shock wave is accompanied by a sudden rise in temperature and hence there is significant difference in the behaviour of solid and porous material. In shock loading of the porous material, the starting sample with specific volume is compressed by means of dynamic pressure to smaller volume. Most of the energy is dissipated by heat. A part of it is stored in the material in the form of lattice defect and distortion.

Increased explosive thickness increases the duration of the pressure pulse. Monolithic materials are produced by densification/compaction of the powder by applying pressure and heat. Densification of powders by shock compression utilizes the extremely rapid and intense deposition of energy over grain boundaries. Densification occurs mainly by pressure. Because of the short duration of the shock wave pulse, new monoliths are produced by densification of powders without changing their unique properties with limited grain growth.

3 Preliminary work done

An extensive literature survey has been carried out before the actual experimentation. Rigorous studies on the phase transformation/synthesis of newer materials have been undertaken after successfully compressing the powders of aluminium, iron and copper to almost 97–98% of their theoretical densities. To achieve this, a number of shock wave experiments have been carried out by changing the explosive to powder mass ratio and also the size of the compaction systems. One such compacted specimen has been shown in figure 2.



Figure 2: Compacted specimen.

4 Experimental work

A number of research workers have used a variety of compaction systems for the powder compaction experiments [3, 4]. The cylindrical compaction system is a metallic tube made of mild steel. It consists of a conical plug at the top and a plain plug at the bottom. Both the plugs are also fabricated out of mild steel.

The cylindrical ampoule is placed in a cylindrical plastic container having a wooden plug at the bottom. The space in between the metallic tube and Plastic container is filled with the explosive. A wooden plug having an electric detonator and booster covers the plastic container from the top. In order to carry out the experiment, the explosive filled compaction cylinder is placed in an earth pit for easy recovery of the compacted specimen. Fig. 3 shows the trial setup before the experiment whereas fig. 4 shows compacted cylinder recovered after the trial.



Figure 3: Trial setup.



Figure 4: Compacted cylinder.

After carrying out the shock compaction trials using aluminium, iron and copper powders and standardizing the explosive to powder mass ratio, nature of explosive and shape and size of the compaction system, further rigorous studies on the phase transformation of Hexagonal Boron Nitride to Cubic Boron Nitride have been undertaken. The explosives such as Torpex 4A, RDX-TNT, PEK-1, Trimonite and ANFO have been used for carrying out the experiments. The X-ray analysis of the shocked samples has been carried out. In these studies, X-ray lines of c-BN with $I/I_0 = 8$ have been observed. Presence of h-BN has not been shown which indicates total conversion of h-BN to c-BN. An X-ray diffractogram of one of the shocked samples is shown in figure 5.

Shock compaction trials have also been carried out with IN 718 and EP 741 NP super alloy powders. The compacted samples have been retrieved from the compaction systems and the specimens are subjected to chemical composition and stress analysis studies. The report shows satisfactory compaction, as the porosity is not present.

The explosive compaction of nanocrystalline nickel base metal powder has been carried out. Alloy consists of 80% Nickel, 15% Iron and 5% Cobalt. This alloy is mainly used for making soft magnets. Before the shock compaction

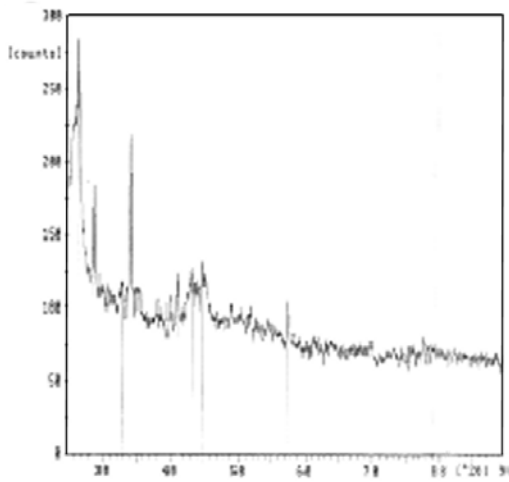


Figure 5: X-ray diffractogram.

experiments, mechanical alloying has been carried out by using a planetary ball mill. Powders are milled together for 125 hours in the Ball mill. Thereafter, the milled powder has been annealed at 500°C for different periods of time. XRD analysis for the grain size of the milled powder shows a 9.2 nanometer size.

5 Results and discussion

The compaction depends upon the ampoule material, tube wall thickness, quantity of explosive, velocity of detonation of explosive and also on the particle size and shape of the powder to be compacted. In the X-ray analysis of the recovered samples of the compacted boron nitride, the X-ray lines of c-BN have been clearly observed. The X-ray lines do not indicate the presence of h-BN. In order to achieve bulk production of c-BN, further shock transformation trials will be carried out in the near future using ampoules of larger size. The X-ray analysis results of the trial specimens have been shown in tables 1 and 2.

One interesting aspect with copper powder and c-BN is that the X-ray lines of both the materials are identical and the only difference lies in the relative intensity (I/I_0) at $d = 1.808$ (Angle $2\theta = 50.4^\circ$) where it is 46 for Cu and 8 for c-BN. In the samples where both c-BN and Cu powder are present, strong lines due to Cu with $I/I_0 = 46$ overshadowed the weak lines due to c-BN of $I/I_0 = 8$ at the same d value. One notable point in these experiments is that the presence of h-BN has not been indicated.

Super alloy powders such as IN 718 and EP 741 NP have been compacted. No porosity has been observed, however, some melting of the central portion has taken place. This problem is being overcome by carefully designing the shock wave experiments. The chemical composition and physical properties of the two alloys have been shown in tables 3, 4, 5 and 6.



Table 1: X-ray analysis results of trial specimens.

S. No.	Explosive used	Typical 'd' values	Relative intensities	Probable Phases	Unidentified lines
1	Torpex – 4A	3.3336 2.5433 2.2943 2.0945 2.0315	91.8 100 46.3 17.4	Cu/CBN	2.5433 2.2943
2	RDX-TNT (60-40)	2.5510 3.3471 2.0274	100 80 41	Cu/CBN	2.5510
3	PEK-I	2.0846 2.0717 1.8073 1.7979	100 72.7 44.1 42.5	Cu/CBN Cu/CBN Cu/CBN Cu/CBN	All lines identified
4	Trimonite	2.0971 1.8147 1.2813 1.0916	100 40 26.6 21.4	Cu/CBN Cu/CBN Cu/CBN Cu/CBN	Only other lines insignificant
5	ANFO	2.0760 1.8003 1.2754	100 39.5 22.9	Cu/CBN Cu/CBN Cu/CBN	Two other lines insignificant
6	ANFO	2.3349 2.0760 2.0248 1.8016 1.2790 1.2757	13 100 14.4 41.8 24.2 27.1	Cu/CBN Cu/CBN Cu/CBN Cu/CBN Cu/CBN	Two other lines insignificant
7	Trimonite	2.0817 1.8036 1.2767	100 34 17.1	Cu/CBN Cu/CBN Cu/CBN	One other line insignificant
8	PEK-I	2.0742 2.0547 2.0367 1.7970 1.7816	100 75 43.4 49 36.7	Cu/CBN Cu/CBN Cu/CBN Cu/CBN Cu/CBN	



Table 2: X-ray analysis results of c- BN and copper.

Copper			CBN		
dA	I/Io	hkl	dA	I/Io	hkl
2.088	100	111	2.088	100	111
1.808	46	200	1.808	5	200
1.278	20	220	1.2785	24	220
1.0900	17	311	1.0901	8	311
1.0436	5	222			
0.9038	3	400	0.9039	2	400
0.8293	9	331	0.8296	3	331
0.8033	8	420			

Table 3: Chemical composition of EP 741 NP, Wt. %.

Element	Powder sample	Specification as per VILS Moscow Russia
Co	15.6	15 – 16.5
Cr	8.8	8 – 10
MO	4.24	3.5 – 4.2
Al	5.6	4.65 – 5.25
Ti	1.64	1.6 – 2.0
W	5.1	5.2 – 5.9
Nb	2.4	2.4 – 2.8
Hf	0.27	0.1 – 0.4
B	0.02	0.02 – 0.06
C	0.03	0.02 – 0.06
O	60 ppm	60 ppm
Ni	Balance	Balance

Table 4: Physical properties of EP 741 NP produced by PREP technique.

Particle shape	Spherical
Mean particle size	70 micron (By sleeve analysis)
Apparent density	5.0 gm/cc (61% of theoretical value)
Tap density	5.4 gm/cc (66% of theoretical value)
Flow rate	13 sec/50 gms

In EP 741 NP, the dendritic structure has been clearly observed in the centre with dendrites oriented in the radial direction that also happens to be the direction of heat flow. This type of the structure is required for the best result. In IN 718, the dendritic structure with in the particle is intact. The structure in the outer portion is better with satisfactory microstructure since the grain boundary has undergone solidification. Successful compaction of nanocrystalline Ni-Fe-Co metal powder has been carried out by using ANFO explosive and 90% of the theoretical density has been achieved. SEM analysis of the milled powder shows



that the particles are flaky rather than spherical and their shape is irregular. TEM analysis indicates that the grain boundaries are not present and the internal structure is a homogeneous solid. SAD pattern shows mix-ring-spots combination but predominantly the ring pattern indicates crystallinity with some degree of amorphous phase due to large number of grain boundaries. Intact compacted sample is obtained after machining the outer shell.

Table 5: Chemical composition of IN 718, Wt. %.

Element	Powder sample (Gas atomized)	Specification as per AMS: 5663
Cr	19.6	17 – 21
Fe	18.9	16 – 20
Nb	4.7	4.75 – 5.5
Mo	3.1	2.8 – 3.3
Al	0.8	0.2 – 0.8
Ti	0.5	0.65 – 1.15
C	0.03	0.08 max.
O	275 ppm	---
Ni	Balance	Balance

Table 6: Physical properties of IN 718 produced by gas atomised technique.

Particle shape	Spherical
Particle size distribution	Mesh size (In micron): (-106+75) (-75+63) (-63+53) (-53+37) (<37) Wt. (%): 10.2 8.5 17.7 27.7 35.9
Mean particle size	50 micron (By sieve analysis)
Apparent density	4.18 gm/cc (51% of theoretical value)
Tap density	5.17 gm/cc (63% of theoretical value)
Flow rate	20 sec/50 gms

Table 7: Physical properties of Ni-Fe-Co milled powder.

Particle shape	Flakes form (irregular)
Average particle size	6 micron
Mean apparent density	1.6197 gm/cc
Mean Tap density	2.5247 gm/cc

In another experiment in which trimonite is the explosive, 89% of the theoretical density has been achieved. The desired crystalline structure is intact in the shock compacted samples. However, to achieve higher densities further shock trials will be carried out in the near future. The physical properties of the nanocrystalline nickel powder have been shown in table 7.



Acknowledgements

The author is grateful to the Director TBRL for his encouragement and permission to present this work. The author also expresses his sincere thanks to all concerned in his working group at TBRL, CGCRI Kolkata and DMRL Hyderabad for their assistance in carrying out experimental trials, X-ray diffraction and stress analysis studies respectively.

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Section 3

Materials characterisation and testing

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Experimental and theoretical investigation of the microstructural evolution in aluminium alloys during extrusion

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Abstract

The purpose of this work is the investigation of the microstructural evolution in aluminium alloys during extrusion at high temperature and subsequent cooling. In particular, the alloy EN AW-6060 of the 6000 series (Al-Mg-Si) is examined here. Subject to such process conditions, the microstructural development in this high stacking-fault material is controlled mainly by dynamic recovery during extrusion and static recrystallisation during cooling. To characterize this development in more detail, EBSD measurements are carried out on different parts of a partly extruded specimen. From this sample, microstructural images are generated and a statistical analysis is performed. Our initial simulation results of the microstructural development during this process show good qualitative agreement with the trends found experimentally via the EBSD investigation.

Keywords: aluminium, microstructure, extrusion, EBSD, subgrains, misorientation.

1 Introduction

Extrusion as a technological process is used to produce profiles with constant cross section from materials such as aluminium, copper, stainless steel, and various types of plastics. The advantages of aluminium and its alloys include high ductility (due to its fcc crystal structure), making it particularly suitable for complex extrusion processes. Additionally, the ideal ratio of the Young's modulus to density of aluminium allows a wide range of applications in automotive and aircraft manufacturing, as well as for lightweight construction in general.

The focus of this short work is to report on the microstructural details of an extruded EN AW-6060 alloy in order to determine the influence of various process



Table 1: Alloy composition of aluminium EN AW-6060 (components in alphabetical order)

component	Cr	Cu	Fe	Mg
%-weight	0.05	0.1	0.1-0.3	0.35-0.6
component	Mn	Si	Ti	Zn
%-weight	0.1	0.3-0.6	0.1	0.15

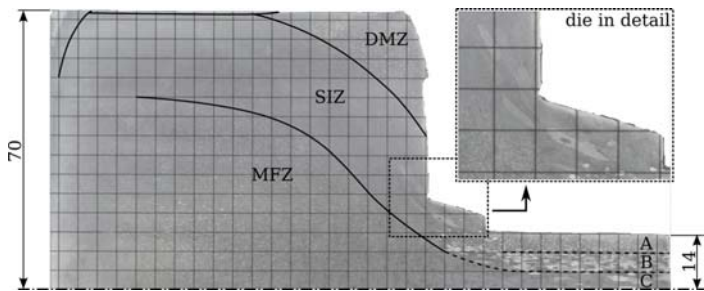


Figure 1: Partly extruded block of aluminium EN AW-6060.

parameters on the resulting microstructure. Aluminium EN AW-6060 is a commonly used industrial alloy with a composition shown in table 1. The main material characteristics are dominated by the components magnesium and silicon and their intermediate phase Mg_2Si which is responsible for the hardening behaviour of this particular alloy [1].

The investigations are performed on a partly extruded block of aluminium EN-AW-6060. After removal from the extrusion press and air cooling to room temperature, the specimen is cut along the middle axis in the extrusion direction. The cut surface is then polished and etched to reveal the grain structures which develop at different stages during the extrusion process.

Fig. 1 shows an etched cross section of the prepared partly extruded block with a block diameter of 140 mm and 28 mm in the extruding rod. The visible black grid is overlayed during the scan of the specimen. Further details about process conditions can be found in Table 2. The temperature in the container and die is determined by the extrusion press used. As indicated, it is generally lower than the initial temperature of the pre-heated block.

2 Microstructure evolution

2.1 Global microstructure overview

In the partly extruded block shown in Fig. 1, three different zones of microstructural development are evident. In the Dead Material Zone (DMZ), which forms



Table 2: Extrusion process conditions.

pre-heated block temp.	450°C
container temp.	350°C
die temp.	350°C
ram velocity	5 mm/s
extrusion ratio	5

a cone at the front of the block, friction between the block, container and die results in little material deformation and concomittant microstructural development. Indeed, the microstructure in the DMZ remains almost unchanged in its original state. In the neighbouring Shear Intensive Zone (SIZ), however, the material undergoes significant and predominantly shear deformation. As a result, the microstructural evolution in this region is quite complex, both during extrusion and cooling. The central region of the block represents the so-called Material Flow Zone (MFZ). Here, the material flows toward the centre of the extruded block. This material is mainly stretched in direction of extrusion and individual grains elongate into a banded texture [2].

Due to the high stacking fault energy of aluminum alloys such as EN AW-6060 and to the high temperature conditions during the extrusion process, the microstructure evolution, especially in the SIZ, is primary influenced by dislocation climb and dynamic recovery. The existing and additional deformation induced dislocations rearrange into dislocation-poor cells separated by low-angle dislocation-rich walls in the interior of existing grains, resulting in so-called subgrain formation. With further deformation, this results in a systematic decrease in the mean grain and subgrain size. Local shear deformation also leads to an increase of the misorientation angle between subgrains inside a grain. Misorientations larger than 15° indicate the transition from subgrain to grain. In addition, initial grain boundaries become serrated due to the subgrain evolution during grain elongation. In the extreme, this results in the joining of opposing grain boundaries to form new and smaller grains (see marked details in microstructure of point C6 in Fig. 2). Since new grains are formed in this process (at the size of the former subgrains), this mechanism is also known as geometric dynamic recrystallisation (GDX) [3]. Note that this has nothing to do with nucleation-based kinetics-driven dynamic recrystallization, which in comparison to dynamic recovery is energetically-unfavorable in aluminum alloys such as EN AW-6060 under the extrusion conditions of interest here.

The microstructure of the resulting profile can be subdivided into three zones denoted as A, B and C. The central zone C contains material from the MFZ. Here, the minimum stored energy needed to drive static recrystallisation upon extrusion is not generally attained. Consequently, on average, the deformation-dominated elongated-grain texture microstructure developed during the extrusion



process persists after the extrudate exits the die. Only in a few isolated regions near to the middle axis where the temperature stayed at a comparable high level exhibit some recrystallisation. The neighbouring Zone B evolves from the SIZ and is characterised by larger grains resulting from static recrystallisation. Apparently, sufficient energy storage takes place in the SIZ to drive recrystallisation after extrusion. Indeed, combined with faster cooling in regions near the free surface of the extrudate, this leads to recrystallisation becoming energetically more favourable than dynamic recovery. The high distortion energy in the deformed grains leads to a high-angle grain boundary migration starting at certain nuclei forming a new microstructure of dislocation free grains. More toward the interior, cooling below the critical recrystallisation temperature is slower, allowing longer growth of primarily recrystallised grains. This mechanism – called secondary recrystallisation – is now driven by the high surface energy of a fine grained microstructure. In contrast to this, zone A, which is also formed from the SIZ, shows a finer globular microstructure resulting only from primary recrystallisation. This stops when the temperature in this area near the surface drops below the critical recrystallisation temperature. The smooth transition between zones A and B is primarily temperature-related, whereas the one between zones B and C results from a sharp separation of materials from different deformation zones (SIZ and MFZ).

Taking a closer look at the microstructure near the die (see detailed view in Fig. 1) reveals elongated, abnormally large recrystallised grains in this area. This unexpected microstructure is in contradiction with the above mentioned recovery mechanism and is due to special experimental conditions. As shown in Fig. 1 the block is only partly extruded. It took 10 minutes to remove this partly extruded block from the press. During this time it remained heated. Because of this, primary and secondary recrystallisation occurs in the material from the SIZ near the die. This is not expected to occur in the block or in the die region during a continuous extrusion process.

2.2 Microstructure evolution along middle axis

The characterisation here is based on Electron Backscattering Diffraction (EBSD) measurements. These facilitate direct access to the microstructural characteristics like grain misorientation or (sub-)grain size. EBSD measurement results consist of a list of measurement point coordinates together with the Euler angles describing the orientation of the crystal lattice in space at this point. Beside using the commercial program Orientation Imaging MicroscopyTM (OIM), we developed and use our own software to generate images of the microstructure from the EBSD data as shown in Fig. 2. Here, the colours are directly related to lattice orientation and represent distinct grains with a relative misorientation greater than 15°. The original EBSD measurement data also contain several points where no measurement was possible, as well as fragments of over- or underlying grains which are automatically filtered out. All results to follow have been directly generated by our in-house software GRAINPLOT and have been validated via comparison with OIM.



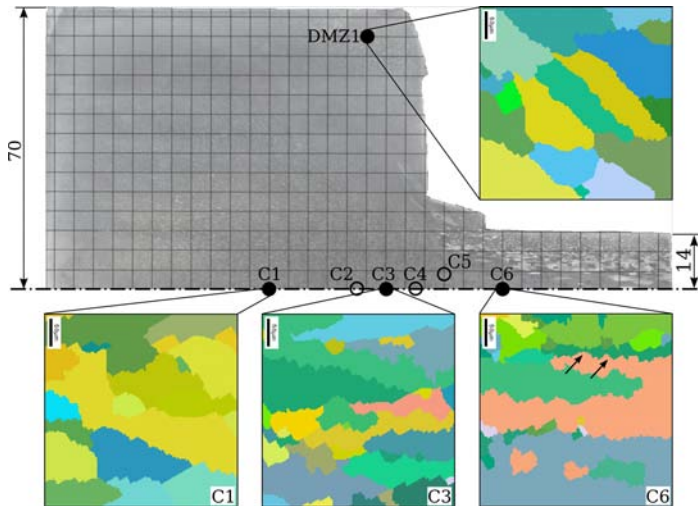


Figure 2: Microstructure evolution along middle axis.

An overview of microstructural evolution in the block is shown in Fig. 2. This is represented by four EBSD measurement points in the block along its axis together with one point in the DMZ. The microstructure of point DMZ1 in the dead material zone serves as an example of the initial microstructure in the block and as a reference for comparison with the microstructure at the other points. The three micrographs below the block in Fig. 2 illustrate the previous discussed elongation and reorientation of grains in the centre of the block. The arrows in the micrograph of point C6 mark the serrated grain boundaries which later lead to a fragmentation into separate grains of former subgrain size.

Exemplary of the general microstructural development as a whole in this region are the results at points C1, C3 and C6. C1 is 40 mm, and C3 10 mm, in front of the die inflow. Further, C6 is located 5 mm beyond the die exit. Each EBSD measurement shown covers an area of $350 \times 350 \mu\text{m}$. The EBSD results for the additional points C2, C4, and C5 are not shown; however, these results are included in the statistical characterisation of the microstructure to follow.

Beside the graphical representation of the microstructure, the EBSD method also allows a statistical evaluation regarding microstructural quantities. For example, Fig. 3 shows the development of the number of grains separated by high-angle boundaries as well as that of their mean and median grain sizes. Clearly indicated here is the decrease of mean grain size during the deformation process. The stagnation and slight increase at point C5 does not fit into this general behaviour. This could be related to the location of C5 at 3.5 mm outside the centre line for reasons of the specimen preparation. The median grain size in Fig. 3 is more robust against outlier values and confirms the general decreasing character of the grain size. Corresponding to the decreasing grain size is an increase in the number of grains along the centre line.



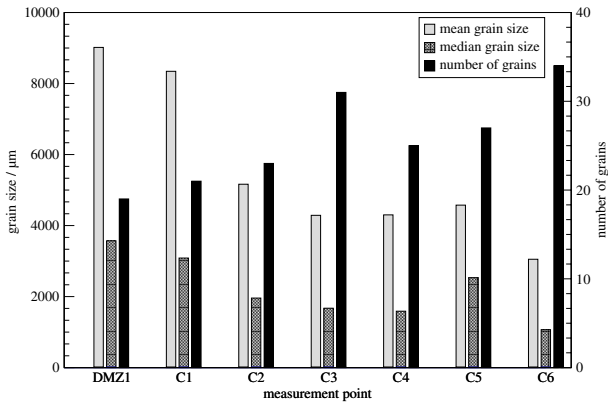


Figure 3: Mean and median grain sizes and number of grains at measurement points.

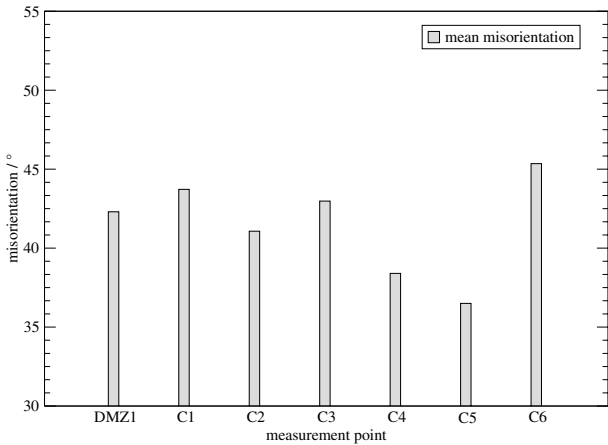


Figure 4: Mean misorientation at measurement points.

The histogram in Fig. 4 shows the statistical results of the misorientation distribution at the measurement points. Following the centre line of the block through to the die, the grains tend to align more and more in direction of the material flow. Hence, the misorientation angle generally decreases from point C1 up to point C6. The increasing value of point C6 located in the extrudate could be explained by static recrystallisation effects which can be sporadically observed in this zone. While interpreting the statistical results one should be aware that these values are based on single measurements where each EBSD data set covers only a region of $350 \times 350 \mu\text{m}$. Further measurements are planned to reduce statistical uncertainties.



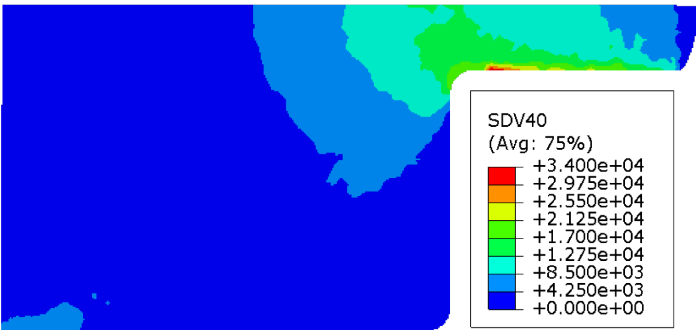


Figure 5: Simulated mean recrystallised grain size.

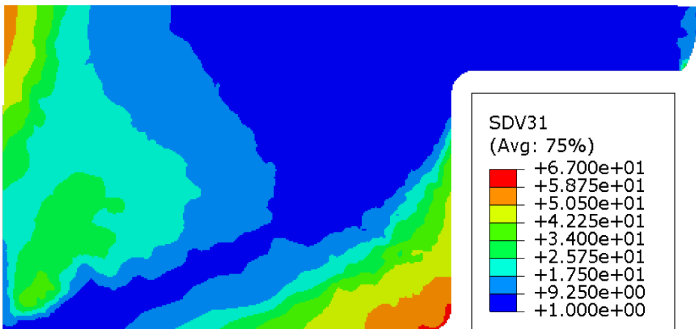


Figure 6: Simulated subgrain size.

3 Simulation

The simulation results presented in Fig. 5 and 6 are produced using a user material (UMAT) model implemented in the commercial Finite Element (FE) solver ABAQUS. The model is based on a formulation introduced by Sellars and Zhu [4] and can also be found in a similar form in [5, 6]. It describes the dependency of the inelastic part of the free energy density on the internal dislocation density, subgrain size, and grain misorientation. For a detailed overview of this model and its implementation refer [7]. In particular, the model is based on a flow rule depending on the Zener-Hollomon-Parameter [8].

Fig. 5 shows the distribution of the mean recrystallised grain size which mainly increases in the region near to the surface of the extrudate. This result corresponds to the general microstructure evolution described in section 2.1. The simulated subgrain size distribution presented in Fig. 6 shows a good qualitative correlation to the micrograph in Fig. 1. While the subgrain size in the DMZ remains near the starting value it significantly decreases in the SIZ which is also directly visible in the etched specimen.



Acknowledgement

This work is embedded into the Transregional Collaborative Research Centre TR30 (see <http://www.transregio-30.com>) funded and financially supported by the German Research Foundation (DFG).

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Fracture toughness K_{IC} of cemented carbide WC-Co

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Abstract

Rotating bending fatigue test was carried out using the cemented carbide WC-Co in ultra-long life. A carbide metal WC has many defects on the boundary. A crack initiates from these defects, and propagates along the boundary. Fatigue limit does not exist. The boundary slips easily, and is weak to sharing force. The fatigue crack propagation rate (da/dN) cannot calculate. But, fracture toughness K_{IC} can calculate from relationship fractal dimension or Hurst number (localized wavelets transformation) and yield area. Yield area of fracture in ultralong $N_f=2.05 \times 10^7$ broad Origin of fracture is surface defects. When $K_{IC} > K_{max}$ in surface stands up, the crack in the plane stress propagate. The fatigue strength of WC cemented carbide is obeyed to weakest link model of defects. Because, even if it supposes that it was worked the cyclic stress over the fatigue strength, the fatigue fracture did not always happen. If $K_{max}/K_{IC} = \text{const.}$ stands up, a small crack is equivalent to a small defect, and fracture of material is induced by initiated crack. By the fractal dimension analysis, the phenomenon of fracture mechanisms will be clear.

Keywords: fracture toughness, cemented carbide WC, double bending S-N curve, fractal dimension, Hurst number.

1 Introduction

Cemented carbide occupies an important position as an element of tool, but is not studied as much as high-hardness, high-toughness carbon steel. As regards the method for evaluating cemented carbide, either transverse fracture strength or fracture toughness by impact value is used. In either case, Palmqvist [1], method which consists of measuring the length of cracks produced at the corner of a



Vickers impression, is used. There are also a variety of other techniques for introducing initial cracks, and each of them has its advantages and disadvantages. According to Chermant et al [2], who studied variations of fracture toughness K_{IC} , due to differences in particle size of WC-Co material which was used in the present study, the larger the particle size of WC the greater K_{IC} , even with the same Co%. One reason for it is the suspected presence of something other than iron-based metals is because the grain boundary binding energy increases. However, the notion of weakest link model is generally accepted against unstable fracture of materials such as ceramics, etc., because most of the factors are represented by intergranular fractures due to second-phase granular action by segregation of Co. As described above, the method of determination of fracture toughness is similar that used in quasi-static tests, and fracture toughness is calculated and defined by the length of the crack. However, because the fracture toughness value variable in depending on whether the point of origin of the crack is on the surface or inside the material, those factors should be determined from the conditions of fatigue fracture mechanisms, its fracture mechanisms was clarified by the small-scale yield area to large-scale yield area based on a fractal dimension analysis as a method of fractography. The boundary determination of the plastic zone was made by noting changes in fractal dimension with reference to the image by using a confocal laser microscope. The method using photographs cannot be said to be an accurate method because it involves a change of dimension, but it enables researchers to pass judgment on whether an unstable fracture has been produced based on whether a position deviated from the linear relation or not.

2 Test specimen and fatigue test

As a test specimen, we used bending fatigue test pieces of smooth rotation finished in the shape and dimension with a parallel portion of 5 mm indicated in Figure. 1.

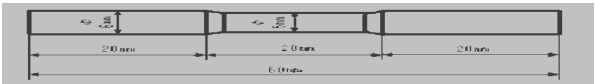


Figure 1: Rotating bending fatigue test piece.

Figure 2 shows a micrographic photo observed at a magnification of 1500 of the test piece cut out in the axial direction after the test and etched with Murakami's reagent.

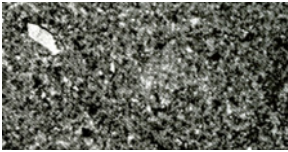


Figure 2: Micrograph of test piece [$\times 1500$].



The white insoluble particles are believed to be residues of Cr. They remain as so-called second-phase particles.

Table 1: Chemical Components of carbided carbon WC.

WC	VC	Cr ₃ C ₂ %	Co %
87.5	0.7	0.8	11

Table 2: Mechanical properties.

Applications	Vickers hardness	Transvers rupture strength	Density	Fracture toughness	Coefficient of thermal expansion	Coefficient of heat conductivity	Young's modulus
Various quality	1690-1725 1708	GPa 3.1	14	MPam ^{1/2} 9.5	× 10 ⁻⁶ /K 5.6	W/mk 63	GPa 550

A lot of pores with fine particles are observed generally. The results of the fracture toughness test by Chermant et al. [2] mentioned earlier agree with the results obtained in the present study.

$$K_{IC} = \phi \sigma \sqrt{a} \tag{1}$$

In that example, calculated values of $a+\Delta a$ obtained by changing the amount of load in the measured values of Vickers hardness are plotted. The axis(x,y) in Figure 3 is arbitrary. From those values, the value of fracture toughness comes to 9 MPam^{1/2} in the case where the particle size of WC is 1 μm. Moreover, mention made of a study used for estimating the maximum strength from the relation with the transverse rupture strength by putting the pores as a defective surface area of $A^{-1/4}(\mu\text{m}^{-1/2})$. This study is subject to the condition that not only the fracture toughness but also the transverse rupture strength are large. In any case, the test method described above is quasistatic, and is not intended for fatigue strength. In the present study, we propose a method for determining the dimensions of plastic zone on the basis of the information which appeared in the fractured face as a result of fatigue test. The value of fracture toughness can be determined from them.

3 Test results and discussion

3.1 Ultra-long of S-N curve

Fig. 3 shows an S-N curve. Two test pieces fractured as a result of fatigue test by rotating bending were prepared by changing the stress level. For the horizontal part, Murakami proposed a method which consists of giving a critical value of progress of crack from the regression.

Statistics of extremes is used in order to provide an estimated value of fatigue test piece from surface area of the pore. This method is currently accepted as $\sqrt{\text{area}}$ method [2]. As a result of calculations made by using the fatigue limit



evaluation formula in the case of the presence of some interposed material, an S-N curve as shown in Figure. 3, in general the shape of a two-stage bent type was obtained. However this cannot be considered as a detailed test result, partly because there is no reason to believe that any stoppage of crack takes place, judging from the fact that a fracture is produced immediately if some crack is initiated. By comparing with the mentioned above test results of other high-hardness , high-strength materials, that reason may be acceptable. However, based on reports of an example in which the material is bent in double stages as SNCM heat-treated material, among various raw materials, it is presumed that the pattern in the shape of stripe observed on the present test specimen shows a trace of progress and propagation of a crack. By the left in Figure 4, we can see that the face with propagation of crack stands on a different level.

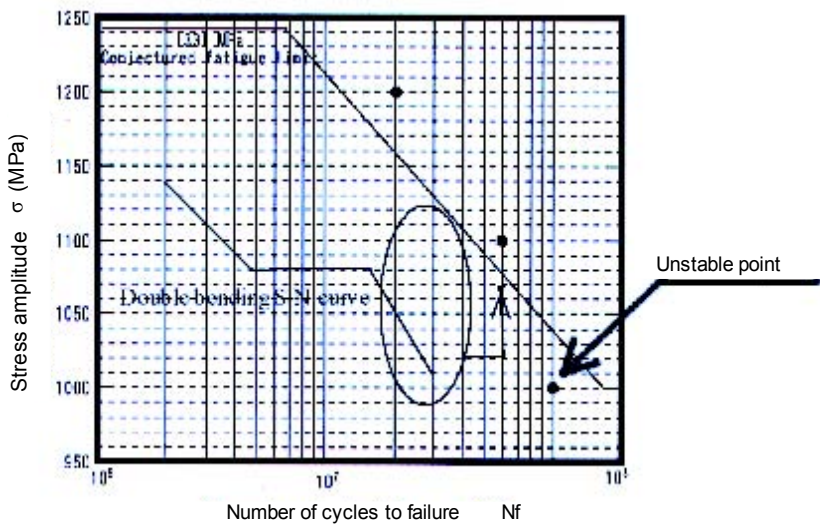


Figure 3: S-N curve in ultra-long Nf.

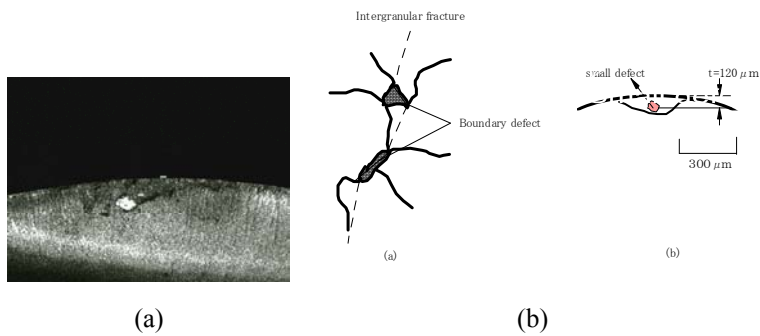


Figure 4: Internal defect of Co.

4 Fracture toughness K_{IC}

4.1 Calculation method of fracture toughness K_{IC}

Description will be made of a method for estimating the fracture toughness value by fractography. A crack propagation pattern is left on the fracture by fatigue. If that information can be obtained quantitatively, it would be useful as a reliability evaluation method. It is often the case that, regarding propagation of cracks, the material characteristics are described from a $da/dN-\Delta K_{IC}$ diagram by checking the propagation rate of cracks on the surface of the specimen. In any case, a method which consists of describing the material characteristics by formulation lacks in description having unified universality. For that reason, we aimed at calculating the fracture toughness value showing the material characteristics by the method of image diagnosis and numerical expression, and studying it as fatigue fracture toughness value. Because fatigue fractures continuously change from small-scale yielding to large-scale yielding and their traces are left on the fracture, this is one of the reasons for adopting them as information. In this regard, a scanning confocal laser microscope is extremely effective. That is because it enables to easily visualize the height information which is one of the characteristics of the confocal type. If time-differential pictures are available, even approximation of the propagation rate of cracks may become possible, but this study does not go that far. A distribution spread of the yield area can be obtained in the form of a picture. Therefore, we applied and performed a method of numerical image analysis regarding finding of the magnitude of yield area. In the micrographic in Figure 4, there is a difference in brightness which seems to indicate formation of a plastic zone. The expanded schematic diagram (B) of the plastic zone away from the starting point shows an example of cracking in shell pattern with formation of intercrystalline cracks. At the central part of the defect, a fine white starting point is found and a black portion of the plastic zone is observed. Its dimension is approximately $25\text{ }\mu\text{m}$ and generally agrees with the results of fractal dimension. Furthermore, in the brittle fracture picture (A) at a position distant from the starting point, black patterns in stripes similar to crazing patterns can be observed. Those black patterns in stripes show spreading in a direction perpendicular to the direction of propagation of cracks, but they are different from ductile fracture type striation. This type of cemented carbide material is quite brittle against shearing, and it is rather difficult to visually find the dimensions of a fine yield area. In the present study, no fine yield area can be observed from Fig. 3, but this is believed to be something counted in the category of fatigue. There is no area showing generation, agglomeration, and propagation of cracks, and it is presumed that an unstable fracture takes place simultaneously as a result of intergranular cracks. In addition, as shown in the schematic diagram in Figure. 4(B), a fine crack (abnormality of Co) of insoluble metal compound, indicated in Figure. 4(A), which existed at a position approximately $120\text{ }\mu\text{m}$ from the surface in the case of cyclic stress of $\sigma_s = 1100\text{ MPa}$, was observed. Therefore the method of calculation of surface area of the defect as well as of the fracture toughness value will be described briefly. It



consists of checking the relationship between the fractal dimension and the dimension of fine yield area by grid-square analysis by transforming a 3-dimensional image of the scanning confocal laser microscope into peak-to-peak.

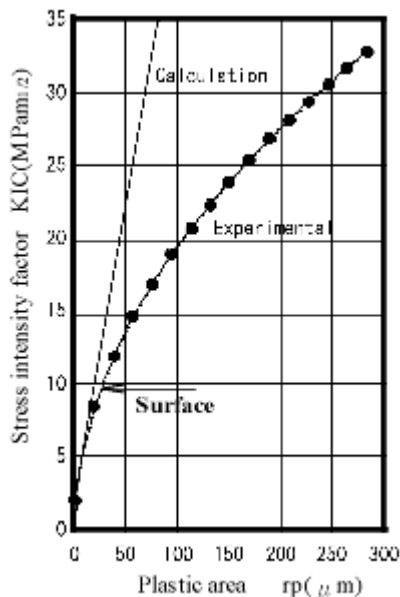


Figure 5: Relationship fracture toughness K_{IC} and plastic zone r_p (internal origin).

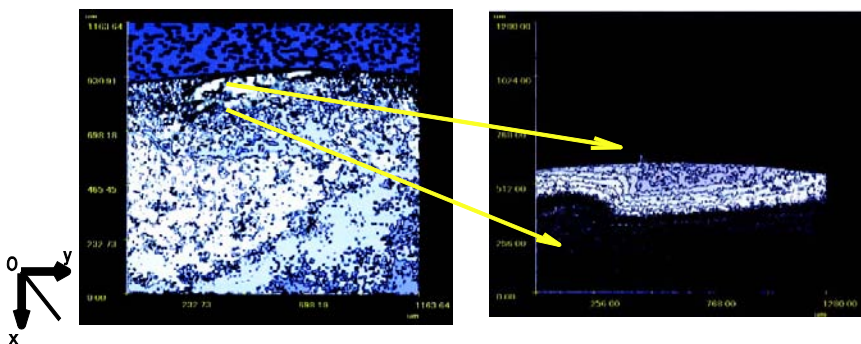


Figure 6: Photograph of surface origin [$\sigma_s=1100$ MPa].

height information, and calculating the fracture toughness value by the following formula:

$$w_p = \frac{\pi}{8} \left(\frac{K_{IC}}{\sqrt{3} \sigma_Y} \right)^2 \quad (2)$$



where, formula (2) is an effective formula, σ_y is an effective value, and r_p is a half length of fine yield area.. In addition, as maximum allowable stress:

$$K_{\max} = F \sigma_0 \sqrt{\pi a} \tag{3}$$

where, F is a correction coefficient, set for $a < w_p$

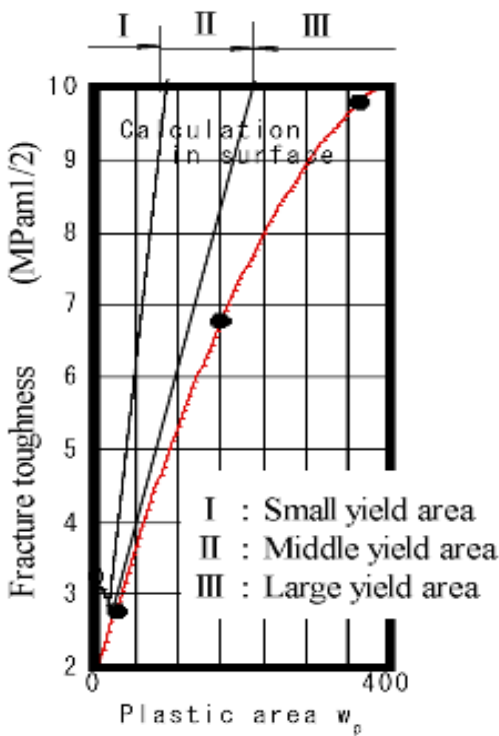


Figure 7: Relationship fracture toughness and plastic zone w_p (surface origin).

If $K_{IC} > K_{\max}$ is established, it is defined as non fracturing stress. At that time, dimension of the defect is given as one, $K_{\max}$ it becomes a very small value. If you define the fine yield area as $Wp=x_a+r_p$ from the Dugdale model, the calculation is made by using $a+r_p$, on the condition of $r_p \gg a$. In the case of $K_{IC} = K_{\max}$, it shows that the crack does not propagate beyond this area. Namely, formula (4) gives conditions of unstable fracture. By calculating $K_{\max} / K_{IC}$ from the relation of Figure. 5, one obtains $a = 1.1215$ which satisfies the conditions. The spreading of the yield area is not clear from Fig. 6(a), but a pattern in stripe due to a difference of height appears.

The distribution of spreading can be understood if the image is turned into a confocal image, however, it is impossible to read up to the dimension r_p of

small-scale yielding. We therefore decided to determine the fractal dimension and a for it, to find the K_{IC} value. In that case, the fracture toughness value taken seems to be the value at $r_p = 25 \mu m$ and approximately $3 MPam^{1/2}$. In this way, a difference is produced in fracture toughness value between surface type and

$$s_0=1.390s_y \dots\dots\dots (4)$$

internal type, and one of the reasons for it is that the fracture toughness value is determined by the surface stress and the state of surface strain. If the fracture toughness value is the same , the relation of K_{IC} (inter) = 1/9 K_{IC} (surf) is about established.

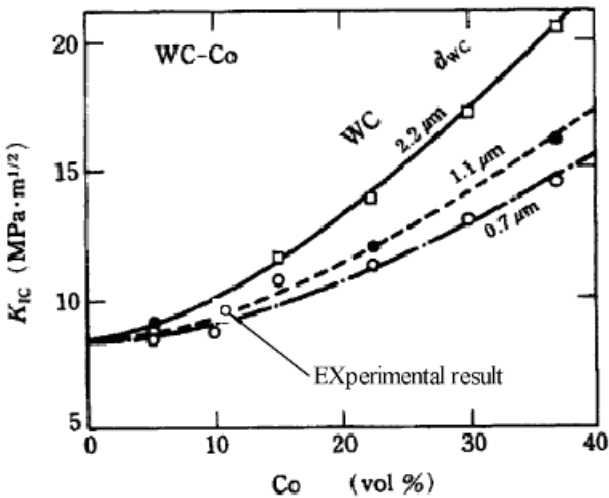


Figure 8: Typesetting author's value on Chermant et al. [2].

5 Observations

In the present study, we proposed a method of calculating the fracture toughness value from the yield area of a fracture by fractal dimension analysis. To check the characteristics of the fracture in more detail, it is necessary to expand the calculation up to the Hurst number. However, since the numerical values are smoothened to average the changes if the calculation is expanded up to the Hurst number, we deleted the noise on the way by moving the average in a way to show the peak-to-peak height. In this connection, we obtained 0.3 ($0 < d_H < 1$) as the Hurst number by calculation. If the Hurst number comes close to 1, it causes fluctuation and there is progress. From the stand point of analysis of numerical image, it becomes meaningless because the high information is smoothed. Therefore, we tried a method enabling us to make proper analysis without destroying the information characteristics of the fracture. Because the original information is that of roughness parameters we made by fetching surface roughness into the basic information, we obtained excellent Figures 5 and 7.

Those results were transplanted in Figure 8 of Chermant et al. The fracture toughness value calculated on the basis of the data obtained from the results of fatigue test turned out to be an excellent one, clearly showing that there is no need of performing any particular fracture mechanical experiment. However, ambiguity of fractal dimension analysis makes it necessary to calculate from a distribution chart in the direction q by fixing a coordinate centering on the starting point. Data processing was simplified by a method of collectively handling peak coordinates, which is used as one of the methods for omitting such troublesome steps. Although the fatigue limit estimation method of S-N curve described in paragraph 3.1 gives a description of approximately $s_w=1330$ MPa, from the scope of the present study, there is a report that, in reality, that figure comes to approximately 1600 MPa. There is also a report that the fatigue limit stress obtained from a rotation bending fatigue test is approximately 1000 MPa. We would like to mention that, in the present study, we determined the fatigue limit stress by applying the maximum defect distribution of regression values from extreme-value statistics, and came to the conclusion that a value of approximately 1600 MPa is appropriate. From the information regarding fracture of sintered alloy, there is no process of generation and propagation of cracks, and this is useful because the yield stress can be calculated by tracing back from the fracture toughness value if only the starting point is known. In the boundary of fractal dimension, by putting as $K_{\max}$, K_{IC} , $w_p=a+r_p$ from formula (2),

$$s_0=1.390s_y \quad (5)$$

The yield stress comes to about 70% of the repetitive stress. The crack propagation mechanism is different on the surface side from that with the internal starting point type. The fracture toughness value of the internal starting point type is approximately 60% of the value on the surface side. This is interpreted as resulting the difference in the state of plane strain and the state of plane stress.

Here is a summary of what has been described above.

(1) Height information by fractal dimension is an extremely important factor for knowing the form of fracture. If the distribution of 2-dimensional fracture at the same time is checked, it is useful because it enables us calculate the stress at any desired point $P(x, y)$ at a distance r from the starting point.

(2) In the present study, we determined the dimension of plastic zone from Dugdale model, given by the following formula with crack propagation rate curve, i.e.

$$K_{\max} = \frac{\Delta K}{(1-R)} \geq K_{IC} \quad (6)$$

Formula (6) gives the condition of unstable fracture.

(3) The distribution chart in Fig. 5 indicates that breaking took place because of a crack produced in a very early period. Further progress into the shape of secondary curve can be understood from the fact that turning up was observed with the left and right test pieces because of a difference in the gradient of height.



(4) From Fig. 5, the fracture toughness value increases on the surface of the test piece. What is important is the point of separation and breaking, and the fracture toughness value at that point comes to approximately $9 \text{ MPam}^{1/2}$. This value agrees well with the value determined by CT test.

Figure 2 shows a micrographic photo observed at a magnification of 1500 of the test piece cut out in the axial direction after the test and etched with Murakami's reagent.

(5) Because one obtains $a = K_{\max}/K_{IC} = 1.1215 := \text{const}$ and the Hurst number takes a low value of 0.3 or so, the fluctuation of height can be presumed to be rather small.

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Characterisation of natural Zeolite and the feasibility of cations and anions removal from water

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Abstract

There are great resources of natural zeolite in Iran. Zeolite, an inorganic ion exchanger, may be used as a suitable technical-economical solution for water treatment in many regions in Iran.

In this research, the characterization of Zeolite in the east region of the country and the feasibility study for removal of hardness, cations and anions was investigated as follows: (1) determination of Zeolite composition and type by using X-Ray Fluorescence (XRF), thermal analysis and infrared spectrometer methods. (2) determination of cation exchange capacity (CEC) and its impact on water hardness reduction. Determination of isotherm curves for Fe, Cr, Al, Bi, Cd, Mn, Ca, Mg, Ag, Ni, Zn, Cu, Pb and their disposition to Zeolite phase, also determination of removal rate of the mentioned cations in analyzed water samples. (3) Zeolite structure rectification by using surfactant (HDTMA) for anions removal.

Keywords: natural Zeolite, characterization, water treatment, cations and anions removal.

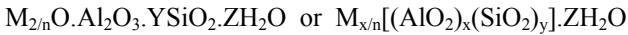
1 Introduction

Using new materials for economical-technical optimization of water treatment process is always under close investigation.



Zeolite is a microporose rigid crystalline with pore, cleft and a micro canal diameter of 3-10 angstrom. It is an inorganic ion exchanger belonging to crystalline alum silicates classification and its crystalline lattice consists of SiO_4 and AlO_4 units with common oxygen. The absence of one positive valence because of existing 3 valence aluminium ions causes access possibility of alkaline ions. It must be mentioned that these ions don't have a stable condition in crystalline lattice and their exchange with cations is probable. Ten-twenty percent of Zeolite's weight relates to existing water. All or part of this water can be removed by heating up to 350°C without destructing of the crystalline lattice.

The applied formula of Zeolite is:



M = metal cation, n = cation's valence, x = 2-10, y = 2-7.

In general, Zeolite consists of following three main segments: (1) aluminium silicate framework (in bracket), (2) vacuous pores of crystalline lattice containing exchangeable cations, (3) water molecules as a surround phase. The natural and synthetic Zeolites are categorized due to secondary structural units including S_4R , S_6R , D_4R , D_6R , T_5O_{10} , T_8O_{16} and $\text{T}_{10}\text{O}_{20}$ [1,2,4,5]. One of the major sources of Zeolite is located in the east of Iran (fig. 1).

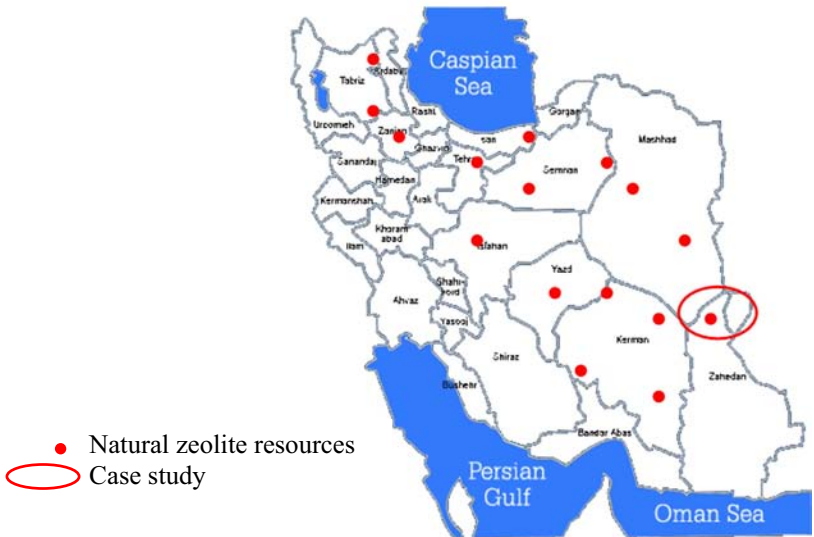


Figure 1: The location of Zeolite sources in Iran [3].

2 Characterization of natural Zeolite

The characterization of investigated natural Zeolite resulted from the following methods: (1) Thermal weighting analysis (fig. 2). (2) Ultra red analysis with SHIMADZVIR-470 spectrometer (fig.3). (3) X-Ray D analysis (fig. 4). The results are showing a certain conformity with Natrolite ($\text{Na}_4\text{Al}_4\text{Si}_6\text{O}_{20}\cdot 4\text{H}_2\text{O}$) [6].

3 Hardness removal

Due to the importance of water hardness as a quality parameter, particularly for groundwater resources, its reduction via natural Zeolite was investigated.

3.1 Materials and method

Two gram agitated Natriumzeolite in 100 mL water and 24 hours detention time in a shaker was used for determining of total, temporary and permanent hardness via EDTA titration method.

3.2 Results

The results show considerable efficiency (ability) by using Zeolite for hardness removal (fig. 5).

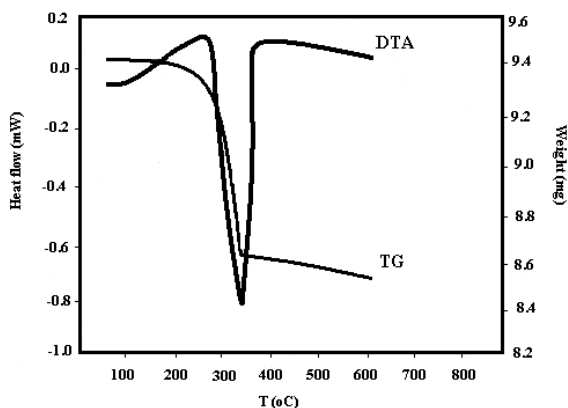


Figure 2: Thermal weighting analysis diagram of investigated Zeolite [6].

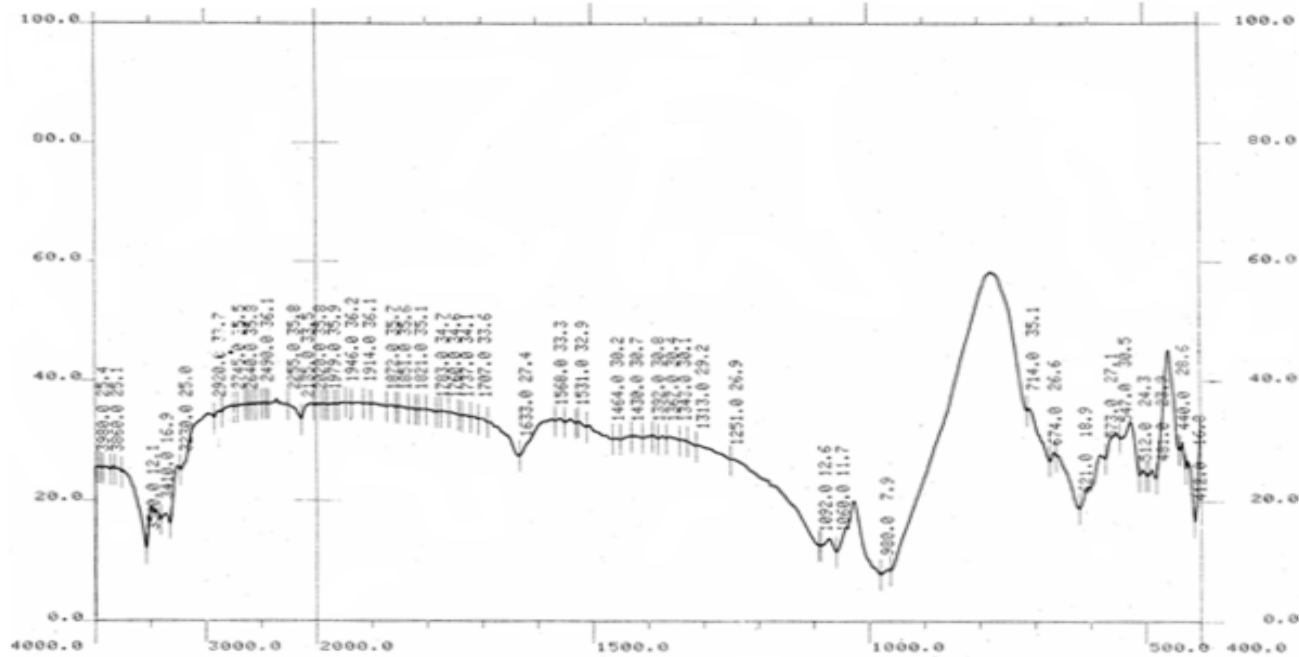


Figure 3: IR spectrum of investigated Zeolite [6].

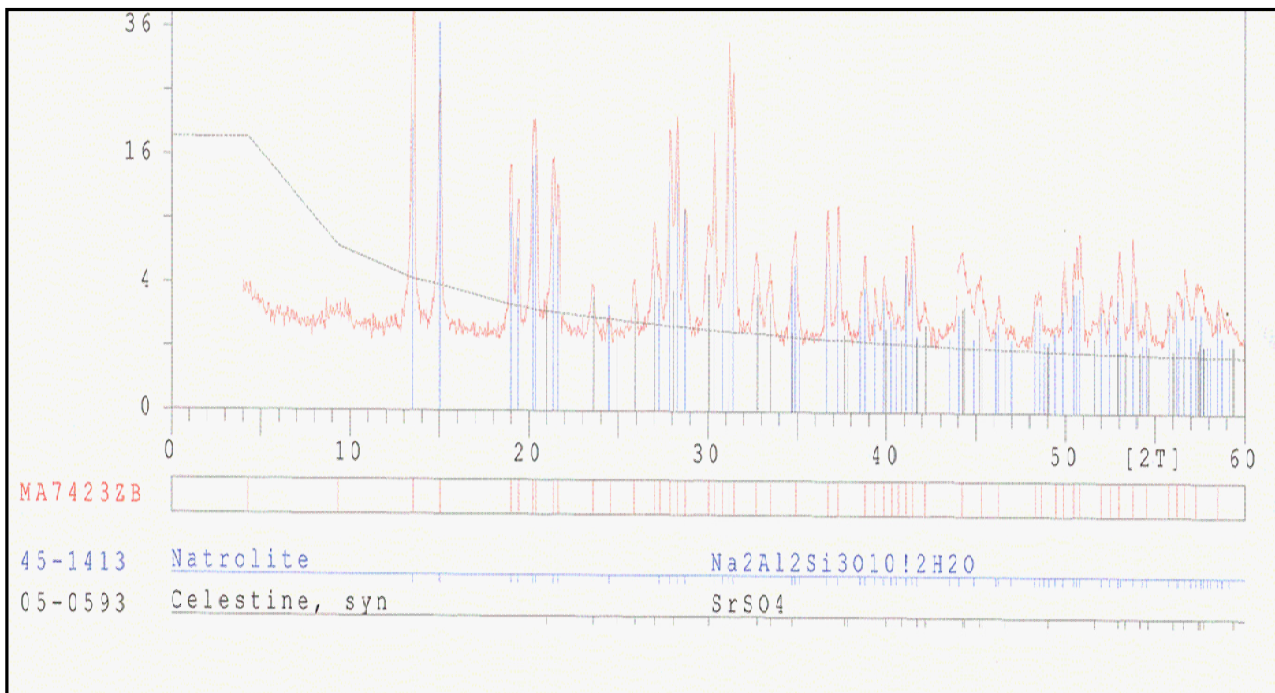


Figure 4: XRD spectrum of investigated Zeolite [6].

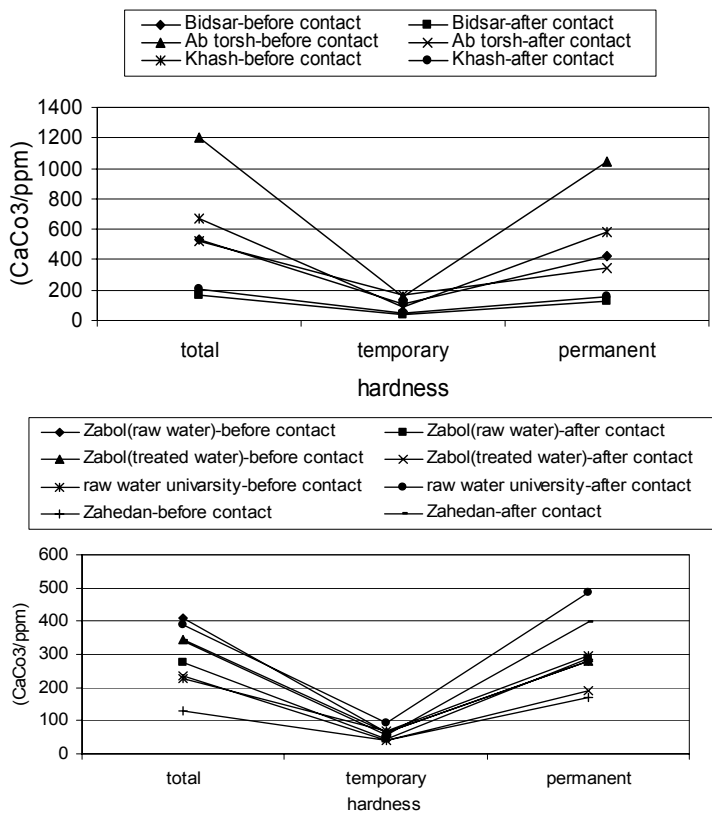


Figure 5: Water hardness removal, 7 different water samples [6].

4 Cations removal

4.1 Materials and method

Zeolite samples, mesh 80, were used after mixing with 4M Natrium chloride for 24 hours and decantation of upsides liquid. After washing the Zeolite with distilled water (2 times distillation) and removing remaining salt, and then drying, the process was performed. Considering the adsorption coefficient importance of each adsorbent phase, the adsorption isotherms were determined, due to Freundlich isotherm. For this purpose, 1 gram of Zeolite was mixed with 50 mL of liquid of different analytes with different concentrations for 48 hours. The remaining concentration of analyte was determined via an atomic adsorption spectrometer.



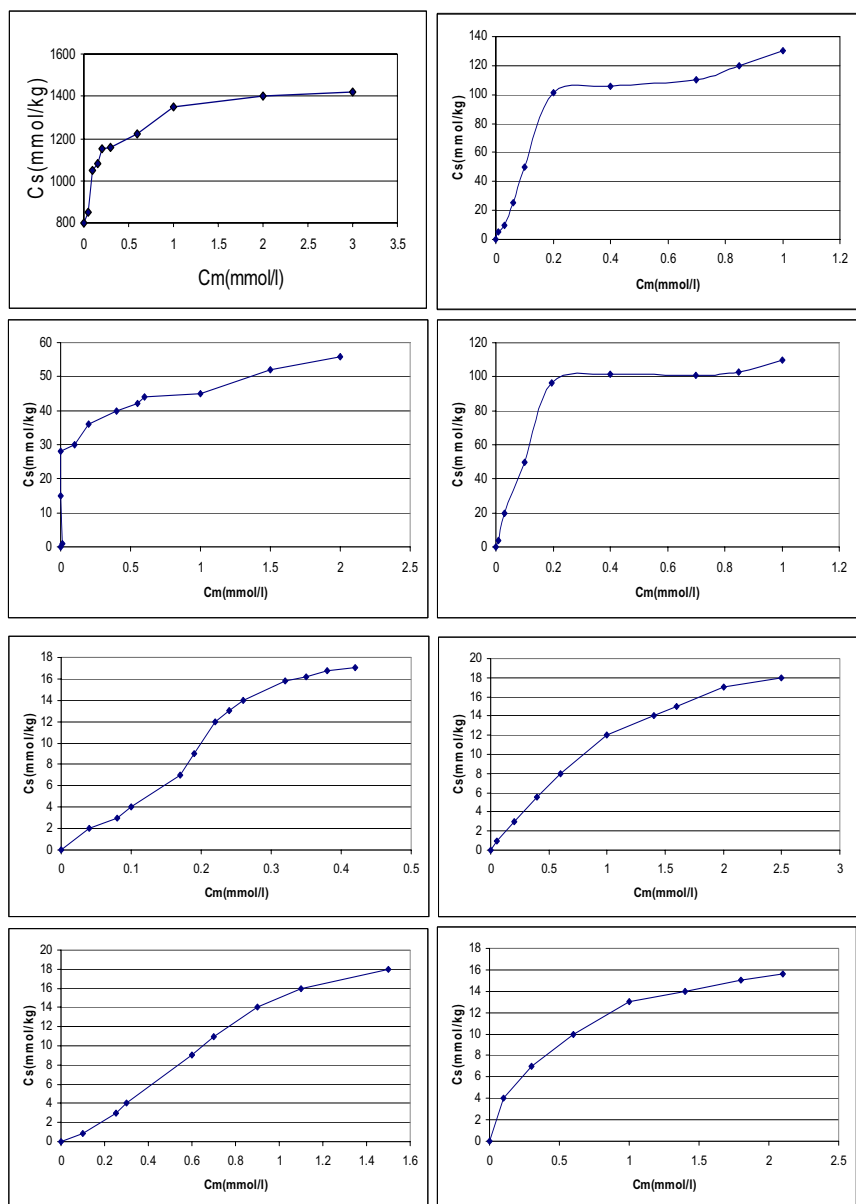


Figure 6: Isotherm curves of investigated cations, in order Fe, Cr, Bi, Al, Cd, Mn, Ca, Mg, Pb, Ni, Ag, Zn, and Cu [6].



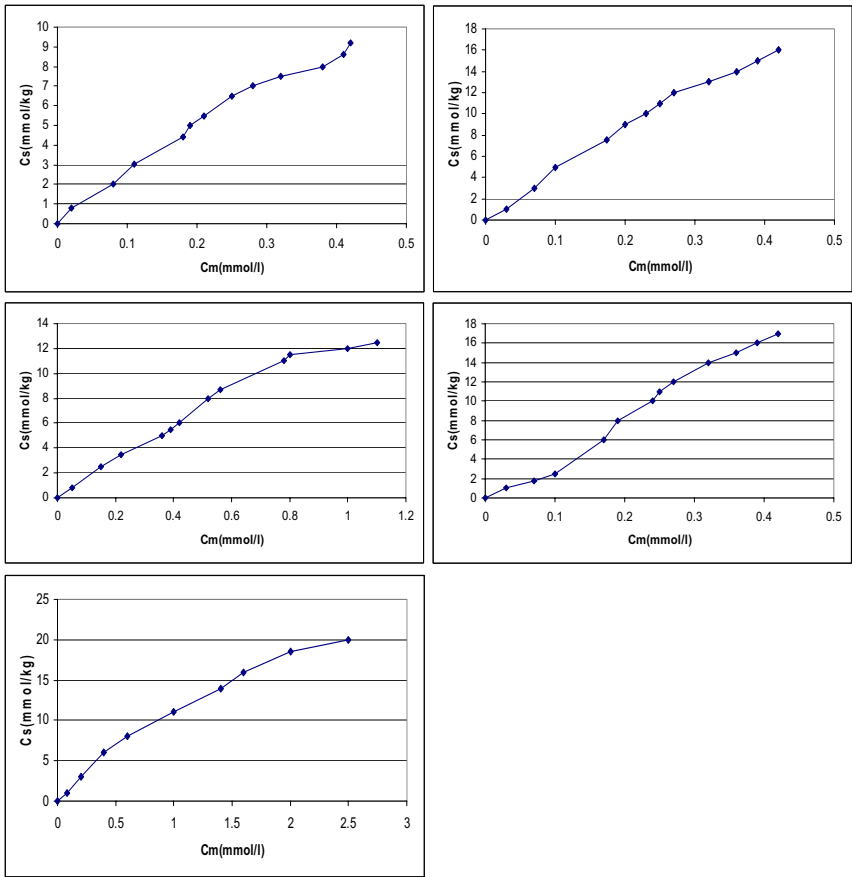


Figure 6: Continued.

4.2 Results

The obtained isotherm curves are shown in Figure 6. Due to the results, the classification of different cations in accordance with their affinity to Zeolite is: $\text{Fe}^{3+} > \text{Cr}^{3+} > \text{Al}^{3+} > \text{Bi}^{3+} > \text{Cd}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} \sim \text{Ag}^{2+} \sim \text{Ni}^{2+} \sim \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Hg}^{2+}$.

Considering high concentrations of heavy metals like Fe, Cr and others in several groundwater resources, it is an economical-technical advantageous possibility to use natural Zeolite for groundwater treatment.

4.3 Cations removal from water

4.3.1 Materials and method

An amount of 10 gr Zeolite was added to 100 mL synthetic water sample with different cations (concentration of each cation equals 100 ppm). After 24 hours



of mixing and thereafter filtrating, the remaining concentration of each cation was determined via an atomic adsorption spectrometer.

4.3.2 Results

The results are shown in Figure 7. Due to the results, the investigated natural Zeolite is particularly appropriate to remove Fe, Bi, Cr, Mg and Ca cations.

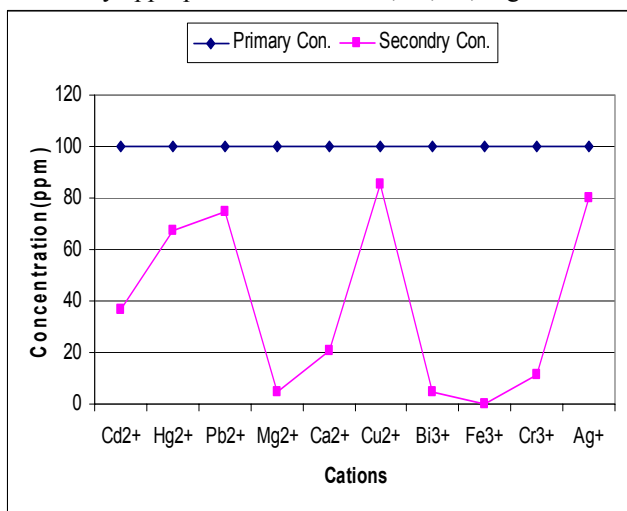


Figure 7: Cations removal abundance from synthetic water sample by using investigated Zeolite (Natrolite) [6].

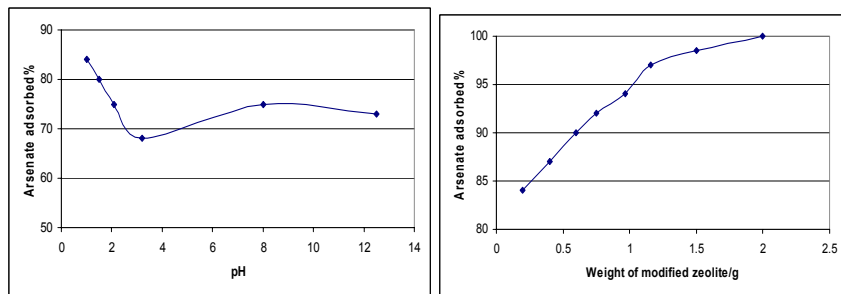


Figure 8: Arsenic removal depends on pH and required Zeolite [6].

5 Anions removal from water

Considering the existing active agent in anionic structure of Zeolite, cations can only be adsorbed. Hence, it must be remediated by using surfactants, especially HDTMA-bromide for organic compounds and inorganic toxic anions removal for instance chromate, nitrate, arsenate, selenate and sulphate.



5.1 Materials and method

In each phase, 10 gr Zeolite was mixed with 40 mL HMNDA compound(-N,N,N,N',N',N'-hexamethyl-1/9-nonanediammonium bromide, $2/72.10^{-4}$ molar) in 65 percent ethanol liquid. After 48 hours detention time in mixer, the Zeolite's colour was changed from white to grey. The remediate material must be removed via washing by water which is distilled twice and ethanol liquid (65%) for several times. Then, this Zeolite was made dry (24 hours in open air).

5.2 Results

Since groundwater resources contain arsenic, especially in the West and Northwest of Iran, the removal of arsenic ions was investigated. The results are shown in figure 8 and show that the optimized pH equals 1.5-2 and required Zeolite for removal process equals 2 gr.

6 Conclusion

Natural Zeolite can be used as a suitable material for groundwater treatment. The investigated natural Zeolite is characterized as Natrolite. It is concluded that this Zeolite has a considerable ability to remove hardness, 3 valence cations and also it is particularly appropriate to remove anions like arsenic that depends on pH and HMNDA.

Acknowledgement

This study was supported by the Sistan and Belouchestan Water and Wastewater Company (SBWWC) and National Water and Wastewater Company Iran (NWWC).

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Resonant ultrasound spectroscopy for investigation of thin surface coatings

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Abstract

In this paper, we analyze the possibility of determination of all in-plane independent elastic coefficients of an anisotropic surface coating on a known substrate by means of resonant ultrasound spectroscopy (RUS). A novel approach based on perturbation theory is presented, which enables direct determination of the elastic coefficients of the coating from the shift of resonant frequencies induced by the deposition of the layer. The reliability of the proposed concept is investigated by numerical simulations as well as verified by experiments.

Keywords: ultrasound spectroscopy, thin coatings, perturbation theory, non-destructive evaluation, in-plane anisotropy.

1 Introduction

Reliable determination of elastic coefficients of thin surface layers and coatings is one of the most challenging topics of today's experimental mechanics. Conventional micro/nanoindentation techniques are usually neither able to distinguish clearly which part of the elastic response is inherent to the coating and which to the underlying substrate, nor suitable for determination of all independent elastic coefficients of anisotropic coatings. A promising alternative to these highly local techniques are the ultrasonic methods, which may be either the methods based on surface elastic waves (SAW), or the resonant ultrasound spectroscopy (RUS) where the sought elastic coefficients are determined from measurements of resonant spectra of free elastic vibrations of a specimen of the examined material. The latter will be discussed in this paper.

Nowadays, the RUS is one of the most widely used methods for determination of elastic coefficients of bulk anisotropic materials. This method has found its very first applications in geophysics as early as in late 1960s, where the elas-



tic coefficients of rocks and minerals were determined from resonant spectra of spherical samples (so-called *resonant sphere technique*, RST [1]) or small cubes [2] of the examined material. Later on, the method was significantly improved by Ohno and his coworkers, enabling determination of anisotropic elastic coefficients up to orthorhombic [3] and trigonal [4] symmetry class from measurements on a rectangular parallelepiped (so-called *rectangular parallelepiped resonance*, RPR). In early 1990s, Migliori et al. [5] introduced this method to solid state physics community, and applied it immediately to in-situ monitoring of elasticity changes of high temperature superconductors when undergoing transitions to the superconducting state [6]. In these pioneering works, also the more general abbreviation RUS started to be used. The measurements were further improved by scanning the surface of the resonating specimen by a laser vibrometer, thus not only the resonant frequencies but also the shapes of vibration modes became available. In 2002, Ogi *et al.* [7] used this improvement for reliable identification of individual modes in the obtained spectrum, which was the approach further developed by the authors in the past few years [8–12].

As far as the investigation of thin surface layers and coatings is concerned, the first attempt to modify the RUS technique for such problems can be found in Visscher's paper [13], where, among many other general shapes of the specimen, also a 'sandwich' (a specimen consisting of two parallel layers) is discussed. By decreasing the thickness of one of the layers, such 'sandwich' obviously limits to a substrate-coating system; this idea was utilized by So et al. [14], who used the concept outlined in [13] for modeling of free vibrations of a SrTiO_3 substrate coated by a thin magnetoresistant film.

Extensive experimental literature on RUS investigation of thin surface layers was published by Ogi and his coworkers. It covers a huge variety of substrate-coating systems ranging from superlattice thin films (Co/Pt multilayer in [15]) to diamond coatings deposited by CVD [16, 17]. The main improvement brought by the Ogi's group to the experimental embodiment of RUS lies in a novel experimental scheme, so-called tripod scheme (e.g. [7]). In this scheme, the investigated specimen is freely laid in a tripod of thin, rod-like piezoelectric transducers (one of them is used for generation of vibrations, the others for detection of the specimen's response). Compared to the classical scheme used in earlier works (e.g. [5]), where the specimen is clamped between two transducers, the tripod scheme ensures that the vibrations of the specimen are very close to free vibrations (the clamping force is eliminated, which is crucial particularly for thin plates or shells). For mathematical description of the vibrating substrate-coating systems, the Ogi's group uses full 3D–3D 'sandwich' models based on the concept of Visscher [13], often utilizing an interpolation method developed by Heyliger [18].

In this paper, novel theoretical and the experimental approaches will be discussed. Unlike to the 'sandwich' concept from [13], our approach reflects the multiscale character of the problem, treating the surface layer as a 2D object deposited on a 3D substrate. In the experimental part, a fully non-contact setup [11] is presented, where the vibrations of the specimen are both generated and detected by lasers. As it will be shown, these novel approaches lead to reliable, reproducible



and straightforward determination of elastic coefficients of the examined surface layer.

2 Theory and preliminary numerical tests

The main idea of RUS measurements is following: First, the resonant spectrum of vibrations of the examined specimen is measured and individual resonant frequencies are localized. Then, the elastic coefficients are determined *inversely*, which means that they are tuned such that the resonant frequencies computed for them fit the experimentally obtained spectrum in some optimal way. For such procedure, one must be able to solve the so-called *direct problem*, i.e. to evaluate the resonant frequencies of the specimen for known elastic coefficients. For homogeneous, bulk specimens of simple geometry, this can be easily achieved by finding stationary points of the Lagrangian energy of the vibrating specimen (a simple variational problem, which can be easily solved by Ritz method, see e.g. [5, 7, 10, 12]). In the following section, the direct problem will be posted and solved for a substrate–coating system.

2.1 Perturbation model of a vibrating substrate–coating system

Consider now a vibrating substrate (a rectangular parallelepiped with edges aligned to cartesian coordinates $\mathbf{x}_1$, $\mathbf{x}_2$ and $\mathbf{x}_3$) on which a thin coating is deposited (on a face normal to the $\mathbf{x}_3$ axis). The kinetic and potential energy of the substrate are

$$E_k = \frac{1}{2} \int_{V_s} \rho_s \dot{u}_i \dot{u}_i dV_s \quad \text{and} \quad E_p = \frac{1}{2} \int_{V_s} C_{ijkl}^{(s)} \frac{\partial u_i}{\partial x_j} \frac{\partial u_k}{\partial x_l} dV_s, \quad (1)$$

where, $\mathbf{u}$ is the displacement field, ρ_s is the density, $C_{ijkl}^{(s)}$ are the elastic coefficients and $V_s = \langle -d_1/2; d_1/2 \rangle \times \langle -d_2/2; d_2/2 \rangle \times \langle -d_3/2; d_3/2 \rangle$ is the volume of the substrate. By taking polynomial approximation of the displacement field

$$u_i = \sum_{k=1}^N \alpha_k^{(i)} \psi_k(x_1, x_2, x_3) \cos(\omega t) \quad (2)$$

(where ω is the angular frequency of harmonic vibrations and the basis ψ_k can be advantageously chosen as orthonormal Legendre polynomials), it can be easily shown (e.g. [5]) that the problem of finding stationary points of the Lagrangian of the substrate $L = E_k - E_p$ can be rewritten as a generalized eigenvalue problem of the following form:

$$\mathbb{K} \vec{\alpha} - \omega^2 \mathbb{M} \vec{\alpha} = \vec{0}, \quad (3)$$

where $\vec{\alpha}$ is a vector of coefficients from approximation (2) and the matrices $\mathbb{K}$ and $\mathbb{M}$ are given by the geometry, density and elastic coefficients of the substrate [5, 7, 10, 12].



Let us now incorporate the presence of the coating in this model. The kinetic and potential energy of the coating (understood here as small perturbations δE_k and δE_p) are considered now as fully given by the displacement field $\mathbf{u}$ at the surface of the substrate where the coating is deposited. For h standing for the thickness of the coating, a possible assumption is to take this displacement field (denoted here as $\mathbf{v}(x_1, x_2, t)$) as an extrapolation of displacement field $\mathbf{u}$ in the midplane of the coating (e.g. in distance $h/2$ above the surface of the substrate) (in this simplification, we neglect the fact that the derivatives of $\mathbf{u}$ can be discontinuous over the substrate–coating interface) which reads

$$v_i(x_1, x_2, t) = u_i(x_1, x_2, x_3 = d_3/2, t) + \frac{h}{2} \frac{\partial u_i}{\partial x_3}(x_1, x_2, x_3 = d_3/2, t) \quad (4)$$

for $i = 1, 2, 3$. This leads to the following simplified expressions

$$\delta E_k = \frac{h}{2} \int_{S_c} \rho_c \dot{v}_i \dot{v}_i dS_c \quad \text{and} \quad \delta E_p = \frac{h}{2} \int_{S_c} C_{ijkl}^{(c)} \frac{\partial v_i}{\partial x_j} \frac{\partial v_k}{\partial x_l} dS_c, \quad (5)$$

for the kinetic and elastic energy of the coating respectively, where the subscripts c and superscripts (c) denote the quantities related to the coating. Using the approximation (2) again, a *perturbed eigenvalue problem* can be arrived, relating the perturbation of matrices $\mathbb{K}$ and $\mathbb{M}$ to the small changes in the angular frequencies $\delta\omega^2$ as

$$(\mathbb{K} + \delta\mathbb{K})(\vec{\alpha} + \delta\vec{\alpha}) - (\omega^2 + \delta\omega^2)(\mathbb{M} + \delta\mathbb{M})(\vec{\alpha} + \delta\vec{\alpha}) = \vec{0}. \quad (6)$$

In this first, linear approximation, is $\vec{\alpha} \perp \mathbb{M}\delta\vec{\alpha}$ and thus, after some additional algebra, the perturbation of the resonant frequency of the i –th mode ($\delta\omega_i^2$) can be expressed as

$$\delta\omega_i^2 = \frac{\vec{\alpha}_i^T (\delta\mathbb{K} - \omega_i^2 \delta\mathbb{M}) \vec{\alpha}_i}{\vec{\alpha}_i^T \mathbb{M} \vec{\alpha}_i}. \quad (7)$$

This formula directly relates the shifts of the resonant frequencies to the elastic coefficients, the density and the thickness of the coating (embodied here by the perturbations $\delta\mathbb{K}$ and $\delta\mathbb{M}$.) In other words, it enables $C_{ijkl}^{(c)}$ to be determined directly from the shifts $\delta\omega_i^2$, without solving the full eigenvalue problem (6) within every step of the inverse procedure. This makes the use of the perturbation model not only enormously less computation-time-consuming than the classical approaches, but more lucid for further theoretical analysis (e.g. estimation of the experimental errors).

It is more than obvious that the shifts $\delta\omega_i^2$ cannot contain sufficient information on all the elastic coefficients $C_{ijkl}^{(c)}$. In the potential energy δE_p , all the products $C_{ijkl}^{(c)} \varepsilon_{ij} \varepsilon_{kl} = \sigma_{kl}^{(c)} \varepsilon_{kl}$ give zero whenever k or l equals to 3 (plane stress conditions in the coating), which decreases the number of the involved elastic coefficients from 21 down to 6. These coefficients can be arranged into a symmetric 3×3 matrix $\mathbb{Q}$, which represents a linear relation between the non-zero components of the stress tensor (σ_{11} , σ_{22} and σ_{12} only) to the in-plane components of the strain



tensor (ε_{11} , ε_{22} and ε_{12}), i.e. $[\sigma_{11}, \sigma_{22}, \sigma_{12}]^T = \mathbb{Q}[\varepsilon_{11}, \varepsilon_{22}, 2\varepsilon_{12}]^T$. It can be easily shown that

$$\mathbb{Q} = \begin{pmatrix} (C^{-1})_{1111}^{(c)} & (C^{-1})_{1122}^{(c)} & (C^{-1})_{1112}^{(c)} \\ & (C^{-1})_{2222}^{(c)} & (C^{-1})_{2212}^{(c)} \\ \text{symm.} & & (C^{-1})_{1212}^{(c)} \end{pmatrix}^{-1}, \quad (8)$$

where $(C^{-1})_{ijkl}^{(c)}$ is a compliance tensor. Further in this text, we will use this matrix $\mathbb{Q}$ for characterization of in-plane elastic coefficients of the coatings, i.e. of those elastic coefficients of the coatings theoretically obtainable from RUS measurements on the substrate-coating system.

2.2 Numerical comparison to a full 3D-3D model

The above proposed perturbation model can be expected to work properly for $h \ll d_3$. Indeed, both the perturbations of the energetic quantities, δE_k and δE_p , are linearly proportional to the thickness of the coating, so limiting $h \rightarrow 0$ increases the validity of our assumptions. A natural question arises, how thin the coating must be to justify the use of the perturbation model, i.e. to ensure that this model provides the frequency shifts with some satisfying accuracy. To investigate this, and in order to verify the correctness of our model, we made the following preliminary numerical tests prior to applying the perturbation model to real experimental data:

1. We considered a homogeneous specimen (a 4mm×5mm×1mm single crystal of silicon cut along the principal directions) with the smallest dimension slightly increasing, and analyzed whether the changes of the resonant frequencies due to the thickening (evaluated by solving the eigenvalue problem (3) for different d_3) can be captured by the perturbation model. In other words, we analyzed a substrate-coating system, where the coating had exactly the same elastic properties as the substrate.
2. We assumed a full 3D-3D 'sandwich' model (similar to [13] but using an orthogonal basis) as a reference and compared the frequency shifts predicted by this model to those evaluated by relation (7). The analyzed system in this case was a CVD deposited diamond coating on the same substrate as in the first example.

For both these systems, shifts of the first thirty resonant frequencies of the substrate were evaluated. The results are shown in Fig. 1. In the upper row, the frequency shifts are shown for two chosen modes (the 1st and the 12th mode in the spectrum; circles denote the full 3D-3D models, solid lines are the shifts determined by relation (7)), in the lower row, the difference between the shifts predicted by the both models for all analyzed thirty modes is plotted versus the thickness and the mode number. The results are shown for the thickness of the coating ranging from 10nm to 100 μm .

Obviously, there is a significant difference between the two analyzed systems. Except of three or four modes, the perturbation model sufficiently approximates



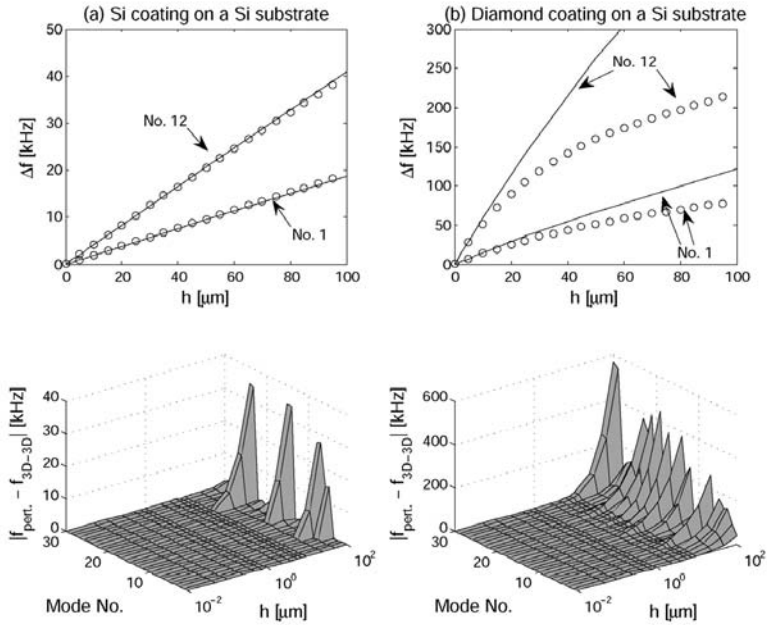


Figure 1: Comparison of the perturbation method to a full 3D–3D model. Upper row: Frequency shifts for the 1st and the 12th mode depending on the thickness of the coating h . (Circles denote the full 3D–3D models, solid lines the perturbation method). Lower row: Differences between the two discussed models for the first 30 modes.

the frequency shifts for the silicon substrate with changing thickness up to $h = 100\ \mu\text{m}$, whereas the silicon–diamond system is reasonably described by the perturbation model for $h \leq 10\ \mu\text{m}$ only. The reason may be found in the disproportion between the elastic properties of silicon and of the deposited diamond. The cubic single crystal of silicon has $c_{11} = 166\ \text{GPa}$, $c_{12} = 64\ \text{GPa}$ and $c_{44} = 80\ \text{GPa}$; for the isotropic diamond coating (polycrystal aggregate), the bulk coefficients $c_{11} = 1143\ \text{GPa}$ and $c_{44} = 530\ \text{GPa}$ were taken from [7]. Thus the diamond is nearly seven times ‘tougher’ in tension than the silicon substrate itself. That is the reason why the potential energy of a $100\ \mu\text{m}$ thick diamond coating cannot be ever taken as a small perturbation of the potential energy of the 1mm thick silicon substrate, and the perturbation approach fails. We can conclude that any estimation of limiting thickness h for which the perturbation approach reliably works is impossible without taking the ratio between elastic moduli of the substrate and the coating into account.



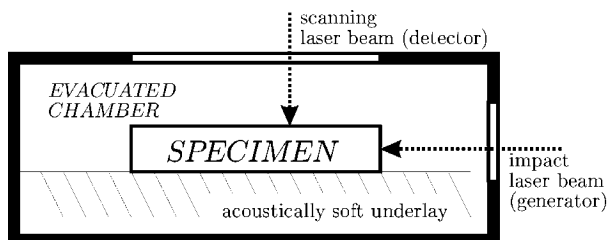


Figure 2: Outline of the non-contact experimental scheme of RUS.

3 Experiment

In this final section, the above outlined approach will be verified experimentally. The experiment (the setup and instrumentation) will be briefly described, and the results for two testing materials will be presented and discussed.

3.1 Experimental setup

For the RUS measurements described in this paper, a fully non-contact scheme [11] was used. In this scheme, the specimen is excited by an impact of a focused laser pulse (so-called thermoacoustic source) and the vibrations are detected by laser-Doppler interferometer scanning the surface of the excited specimen. The specimen itself is laid on an underlay which must be extremely acoustically soft (i.e. its acoustic impedance must be incomparably smaller than the impedance of the specimen) to ensure a good approximation of the free-surface boundary conditions. To minimize the damping of the specimen, the whole measurement is performed in an evacuated chamber with two silica-glass windows, one for each of the used laser beams (see Fig. 2 for an outline). The used instrumentation was following: The elastic vibrations in the specimen were excited by sequences of pulses of a focused infrared laser beam (pulse duration 8 ns, energy 25 mJ, Quantel ULTRA Nd:YAG Laser system, equipped by fiber optic – FOLA options). The displacement response was detected in a mesh of points on the sample surface by Polytec Micro System Analyzer MSA-500 (using the OFV-5000 controller and the sensor head OFV-551).

This scheme was inspired by measurements by Zadler [19], who used lasers to excite specimens hanging on thin silica wires. However, the use of the acoustically soft underlay proposed by the authors seems to provide adequately good approximation of the free-surface conditions, but with much easier specimen mounting and replacement. This experimental concept was already successfully applied to determine elastic coefficients of various bulk materials [11, 12], and was shown to be especially suitable for quantitative measurements of ultrasound attenuation [20].



3.2 Experimental verification of the perturbation model

The non-contact experimental scheme of RUS was used to verify the perturbation model. To know the sought elastic coefficients of the examined layers with the highest possible accuracy, and thus, to be able to analyze how reliably these coefficients can be determined by relation (7), we decided to use the same approach as in the first of the preliminary numerical tests, i.e. to perform the measurements on homogeneous specimens where the presence (or absence) of the surface coating is represented by a change in thickness.

Two different materials were used for such experiments. The first was a single crystal of silicon (a $2.1 \text{ mm} \times 3.6 \text{ mm} \times 3.1 \text{ mm}$ rectangular parallelepiped cut along the principal crystallographic axes) and the second a reaction-bonded silicon carbide Si-SiC ($1.8 \text{ mm} \times 2.5 \text{ mm} \times 2.8 \text{ mm}$ rectangular parallelepiped). These specimens were taken as substrates *with* surface layers; the resonant spectra of these specimens were measured (covering always about the first thirty modes) and individual modes of vibration within the spectra were identified. After that, the considered surface layers were removed by polishing: $32 \text{ }\mu\text{m}$ thick layer was polished out from the single crystal of silicon, $8 \text{ }\mu\text{m}$ thick layer from the specimen of the reaction-bonded silicon carbide. This approach simulated the issue of determination of elastic properties of a $32 \text{ }\mu\text{m}$ thick cubic surface coating and a $8 \text{ }\mu\text{m}$ thick isotropic surface coating. The resonant spectra of the specimens *without* the 'coatings' were measured and the frequency shifts $\delta\omega^2$ for particular modes were identified (in this point, the identification of the modes from scanning laser-Doppler interferometry is obviously crucial, as the original order of the resonances can be shuffled when the layer is deposited/removed).

To verify the reproducibility of the measurements, the spectra of the specimens before the layers were polished out were measured repeatedly under slightly different conditions (the impacting laser was focused on different places of the specimen, the specimen was removed from the chamber and put back again etc.). In Fig. 3, the spectra obtained by two different measurements of the specimen before polishing (solid lines) are compared to the spectrum of the specimen without the examined layer. Obviously, the reproducibility of the measurements is extremely good and all the shifts of individual peaks in the spectrum can be reliably ascribed to the presence/absence of the surface layer.

Our aim was to determine the elastic coefficients of the removed layers Q_{ij} by inverting the perturbation formula (7). This was done in two different ways:

1. The symmetry class of the examined material was considered as known, i.e. only three independent coefficients for cubic silicon were sought (Q_{11} , Q_{12} and Q_{33}) and two (Q_{11} and Q_{33}) for the isotropic silicon carbide.
2. Full elastic anisotropy of the layer was considered, which means six independent elastic coefficients Q_{ij} . However, as all the modes of vibration of the examined layer were forced by free vibrations of the specimen, the layers were loaded only in modes having the same symmetry as the substrates (i.e. in modes symmetric or antisymmetric with respect to symmetry planes of the substrates). This obviously precludes reliable determination of the coef-



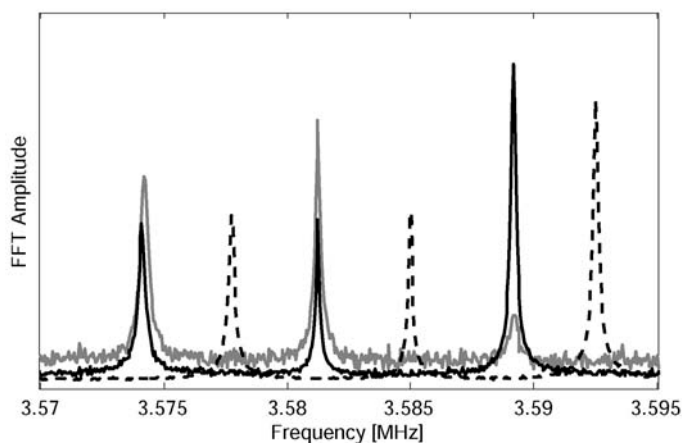


Figure 3: A selected part of the obtained spectrum (Si-SiC specimen) illustrating the reproducibility of the non-contact RUS measurements and the shifts induced by the absence of the surface layer. Solid lines (black and gray) correspond to two independent measurements of the original specimen, the dashed line shows how the resonant frequencies change after a $8\mu\text{m}$ thick surface layer was removed.

ficients Q_{13} and Q_{23} , so only Q_{11} , Q_{22} , Q_{12} and Q_{33} were sought. (The coefficients Q_{13} and Q_{23} could be, however, determined by measurements on less symmetric substrates.)

In both cases, the sought coefficients Q_{ij} were calculated by numerical inversion of relation (7), where to the measured shifts of resonant frequencies were fitted in the least-square sense. In Tab. 1, the results are listed and compared to coefficients $Q_{ij}^{(s)}$ determined from the elastic coefficients of the substrate $C_{ijkl}^{(s)}$ by formula (8). The experimental errors displayed in Tab. 1 result from the accuracy of measurements of the removed layer, which was estimated to be about $1\mu\text{m}$.

In the case of the single crystal of silicon, this table shows how powerful tool the perturbation model can be. Not only that all the elastic coefficient for the known class of symmetry were determined with satisfying accuracy (especially when the uncertainty given by the thickness of the layer is taken into account), but also the cubic symmetry can be reliably identified: For cubic silicon, the constants Q_{11} and Q_{22} differ by less than 2%. For silicon carbide, the results are less satisfying. Although for the given symmetry class, the results are quite good, the isotropy requires $Q_{11} = Q_{22} = Q_{12} + 2Q_{33}$, which is here not fulfilled (difference larger than 10%). This may be ascribed to heterogeneity or porosity of the material or to the fact that for $h = 8\mu\text{m}$, the uncertainty in the thickness (and plan-parallelism) of the removed layer is more significant.

		Bulk material			Layer (perturbation model)		
Examined material	h [μm]	$Q_{11}^{(s)}$ [GPa]	$Q_{12}^{(s)}$ [GPa]	$Q_{33}^{(s)}$ [GPa]	Q_{11} [GPa]	Q_{12} [GPa]	Q_{33} [GPa]
Silicon	32 ± 1	141.5	39.5	79.7	142.0 ± 4.3	37.4 ± 1.2	82.8 ± 2.6
Si-SiC	8 ± 1	412.2	- - -	168.6	436.2 ± 54.5	- - -	192.7 ± 24.1

		Layer (perturbation model, full anisotropy)					
Examined material	h [μm]	Q_{11} [GPa]	Q_{12} [GPa]	Q_{13} [GPa]	Q_{22} [GPa]	Q_{23} [GPa]	Q_{33} [GPa]
Silicon	32 ± 1	140.9 ± 4.4	36.4 ± 1.1	N/A	143.1 ± 4.5	N/A	82.8 ± 2.2
Si-SiC	8 ± 1	422.4 ± 52.8	32.6 ± 4.1	N/A	454.4 ± 56.8	N/A	179.0 ± 22.4

Table 1: Comparison of in-plane elastic coefficients Q_{ij} determined by RUS on bulk specimens and by the perturbation model.

4 Conclusion

By introducing the perturbation theory into the RUS of thin surface coatings, the in-plane elastic coefficients of isotropic and cubic coatings can be easily and reliably determined. In future, the authors would like to focus on the effect of the disproportion between the elastic properties of the substrate and the coating (see paragraph 2.2) and the the analysis of the experimental errors of the obtained coefficients in dependence on various factors, such as symmetry of the substrate, etc.

Acknowledgements

This work was financially supported by the Czech Science Foundation (project No.202/09/P164), the Grant Agency of ASCR (project No. A200100627), the Czech Ministry of Education (project No. 1M06031) and the institutional project of IT ASCR CEZ: AV0Z20760514.

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The effect of cerium solutions on 316L stainless steel

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Abstract

Surface passivation is a technique for improving the corrosion resistance of stainless steel. In this work, we studied the effect of cerium treatment on 316L SS. Characterization techniques such as anodic polarization test, electrochemical impedance spectroscopy, and X-ray photoelectron spectroscopy were employed to correlate the corrosion behavior to surface treatments. Results showed that cerium passivation treatment increase corrosion protection of alloy due to the formation of amorphous oxidation that leads to diffusion control. This improvement is attributed to a more uniform and compact layer which is composed of oxide particles with higher oxygen and chromium concentrations.

Keywords: passive layer, 316L stainless steel, cerium, chemical treatment, electrochemical, SEM, XPS.

1 Introduction

Resistance of passive layer of stainless steel depends on the alloy composition and conditions in which it is generated. Chemical treatment on steel parts could improve passive layer [1]. Well-known method of surface modification involves the use of dichromate, a substance which is now recognized as both highly toxic and carcinogenic. The search for more environmentally acceptable alternatives has lead to the identification of rare-earth metal species as possible replacements for the chromium [6].

The anodic dissolution behavior of active-passive metals in the presence of oxidizers is illustrated in figure 1, which shows a typical active-passive metal M



immersed in an electrolyte containing a redox agent R. The effect of increasing the amount of oxidizer is to shift reversible potential in the positive direction according to the Nernst equation. The increase in oxidizing agent from concentration 1 to 7 is represented by curve 1 to 7.

Initially, metal M corrodes in the active state at a rate corresponding to point A. As the concentration of oxidizer is increased from 1 to 3, corrosion rate continuously increases from A to C. In this particular range of oxidizer concentration, metal M acts like a nonpassivating metal; its corrosion rate increases with oxidizer concentration. At a concentration corresponding to the curve 4, there is a rapid transition in corrosion potential from point D in the active state to G in the passive state. As oxidizer concentration is increased from 4 to 5, metal remains in the passive state and its corrosion rate remains low and constant. As the concentration of oxidizer is increased further, the transpassive region is intersected and corrosion rate increases rapidly with increasing oxidizer concentration, as shown by curve 6 and 7 in figure 1.

This analysis leads to a very useful, practical rule. To safely maintain passivity, oxidizer concentration should be equal to or greater than the minimum amount necessary to produce spontaneous passivation.

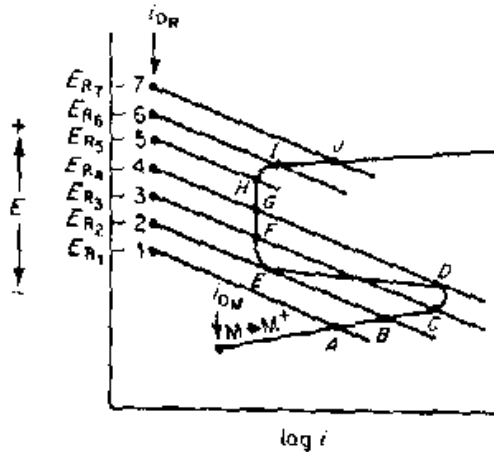


Figure 1: Effect of increasing oxidizing solution concentration on the electrochemical behavior of active-passive metal

The passive layer is formed by an oxidation-reduction reaction in which the chromium and iron are oxidized, and the passivating agent is reduced. An essential of the passivity of iron is the presence of H and OH groups which impart the property of amorphousness, nonstoichiometry, and protectivity. The principal feature is the amorphousness and nonstoichiometry, leading to defect states associated with proton deficiency and a concentration gradient of the ionic species [21].

In this work, the behavior of 316L stainless steel following post cerium treatments was studied in an effort to examine the additional level of corrosion protection afforded by it.



2 Experimental

Specimens used in this study were 316L stainless steel. The composition in wt% was 0.021% C, 17.61% Cr, 12.45% Ni, 2.29% Mo, 0.069% Si, 1.05% Mn, 0.020% S, 0.031% P, and bal. Fe. They were mounted with an exposed area to $1 \times 1 \text{ cm}^2$. The surface was mechanically polished starting with 220 grit silicon carbide paper following 320 / 400 / 800 / 1000 grit paper to have a comparable surface roughness. They were then rinsed with deionized water.

Passivation treatments were conducted on specimens using immersion in $\text{K}_2\text{Cr}_2\text{O}_7$ for 20 minutes at room temperature with $\text{pH}=4$. The original specimen was studied as-received, without passivation treatment as reference and for comparative purposes.

Immediately after removal from the passivating solution the specimens were thoroughly rinsed, using spray washes [5].

The corrosion properties of the passive layer were studied using DC polarisation and electrochemical impedance spectroscopy (EIS). Electrochemical tests were conducted using Potentiostat, Model Zahner, in 3.5% NaCl solution at room temperature opening air. Saturated calomel electrode (SCE) used as reference electrode and platinum used as auxiliary electrode. Potentiodynamic polarisation curves were plotted from $-200\text{mV}_{\text{SCE}}$ to $+200 \text{ mV}_{\text{SCE}}$ at a polarisation scan rate of 0.1 mV/s ; EIS measurements were performed in the frequency range from 100 mHz to 100 kHz with a logarithmic sweeping frequency of 4 steps/decade. EIS involved the imposition of a 10mV amplitude sine-wave and the measurements were carried out at the E_{corr} .

Then the microstructure and composition of those specimens were investigated using X-ray photoelectron spectroscopy (XPS) to determine cause for this behavior. The XPS spectra were obtained with a VG Microtech electron spectrometer, model MT 500, using an Mg $\text{K}\alpha_{1,2}$ anode X-ray source ($h\nu = 1253.6 \text{ eV}$) with a primary beam energy of 15 kV and an electron current of 20mA. The pressure in the analysis cabinet was maintained at 1×10^{-9} Torr throughout the measurements.

The specimens were analyzed by means of argon-ion sputtering on the original surface and after 30, 90, 200 and 390s argon-ion sputtering was carried out with primary beam energy of 5 kV and an ion density of $1 \mu\text{A}/\text{cm}^2$.

3 Results and discussion

3.1 Electrochemical tests

Fig. 2 shows polarisation curves for specimens tested in a 3.5% NaCl solution. To determine the corrosion rate from such polarization measurements, the tafel region is extrapolated to the corrosion potential and this point is corresponded to the corrosion rate of the system expressed in terms of current density. The E_{corr} and I_{corr} of each specimen are mentioned in table 1 [2].

As shown in fig. 2, electrochemical impedance spectra of an air passivated specimen (tested in a 3.5% NaCl solution) in complex plane presentation are



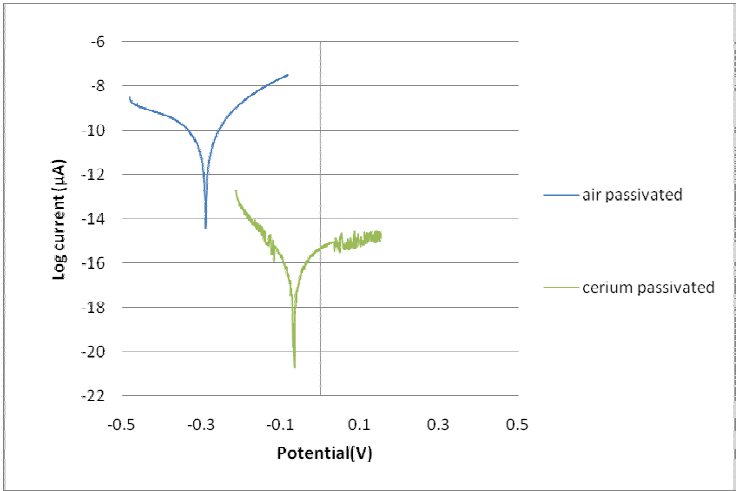


Figure 2: Polarization curve of specimen: (i) air passivated, (ii) cerium passivated.

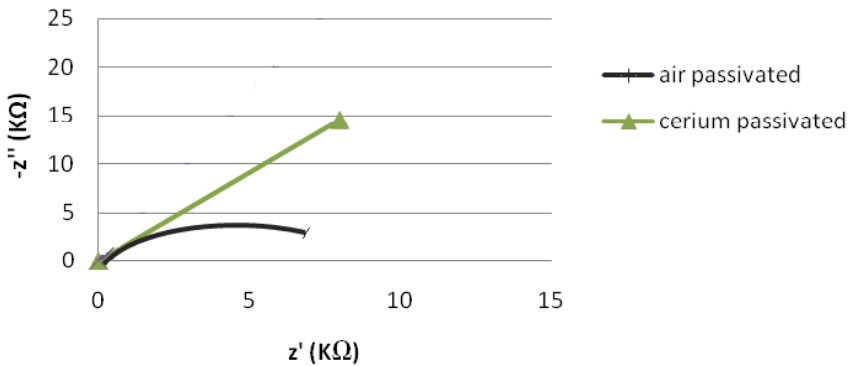


Figure 3: Nyquist plot of specimens: (i) air passivated, (ii) cerium passivated.

characterized by one semicircle, whereas spectra of cerium passivated specimen is straight line.

The quantitative analysis of the electrochemical impedance spectra must be based on a physical model of the corrosion process. Fig. 3 shows Randles Simple model includes the electrochemical resistance (R_p) in parallel to the double layer capacitance (C) connected with the resistance of the electrolyte (R_s) [8, 9]. Equation (1) represents a semicircle in the complex plane plot with R_p as diameter:

$$\left(Z' - R_s - \frac{R_p}{2} \right)^2 + (Z'')^2 = \left(\frac{R_p}{2} \right)^2 \quad (1)$$



However, imaging impedances of cerium-passivated specimen showed it does not increase and capacitive semicircles are not completed. This behavior indicates the reaction is under diffusion control. Therefore the Warburg diffusion impedance is an inevitable element in circuit. Also capacitive is replaced with CPE (constant phase element) to fit with the experimental curve [8, 12]. The CPE behaviour could be treated as an “ ω space fractality”, i.e., as manifestation of a self-similarity in the frequency domain [27]. The CPE impedance is given by:

$$Z_{CPE} = \frac{1}{(i\omega)^n A} \tag{2}$$

where A is a proportionality coefficient and n has the meaning of the phase shift, which value can be considered as a measure of the surface inhomogeneity.

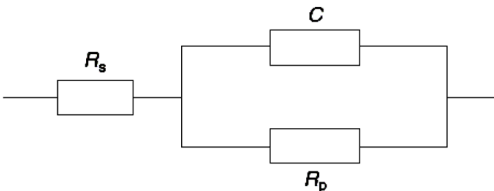


Figure 4: Randles Simple equivalent circuit of air passivated specimen.

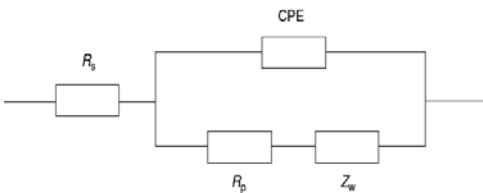


Figure 5: Equivalent circuit of cerium passivated specimen.

Table 1 indicates R_p obtained from the equivalent circuit of each specimen. Electrochemical tests results show cerium treatment improves corrosion resistance of stainless steel.

Table 1: EIS and polarization tests results.

sample	Corrosion potential (mV)	Corrosion rate (nA/cm ²)	Resistance (Ω/cm ²)
Air passivated	-289	5100	1.2×10 ³
Cerium passivated	-90	94	3.6×10 ⁵

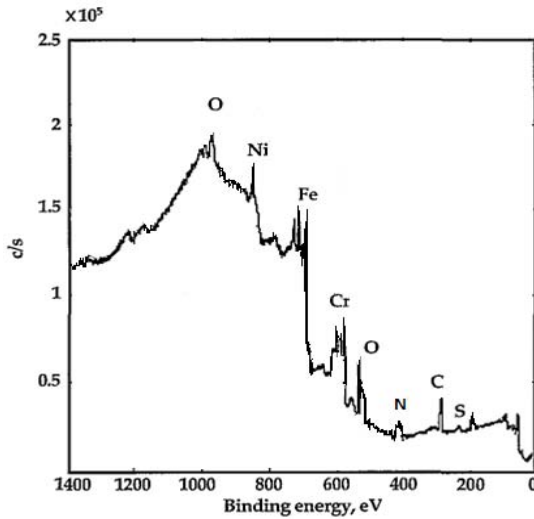


Figure 6: XPS spectra of air passivated specimen.

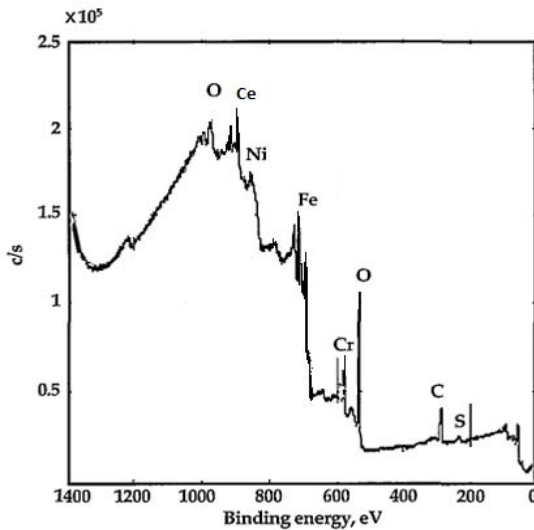


Figure 7: XPS spectra of cerium passivated specimen.

3.2 XPS

XPS analysis of stainless steel surfaces treated by various chemicals can provide valuable information about passivation layer composition.

The “surface atoms” are the atoms which would be in contact with the aqueous solution. A surface atom is drawn and is submitted to the possible events, surface diffusion, dissolution or passivation, according to probabilities



dependent on the nature of the atom (Cr or Fe) and on its chemical environment. The surface is then modified accordingly.

The XPS of spectrums of the passive film formed in air and cerium solution are shown in figures 6 and 7. It was found that there was the obvious Cr signal on the surface of the cerium treated and slightly reduced Cr signal on the surface of the air-passivated [3].

The depth profile of the atomic concentration of each element can be obtained by high resolution XPS spectra at different argon-ion sputtering time. Figures 8 and 9 illustrate the concentration of oxygen, chromium, and iron in passive layer of 316L stainless steel corresponding to air and cerium treatment.

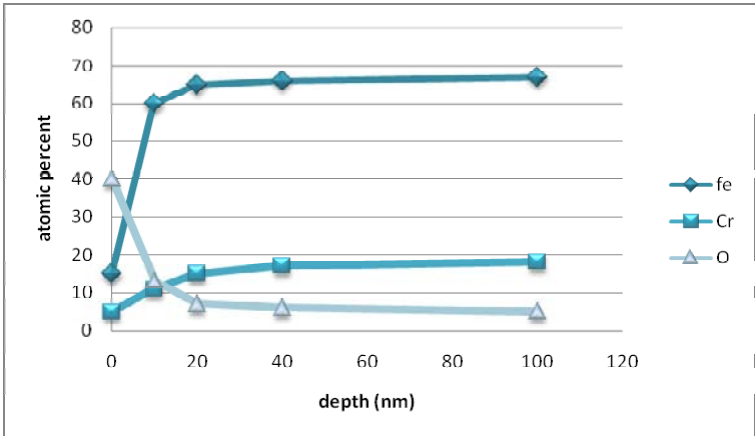


Figure 8: Atomic concentration of oxygen, chromium and ferrous elements for the Air-passivated specimen.

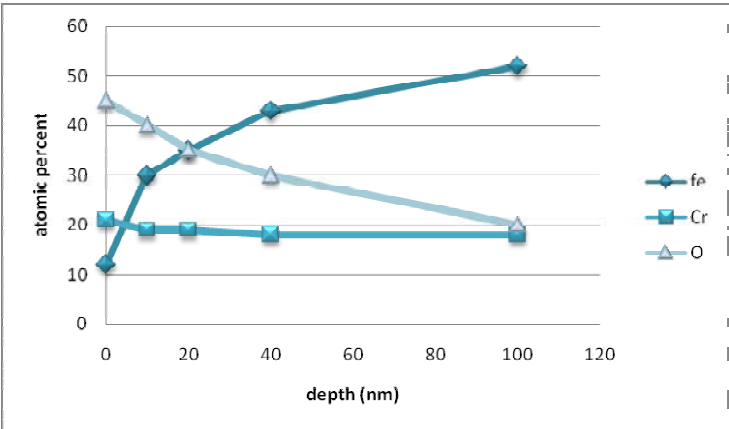


Figure 9: Atomic concentration of oxygen, chromium and ferrous elements for the cerium-passivated.



Chromium is enriched in the surface of passive layer after chemical passivation. Corrosion resistance is the result of protection conferred by a chromium-rich passive layer.

Selective dissolution (of Fe) and surface diffusion lead to the existence of oxide-hydroxide nuclei that will grow to finally cover the whole surface. In other words the passivation is due to formation of “oxide-hydroxide” nuclei, resulting from the presence of local chromium-rich clusters, the formation of which is favoured by selective dissolution of iron and by surface diffusion of chromium.

At the beginning, there is no nucleus on the initial surface. Therefore there is a strong selective dissolution. The surface becomes enriched in chromium, which can diffuse because vacancies have been created by the dissolution. Surface diffusion is necessary to fill up narrow channels that could be developed during dissolution. The surface roughness increases during this process. It also favours the formation of “chromium oxide” nuclei blocking the dissolution (“passivating the surface”), by preferential diffusion of Cr towards clusters of Cr atoms, whereas random diffusion of iron is considered. Small islands of chromium oxide are formed and grow during polarization in the passive region. After a certain time the local Cr concentrations become sufficient to form a number of nuclei. Then the passive layer grows rapidly because of the rapid Cr supply to the existing clusters. A significant amount of Fe is trapped in the passive film.

It suggests that surface diffusion of the chromium in the passive oxide layer is responsible for the chemical composition of passive films (chromium enrichment) in the early stages of passivation.

The chromate film has excellent corrosion protection, and the film is self-healing. Scratches or gouges in the chromate film will reseal themselves upon contact with water or humidity.

Also cerium treatment promotes formation of $\text{Ce}(\text{OH})_3$, CeO_2 and $\text{Ce}(\text{OH})_4$ which are amorphous [3, 10, 11].

4 Conclusion

- The use of a rare earth metal salt, such as cerium nitrate, provides a degree of corrosion protection without incurring the health and environmental risks that are posed by chromates.
- DC measurements shows poor corrosion resistance behavior of air passivated specimen: $R_p=1.2 \text{ k}\Omega\text{cm}^2$ and $i_{\text{corr}}=5.1 \text{ }\mu\text{A}/\text{cm}^2$ respect to enhanced corrosion resistance behavior of cerium-passivated specimen: $R_p=360 \text{ k}\Omega\text{cm}^2$ and $i_{\text{corr}}=0.094 \text{ }\mu\text{A}/\text{cm}^2$
- EIS results indicated cerium passivation treatment lead to diffusion control by considering Warburg diffusion element in equivalent circuit.
- The XPS results indicated that chromium-passivation treatment was advanced in the Cr enrichment on the surface of stainless steel.



Acknowledgements

Special thanks are directed to Dr. Kermaini. This paper was supported by Petroleum University of Technology (PUT), Pars Oil and Gas Company (POGC), and National Iranian Oil Company (NIOC).

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Image analysis application in metallurgical engineering and quality control

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Abstract

Image analysis (IA) is widely used in different areas of science such as medicine, biology and engineering. Quantitative measuring by image analysis has also found application in metallurgical engineering, especially in analyzing metallographic microstructures. The measuring of different microconstituents dimensions based on image analysis, performed in metallurgical investigations is presented in the paper. Determination of the brittle phase content in the function of the heat treatment temperature for the heat resistant Ni-Cr-Co-W alloy, with the aim of obtaining optimal microstructure for repair welding are presented. Results have shown that the best effect of the brittle phases dissolving is obtained at the temperature of 1250 °C. Investigation of the effects of Si (1-10%) and Cu (0.5-4.5 %) content, in the cast Al alloy for automotive application, on secondary dendrite arm spacing (SDAS) in the structure was performed. Results have shown that the higher silicon and copper contents reduced the size of the SDAS, which directly enable better mechanical properties of the cast product. The effect of different energy inputs, in the steel arc welding process, on the dimensions and geometry of the zones in a cross section of the welded joint was investigated. The heat affected zone (HAZ) of the welds is critical for the mechanical properties and weld quality and it is directly dependent on the energy input. The area and width of the HAZ for different heat inputs, from 0.4 to 1.4 kJ/mm, were measured by the IA. The obtained results have shown direct dependence of the measured dimensions from the energy input. The applied methodology enables weld quality control in the case of the automatic welding processes. All presented experimental results are based on a large number of measurements. A statistical analysis was performed and a high correlation of the results was obtained. For the each of the presented investigations and analyzed phenomenon, a statistical mathematical model is suggested with the boundary conditions defined by the investigated intervals of variables.

Keywords: *image analysis, Ni-Cr-Co-W alloys, cast Al alloys, steel welds.*



1 Introduction

Image analysis (IA) is widely used in different areas of science such as medicine, biology and engineering. Quantitative measuring by image analysis has served the automotive, aerospace, semiconductor, metal fabrication, foundry, welding, or other related materials design, fabrication or testing industry. IA also found application in metallurgical engineering, especially in analyzing metallographic microstructures. Structure measurements as cast structure properties, failure analysis, welding structures measurement have received considerable attention in recent years, partly because of development of stereological methods and the importance made in image analysis. Quantitative measurement of microstructure is of great importance in quality control studies as well as in structure property control. For many years, metallurgists have primarily relied on qualitative descriptions of microstructures or rating based on comparison charts. In general, comparison charts lack the sensitivity needed to accurately define differences between samples. The accuracy of this methodology significantly depends on the operator's experience, knowledge and ability to properly estimate some structural features. It is a very subjective method and obtained results are the matter of estimations.

Development of automatic image analysis has greatly increased the use of stereological principles for determining microstructure characteristics. These devices reduce the time necessary for manual measurements, improve accuracy of statistical measurements, reduce time, and eliminate the influence of operator estimation to the minimum level. Application of this apparatus required greater attention to sample preparation, since the software lacks the human ability to separate microstructure features that are not clearly defined.

Quick and easy detection and selection of the microconstituents by shape, size, colour and other criteria is allowed by the IA application. It is applicable for determination of the metal grain size, phase content in powder or non ferrous metals, content of the martensite, pearlite, ferrite, austenite in steel microstructure, shape and content of the graphite in the cast iron, etc.

Quantitative measurements are of great value to the many fields of metallurgy as this paper has demonstrated. Three different metallurgical problems were analysed based on the measuring of the linear or/and areal dimensions of the microstructural/macrostructural components by the IA in relation to the process parameters. Area measuring of the brittle phase in steel microstructure and the area of the weld metal and heat affected zone in the macrostructure of the weld joint were performed. Linear dimensions as secondary dendrite arm spacing (SDAS) in a cast Al alloy and weld metal and heat affected zone width were also carried out. Effects of heat treatment temperature on the brittle phase content in the microstructure of the high temperature alloy, properties of the cast microstructure in function of the Al alloy chemical composition and effects of the heat input on the steel weld joint dimensions were investigated in this work. All tests were performed by a light optical microscope with an automatic image analyser.



2 Experimental

2.1 Brittle phase content in the Ni-Cr-Co-W alloy microstructure

Determination of the brittle phase content in the microstructure of the heat resistant Ni-Cr-Co-W alloy (Supetherm) tube was performed. Centrifugally cast riser tube from an ammonia plant was exposed for about 70000 hours at an operating temperature of 850°C and was fractured. For weld repairing of the tube it was necessary for the alloy to be previously prepared. The usual way for obtaining optimal microstructure for repair welding of the investigated alloys is high temperature dissolving of the brittle phases. For defining the optimal temperature for heat treatment a diffusion annealing at temperatures in the 50°C interval, from 1150°C to 1250°C during 1 and 3 hours was performed. The chemical composition of the analysed alloy and mechanical properties in the untreated alloy are presented in Tables 1 and 2.

Table 1: Chemical composition of analysed Supertherm alloy (in mass. %).

C	Mn	S	P	Si	Ni	Cr	Co	W	Fe
0.48	0.54	<0.02	<0.02	1.38	34.9	25.8	15.7	4.93	rest

Table 2: Mechanical properties of Supertherm alloy in non-treated condition.

Tensile strength	Absorbed energy KV300/1.5	Hardness
MPa	J	HV 30
410	1.5	304

Samples for investigation were prepared for optical microscopy by the classic method of grinding and polishing. Etching was performed in Aqua regia. The light optical microscope has been used. Quantitative metallographic measurements were based on the image analysis. The heat treatment effects on the quantity of brittle (σ) phase and carbides in the microstructure were analysed. Based on the black/white contrast, the total area of brittle phases was determined by image analysis. Applied magnification was 200 times. Ten measurings were performed at each sample, and then the highest and lowest value were rejected and the mean value of the remaining eight measuring were presented as a result.

2.2 Properties of the cast Al alloys microstructure

The most important practical aspect of the cast dendrite structure is the secondary dendrite arm spacing (SDAS) that represents the distance between secondary dendrites in the solidifying structure of cast metals and alloys. In order to investigate the impact of silicon and copper on the size of the SDAS in Al-Si-



Cu alloys, the contents of these two elements have been varied between 1.3 and 9.7 wt.% Si, while copper additions were varied between 0.37 and 4.7 wt.%.

The investigations were performed using Al-Si11 alloy with the trace of Cu, Mg and other elements, which had been diluted by adding certain amount of pure aluminium in order to reach designed content of silicon. The chemical compositions of the resulting eleven alloys, as determined using Optical Emission Spectroscopy (OES) are presented in Table 3.

Table 3: Chemical compositions of investigated Al-Si alloys with different content of silicon.

Alloy	1	2	3	4	5	6	7	8	9	10	11
Si (wt.%)	10.99	9.71	8.59	7.57	6.97	6.05	4.70	3.72	2.75	2.06	1.30
Al (wt.%)	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest

Fe=0.09-0.13, Cu=0.001-0.002, Mn=0.02-0.04, Mg=0.17-0.32, Zn=0.006-0.009.

In order to analyse the effect of the various content of copper on the size of the SDAS nine synthetic Al-Si-Cu compositions were produced by melting a charge of Al-6 wt.%Si-0.002 wt.% Cu base alloy, with the addition of various amounts of pure copper. Table 4 shows the chemical composition of the resulting alloys.

Table 4: Chemical compositions of investigated Al-Si-Cu alloys with different content of copper.

Alloy	1	2	3	4	5	6	7	8	9
Si (wt.%)	6.02	6.09	6.19	6.25	6.15	6.07	6.10	6.21	6.17
Cu(wt.%)	0.37	0.76	1.42	1.76	2.13	2.23	2.60	3.20	4.71
Al (wt.%)	rest	rest	rest	rest	rest	rest	Rest	rest	rest

Fe=0.07-0.08, Mn=0.002, Mg=0.21-0.30, Zn=0.004-0.005.

Previously prepared samples for each targeted alloys are firstly charged in the ceramic cups, loaded in an electric resistance furnace and melted. During all experiments the melt temperature was kept constant at the $700^{\circ}\text{C} \pm 5^{\circ}\text{C}$. After melting down, all samples with masses of approximately $80\text{g} \pm 2\text{g}$ where left to solidify under the same conditions. The thermoelement has been inserted into test sample in order to determine the cooling rate. The temperature range between liquidus and solidus temperature divided with total solidification time has been used to calculate the rate of solidification. The cooling rate for all samples was $0.15^{\circ}\text{C}/\text{sec}$.

Solidified cylindrical samples are sectioned vertically. One half of the sample has been used for chemical analysis while the other half has been used for quantitative measurements of the SDAS by IA. Metallographic samples were prepared by standard grinding and polishing procedures. The light optical microscope has been used in this work for the SDAS measurement.



The SDAS is a measure of the length scale between two adjacent SDAS and it is usually an order of magnitude smaller than the primary arm spacing. In this work the line intercept method was utilized to measure the SDAS. The applied magnification was 25 times. The size of the SDAS has been obtained as an average value of at least 10 measurements.

2.3 Zones dimensions in cross section of the steel welded joint

The steel weld joint consists of different zones, such as: weld metal, heat affected zone and base metal. The heat affected zone (HAZ) of the welds is critical for the mechanical properties and weld quality and it is directly dependent on the energy input of the heat source. The area and the width of the HAZ and weld metal (WM) for different heat inputs in arc welding of the steel plates were quantitatively measured by image analysis.

Five trial bead on plate welds have been produced with the various heat inputs. Test pieces 6x150x300 mm of low alloy Q&T, Ni-Cr-Mo (HY-100) steel have been used as the base plates. The chemical composition and mechanical properties of the steel are given in Tables 5 and 6.

Table 5: Chemical composition of HY-100 steel plate and welding wire.

	Chemical Composition (mass. %)									
	C	Si	Mn	P	S	Cr	Ni	V	Mo	Fe
plate	0.11	0.31	0.27	0.010	0.004	1.01	2.64	0.08	0.28	rest
welding wire	0.09	0.75	1.50	/	/	/	1.10	/	/	rest

Table 6: Mechanical properties of HY-100 steel plate.

Yield Strength Rp _{0.2}	Tensile Strength Rm	Elongation in 50 mm A5	Charpy V-Notch Impact ISO-V min.	Bending $\alpha=180^\circ$
MPa	MPa	%	J	
min. 690	740-940	min. 16	118 at 293K	d=3.0a*

The single pass bead on plate GMA welds were made on an automatic welding device, with which a specified welding speed could be accurately controlled. The shielding CO₂ gas flow was 0.1 dm³ s⁻¹. Chemical composition of an $\varnothing$ 1.2 mm welding wire is given in Table 5. Welding parameters are listed in Table 7.

The width and area of weld metal and HAZ were measured on the samples sectioned from the transverse cross sections of the welded joint. The surfaces of the samples are routinely grounded and polished. The samples were etched in 3% Nital solution and were examined on the optical microscope with image analysis equipment. The quantitative measuring of the HAZ area is determined based on the black/white contrast. The width of the HAZ was measured by the linear



Table 7: Welding conditions for trial bead on plate welds.

Sample	Arc Voltage	Welding Current	Welding Speed	Speed of Welding Wire	Heat Input
	V	A	mm s ⁻¹	mm s ⁻¹	KJ mm ⁻¹
1	27	260	16.7	165	0.4
2	28	198	9.3	140	0.6
3	30	182	6.2	104	0.9
4	28	196	5.1	117	1.1
5	29	232	5.0	146	1.4

intercept method. The size of the width and area of weld metal and HAZ has been obtained as an average value of at least 5 measurements.

3 Results and discussion

3.1 Heat treatment effects on the Ni-Cr-Co-W alloy microstructure

A lot of trial and error is involved when it comes to repair welding of service exposed high temperature cast materials and, depending on the source, different weld repair strategies are proposed and applied. One of the methods used to enhance weldability is solution annealing before welding. The data from literature showed that embrittlement caused with brittle phases, as secondary carbides and σ - phase, could be eliminated and original ductility restored by a solution annealing heat treatment at 1065°C during two hours [1]. This data existed for cast alloy HP, but for investigated alloy Supertherm was not found. Therefore, in the present work, the aim has been to assess the optimal temperature for solution annealing for preparing alloy for weld repairing.

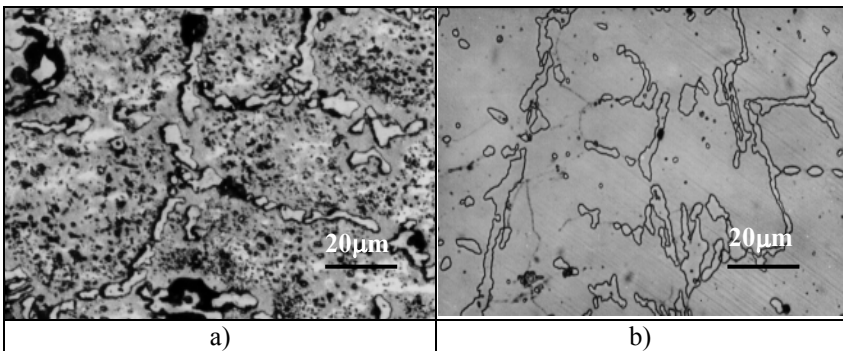


Figure 1: Microstructure samples of the Supertherm alloy investigated by the IA, a) without heat treatment b) after heat treatment at 1250°C/1h, etched in Aqua regia.

The samples of the microstructure for investigations are presented in Figure 1. The sample of the as received microstructure without high temperature heat treatment is shown on Figure 1a), while sample of the treated microstructure at 1250°C for 1h is shown in Figure 1b). The areas of the brittle phases at the grain boundaries and inside the grain were measured.

The results of the quantitative metallographic measurements based on the image analysis are presented. The effects of heat treatment temperature on the quantity of brittle phases as σ – phase and carbides, are presented by diagram in Figure 2. It is evident that with the increase of the annealing temperature there is a decrease of the total area of the σ – phase and carbide particles in relation to untreated condition. Such behaviour is a result of their dissolution in the austenite - (γ) phase.

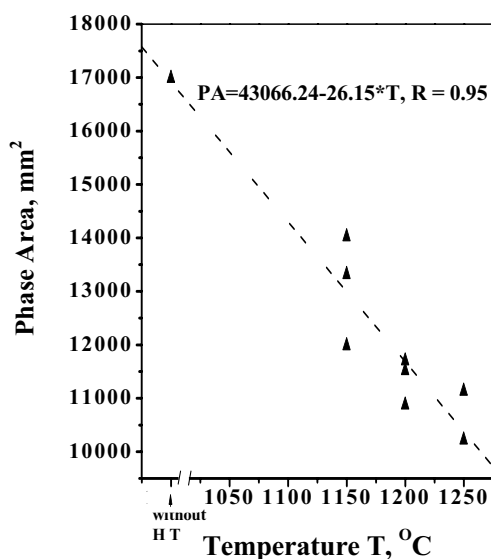


Figure 2: The effect of heat treatment temperature on the overall quantity of σ phase and carbides particles

From the result obtained by IA, it is obvious that the temperature of 1250°C offers the best effects of brittle phases dissolution, and therefore it could be suggested for enhancing weldability and for preparation for repair welding of an investigated material. It has to be noted that this temperature is close to the temperature of liquation of certain Supratherm alloy microconstituents. Therefore, an annealing temperature of between 1150°C and 1200°C is suggested for heat treatment of an investigated alloy.

The results of regression analysis has shown high correlation coefficient R between 0.95 and 0.98, which indicates that the obtained results could be applied for determination of the analysed values in the analysed temperature interval.



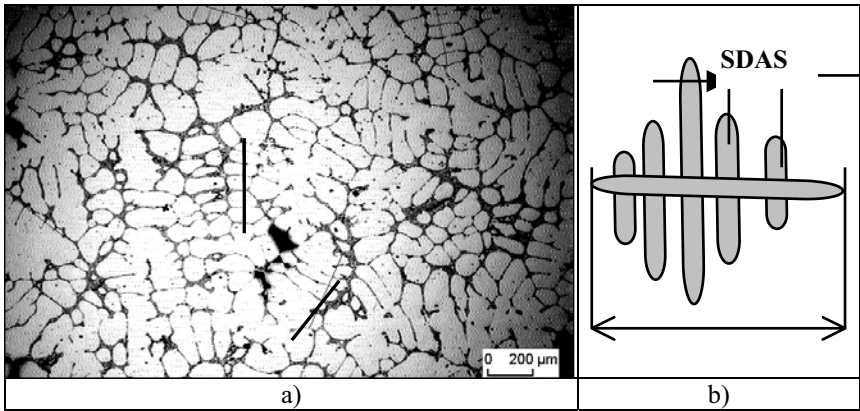


Figure 3: Sample of the analysed aluminium-silicon alloy microstructure a) and b) schematic representation of dendrites showing the difference between primary dendrite arm spacing (DAS) and measured secondary dendrite arms spacing (SDAS).

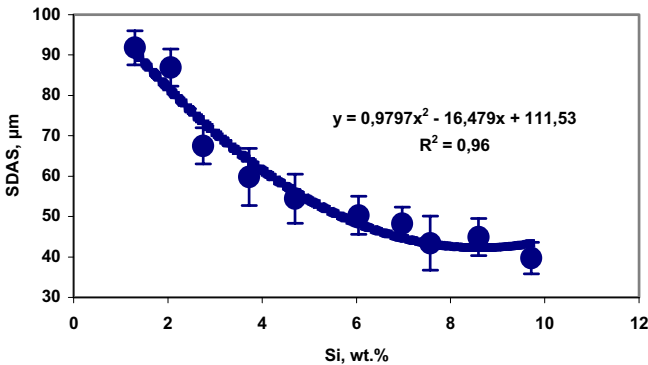


Figure 4: The effect of the various silicon content on the size of the SDAS. There is appreciable refining effect as the content of silicon varied between 1 and 8 weight percent. When the content of silicon increase above 8 wt.%, this effect is insignificant.

3.2 Secondary dendrite arm spacing (SDAS) in cast Al alloys

A comprehensive understanding of melt quality is of paramount importance for the control and prediction of actual casting characteristics. The most important practical aspect of the cast dendrite structure is the secondary dendrite arm spacing (SDAS) that represents the distance between secondary dendrites in the solidifying structure of cast metals and alloys. This quantity is significant because it has been shown that many mechanical properties can be related to it, with the best properties always associated with the smallest SDAS [2]. A sample of the analysed aluminium-silicon alloy microstructure and schematic

representation of dendrites showing primary dendrite arm spacing (DAS) and measured secondary dendrite arms spacing (SDAS) are presented in Figure 3.

A well known effect of varying cooling rates on the size of the SDAS is effusively exploited in the literature. In addition, the effect of alloying elements on the size of the SDAS by aluminium-silicon alloys was not so extensively investigated. Only a few researchers have examined the effect of variation in the Al alloy composition on the size of the SDAS [3, 4].

The influence of various content of the silicon and copper on the size of the SDAS in Al alloy is presented in Figures 4 and 5. The each point on figures corresponds to the average value of the SDAS based on the ten measurements. Vertical bars represent the standard deviations for each series of measurements.

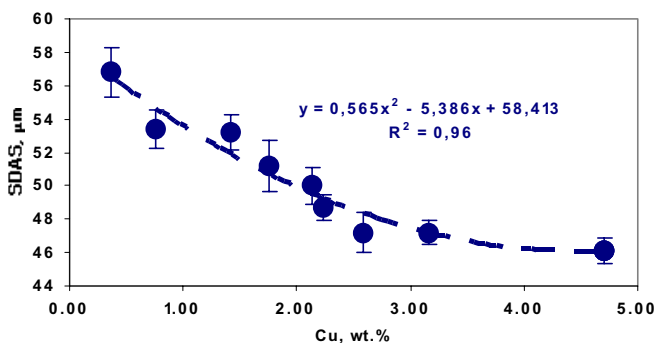


Figure 5: The effect of the various copper content on the size of the SDAS. The increases in the copper content from 0 to 3 weight percent refine considerably the size of the SDAS. Any increase above 3 wt.% of copper refine the dendrite but at a much lower rate.

The higher silicon and copper contents reduced the size of the SDAS. Dependence between the SDAS and silicon or copper content could be expressed by linear equations with high correlation coefficient.

Measurement done by image analysis confirmed that the average size of the SDAS decrease from 91.8 μm to 39.7 μm according to addition of silicon from 1 to 10 wt. % respectively. The effect is more significant until silicon reaches the content of 8 wt.%. Further increase in the content of silicon has almost no effect on the size of this microconstituent. A similar, but considerably smaller effect can be recognized by the addition of copper in the AlSiCu melt. The data presented in Figure 6 shows that the size of the SDAS slightly decreases from 56.8 μm to 46.1 μm when the content of copper in the AlSiCu melt increase to approximately 4.7 wt.%. Theses results are not unexpected. It is well known from the literature that the size of the dendrites is, beside the cooling rate of solidification, dependent on the level of alloying elements present in the melt [2]. From the result it is evident that the effect of the same content of copper is slightly smaller that that of the same content of silicon.

Dependence between the SDAS and silicon or copper content are expressed by polynomial equations with high correlation coefficient $R=0.96$. The presented

equations could be used for SDAS prediction for different Si or Cu contents in the investigated intervals.

3.3 Steel weld joint dimensions

The measured values by IA, as linear and area weld joint dimensions, in the cross section of the bead on plate welded joint in the arc welding process, are presented in Figure 6.

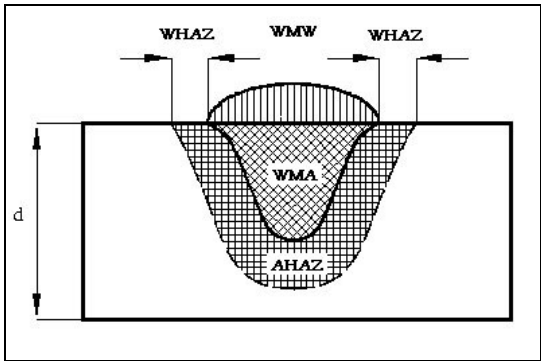


Figure 6: Schematic presentation of the measured bead on plate weld dimensions, WMW – weld metal width, WHAZ – width of the HAZ, WMA – weld metal area, AHAZ – area of the HAZ.

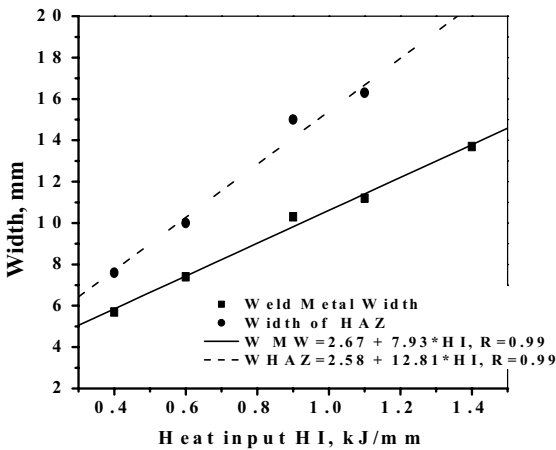


Figure 7: Measured linear dimensions of the steel weld joint as a function of the heat input HI. WMW – weld metal width, WHAZ – width of the HAZ.

The result of the measured critical weld dimensions as: WMW – weld metal width, WHAZ – width of the HAZ, WMA – weld metal area, AHAZ – area of

the HAZ for different heat inputs (HI) during arc welding, from 0.4 to 1.4 kJ/mm, are presented in Figures 7 and 8.

The obtained results have shown direct dependence of the measured dimensions from the energy input. Measured widths, of the WM and HAZ are increased with heat input increasing, as presented on Figure 8. The same dependence is observed for WM and HAZ area in relation to the heat input (Figure 8). It is known from the literature that dimensions of the HAZ directly depend of heat input [5]. For the measured results by IA, correlation coefficients of the linear regression equations are calculated. The high correlation coefficients R , with value of 0.99 are obtained for all performed measurements.

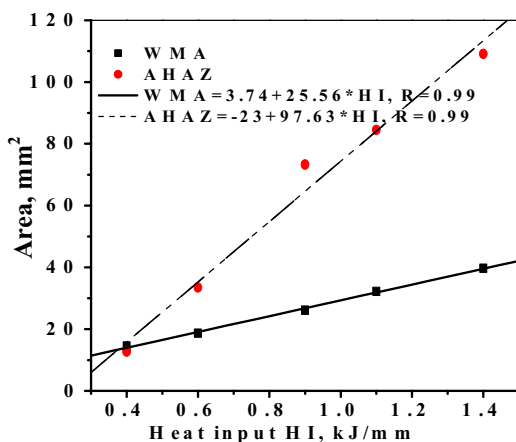


Figure 8: Measured area dimensions of the steel weld joint as a function of the heat input HI. WMA – weld metal area, AHAZ – area of the HAZ.

The presented methodology based on the IA measurements enables quality control of the welds joints in a case of the weld qualification and for the periodical controls in the automatic welding processes.

4 Conclusions

Quantitative measuring by image analysis applied in metallurgical engineering is presented. Three different metallurgical problems were analysed based on the measuring of the linear or/and areal dimensions of the microstructural/macrostructural components by the IA in relation to the process parameters as:

Determination of the brittle phase content in the function of the heat treatment temperature for the heat resistant Ni-Cr-Co-W alloy, with the aim of obtaining optimal microstructure for repair welding are presented. Results have shown that the best effect of brittle phases dissolving is obtained at the heat treatment temperature interval from 1150°C to 1250 °C.



Investigation of the effects of Si (1-10%) and Cu (0.5-4.5 %) content, in the cast Al alloy for automotive application, on secondary dendrite arm spacing (SDAS) in the structure was performed. Results have shown that the higher silicon and copper contents reduced the size of the SDAS, which directly enable better mechanical properties of the cast product.

The effect of different energy inputs, in a steel arc welding process, on the dimensions and geometry of the steel welded joint was investigated. The heat affected zone (HAZ) of the welds is critical for the mechanical properties and weld quality and it is directly depended of the energy input. The area and the width of the HAZ for different heat inputs, from 0.4 to 1.4 kJ/mm, were measured by the IA. The presented methodology enables quality control of the welds joins in a case of the weld qualification and for the periodical controls in the automatic welding processes.

All presented experimental results are based on a large number of areal or linear dimensions measurements by the IA. High correlation coefficients for the regression equations of the results were obtained for the each of the presented investigations.

Acknowledgement

A part of this work was carried out in a scope of the project 19023: "Development of the new repair welding technologies for intervention maintain thermo energetic plants" supported by the Ministry of Science of the Republic of Serbia

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Section 4

New methods

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Ultra-high-performance fiber reinforced concrete: an innovative solution for strengthening old R/C structures and for improving the FRP strengthening method

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Abstract

In this study a new innovative method of earthquake-resistant strengthening of reinforced concrete (R/C) structures is presented for the first time. Strengthening according to this new method consists of the construction of steel fiber ultra-high-strength concrete jackets without conventional reinforcement, which is usually applied in the construction of conventional reinforced concrete jackets. An innovative solution is also proposed for the first time that ensures a satisfactory seismic performance of existing reinforced concrete structures, strengthened by using composite materials. The weak point of the use of such materials in repairing and strengthening old R/C structures is the area of beam-column joints. According to the proposed solution, the joints can be strengthened with a steel fiber ultra-high-strength concrete jacket, while strengthening of columns can be achieved by using CFRPs. The experimental results showed that the performance of the subassembly strengthened with the proposed mixed solution was much better than that of the subassembly retrofitted completely with CFRPs.

Keywords: steel fiber ultra high-strength concrete, reinforced concrete jackets, fiber reinforced polymers, beam-column joints, columns, cyclic loads.

1 Introduction

Damage incurred by earthquakes over the years has indicated that many reinforced concrete (R/C) buildings, designed and constructed during the 1960s



and 1970s, were found to have serious structural deficiencies today. These deficiencies are mainly due to lack of capacity design approach and/or poor detailing of the reinforcement. As a result, lateral strength and ductility of these structures were minimal and hence some of them collapsed [1–3]. One of the most popular pre-and post-earthquake retrofitting methods for columns, beam-column joints and walls is the use of reinforced concrete jacketing. In retrofitting building columns, b/c joints and walls with outer R/C jackets, the usual practice consists of first assembling the jacket reinforcement cages, arranging the formwork and then placing the concrete jacket [4–7]. Shotcrete can be used in lieu of conventional concrete in the repair works and, in some cases, offers advantages over it, the choice being based on convenience and cost.

The wrapping of reinforced concrete members (usually columns, b/c joints and walls) with fiber-reinforced polymer (FRP) sheets including carbon (C), glass (G) or aramid (A) fibers, bonded together in a matrix made of epoxy, vinylester or polyester, has been used extensively through the world in numerous retrofit applications in reinforced concrete buildings. These are recognized as alternate strengthening systems to conventional methods such as plate bonding and shotcreting [8, 9].

The best choice of the appropriate retrofitting method highly depends on the feasibility of the method, on the cost and on the simplicity of the application. Of course, it is well known that the works related to strengthening of buildings have higher difficulties and cost compared to the usual construction works related to the construction of new reinforced concrete buildings.

According to the above conception it would be very interesting to create and introduce in the marketing a new method of retrofitting old reinforced concrete structures, as effective as the methods of retrofitting but simpler in application and more economical. An earthquake strengthening system with the aforementioned qualifications would be very competitive among the others.

Henager [10], successfully replaced all the hoops of the joint region and part of the hoops of the critical regions of the adjacent beam and column of an earthquake-resistant beam-column subassembly, by steel fibers (1.67% fiber volume fraction is used). This replacement involved 50% reduction in building costs.

Fiber Reinforced Concrete or Shotcrete has been successfully applied in many construction applications eliminating or significantly reducing the conventional reinforcement of R/C structures and reducing the construction costs.

The advantages of Fiber Reinforced Concrete has been worldwide recognized, however has not been found yet a reliable way of application of this material in the retrofitting of old reinforced concrete structures, by eliminating or significantly reducing the conventional reinforcement of the R/C jacketings and generally by reducing the cost of retrofitting compared to that involved by the use of other strengthening methods as plate bonding and FRPs. A relatively new process called SIMCON (Slurry Infiltrated Mat Concrete) developed by Hackman et al. [11], seems to be very effective in strengthening applications. SIMCON is made by infiltrating continuous steel fiber-mats, with specially designed cement-based slurry. Nevertheless, SIMCON technique has the same



disadvantages as FRPs. Their strengthening layers wrap usually horizontally the columns and the walls increasing their shear strength and ductility, but these layers are terminating in the slabs of the strengthening reinforced concrete buildings. The strengthening layers could not effectively pass through the slabs, thus these layers could not increase the flexural strength of the columns and walls and could not effectively retrofit the beam-column joint regions. The existing experimental results related to the retrofitting of beam-column subassemblages of reinforced concrete structures demonstrated significant damage concentration in the joint regions, although the subassemblages used were of planar-type, without slabs and the retrofitting works related to SIMCON application were easy [12].

2 The proposed new innovative strengthening method

An important experiment was conducted by Tsonos [13]. An exterior beam-column subassemblage L_3 poorly detailed in the joint region was subjected to unidirectional reversed cyclic lateral loading. The joint region of this subassemblage was representative of the joint regions of old structures built during the 1960s and 1970s. The subassemblage was reinforced in the joint region by one hoop of diameter 8mm instead of the five hoops of the same diameter required by the ACI-ASCE Committee 352 (ACI 352R-02) [14]. The joint shear stress of the specimen was higher than the maximum allowable joint shear stress by the same Committee ($\tau_{\text{joint}} = 1.36 \sqrt{f'_c} > \tau_{\text{permitted}} = 1.0 \sqrt{f'_c}$). As expected, this specimen failed in pure and premature joint shear failure from the early stages of the seismic-type loading. The removal and replacement of the damaged concrete in the joint by a non-shrink, non-segregating steel fiber concrete of high-strength with only 0.5% fiber volume fraction and the removal and replacement of the damaged concrete cover of part of the columns' critical regions with the same steel fiber high-strength concrete, resulted in a pure beam failure, when the repaired subassemblage RL_3 was imposed to the same loading as the original control subassemblage L_3 .

The above experiment led us to the idea of using the same non-shrink, non-segregating steel fiber high-strength concrete for the strengthening of old reinforced concrete buildings, by jacketing not with the use of conventional reinforcement, longitudinal bars or hoops [15]. For this purpose and for best results, it was decided to increase the fiber volume fraction and to increase the compressive and tensile strengths of the steel fiber concrete. The following large experimental program was implemented. Four identical exterior beam-column subassemblages were constructed, using normal weight concrete and deformed reinforcement. The test specimens were 1:2 scale models of the representative 40cm×40cm square columns and beam-column joints which are usually found in building constructions within Greece and Europe in general. The columns and b/c joints of these specimens were poorly detailed in order to represent columns and b/c joints of old buildings built in 1960s and 1970s. In figure 1 are shown the dimensions and cross-sectional details of these specimens. Their columns had



less longitudinal and transverse reinforcement than the modern columns and their joint regions had not joint hoops, the joint shear stress were $2.20 \sqrt{f'_c}$ MPa $> 1.0 \sqrt{f'_c}$ MPa, and the flexural strength ratios of these specimens were lower than 1.0. The concrete compressive strength of these original specimens was approximately 8.50MPa. Thus, a premature joint shear failure is expected for all these subassemblages during a seismic type loading. All these original specimens were subjected to cyclic lateral load histories so as to provide the equivalent of severe earthquake damage. In figure 2 is shown the failure mode of the representative specimen O_3 and its hysteresis loops. The failure of O_3 was concentrated mainly in the joint which lost almost all of the core's concrete.

In the following are described in brief the retrofitting works for specimens O_3 , W_2 , M_1 , and M_3 .

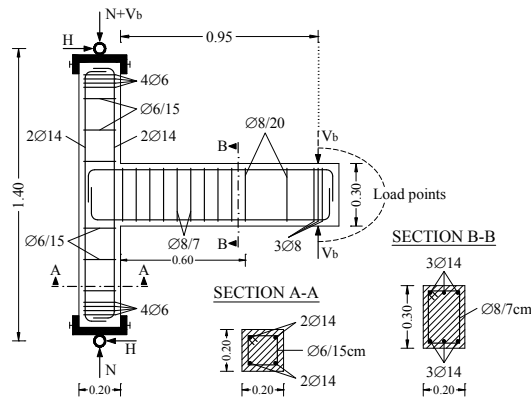


Figure 1: Dimensions and cross-sectional details of original subassemblages O_3 , W_2 , W_3 , M_1 , and M_3 .

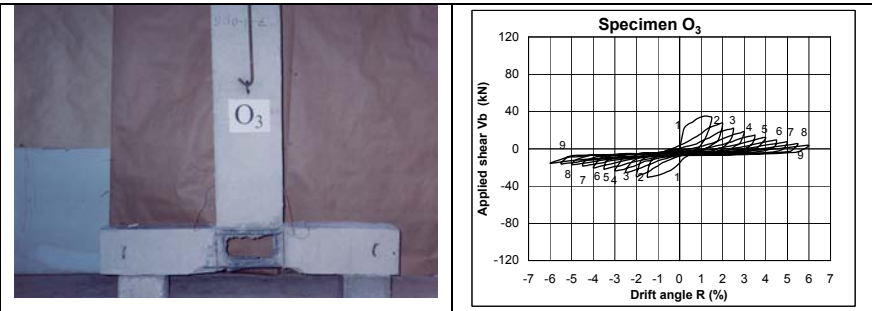


Figure 2: Plots of applied shear versus drift angle and failure mode of the original subassemblage O_3 .

1. Specimen O_3 was retrofitted by reinforced concrete jacket in the columns and beam-column joint region. The compressive strength of the jacket's concrete was 31.70MPa. Deformed bars were used for the construction of the steel cage of the jacket. After the interventions this specimen was designated SO_3 . In figure 3 is shown the jacketing of column and beam-column connection of subassemblage SO_3 .
2. Specimen W_2 was strengthened by a high-strength fiber jacketing in the joint region and on the columns (see figure 3). The damaged concrete of the joint region of specimen W_2 was removed and replaced by a premixed, non-shrink, rheoplastic, flowable and non-segregating concrete of high-strength. The repaired and subsequently strengthened specimen was named FW_2 . The design for the retrofit process with carbon fiber-reinforced polymer sheets (CFRPs) was based on $E_f = 235\text{GPa}$, $t_f = 0.11\text{mm}$ (t_f = layer thickness) and $\varepsilon_{fu} = 1.5\%$ (ε_{fu} = ultimate FRP strain).
3. Subassemblage M_1 was strengthened by jacketing with ultra high-strength steel fiber-reinforced concrete (UHSFC) with 1.5% fiber volume fraction in the columns and in the joint region. The thickness of the jacket was only 4.0cm. The repaired and subsequently retrofitted specimen was named $HSFM_1$ (see figure 3).
4. Subassemblage M_3 was retrofitted by jacketing with UHSFC with 1.0% fiber volume fraction, in the columns and in the joint region. The thickness of the jacket was 6.0cm. The repaired and strengthened specimen was named $HSFM_3$ (see figure 3).

The compressive strengths of the UHSFC used for the strengthening of $HSFM_1$ and $HSFM_3$ were 106.33MPa and 102.30MPa respectively. The tensile strength of the UHSFC used, was approximately equal to 12MPa. The steel fibers used were Dramix ZP 30/0.6.

All the above strengthened subassemblage SO_3 , FW_2 , $HSFM_1$ and $HSFM_3$ were imposed to the same loading as that of their original subassemblages. All strengthened specimens demonstrated increased strength, stiffness and energy dissipation capacity as compared to those of their original specimens (compare hysteresis loops between the original and the upgraded subassemblages in figures 2 and 4 e.g. O_3 – $HSFM_1$). However, the failure mode of SO_3 and FW_2 was quite different from that of all upgraded specimens by the new proposed jackets $HSFM_1$ and $HSFM_3$. Thus although, the beams of both SO_3 and FW_2 yielded, the majority of the damage was concentrated in their joint regions, see failure modes of specimens in figure 4. On the contrary, the failure mode of both specimens $HSFM_1$ and $HSFM_3$ was the optimum one. Formation of plastic hinge in their beams was observed from the first cycles of loading, while the following cycles resulted in damage concentration only in the critical regions of their beams near their joints. A mixed flexural – shear failure mode was observed in their beams at the end of the tests, which was accompanied by severe buckling of the longitudinal beam reinforcement. The joints and the columns of both these specimens were intact at the conclusion of the tests. This excellent seismic performance of both the $HSFM_1$ and $HSFM_3$ subassemblages was demonstrated both in their failure modes (figure 4) and in their hysteresis loops (figure 4).



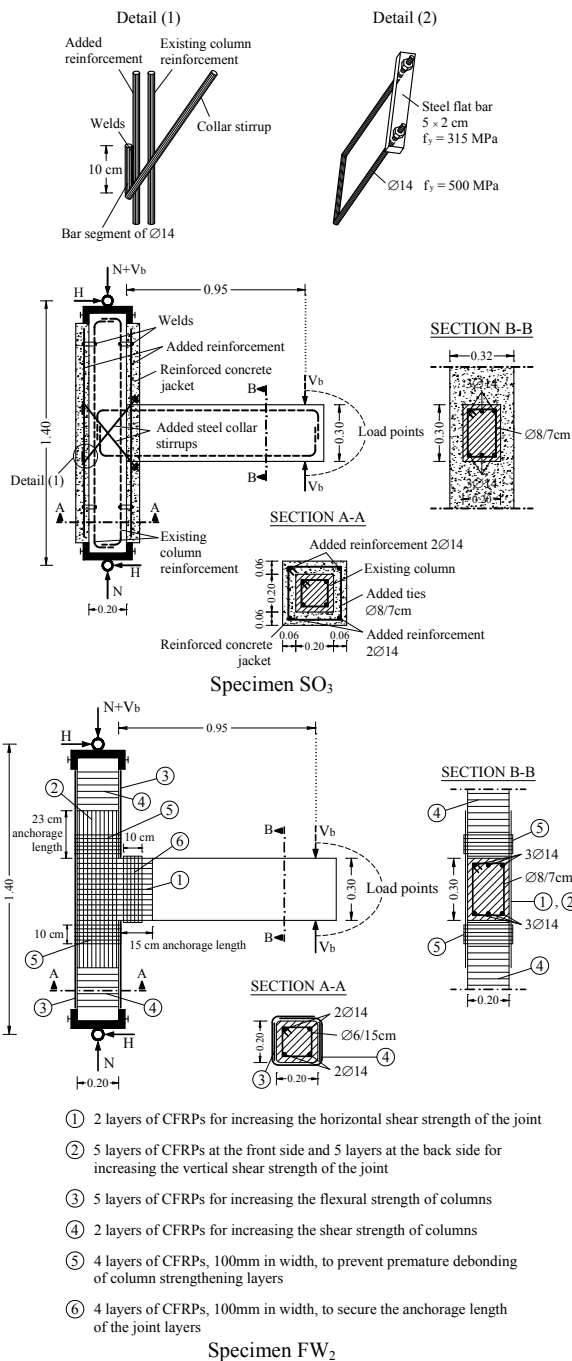


Figure 3: Jacketing of column and beam-column connection of subassemblages SO₃, FW₂, HSFM₁, and HSFM₃.

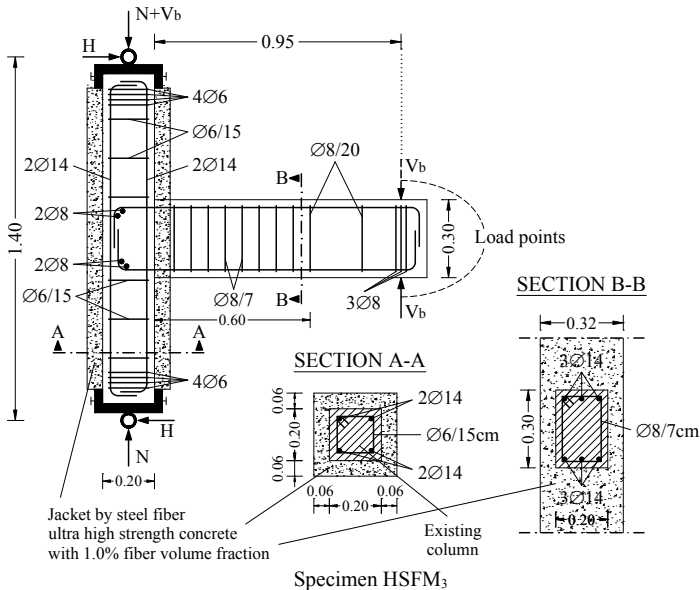
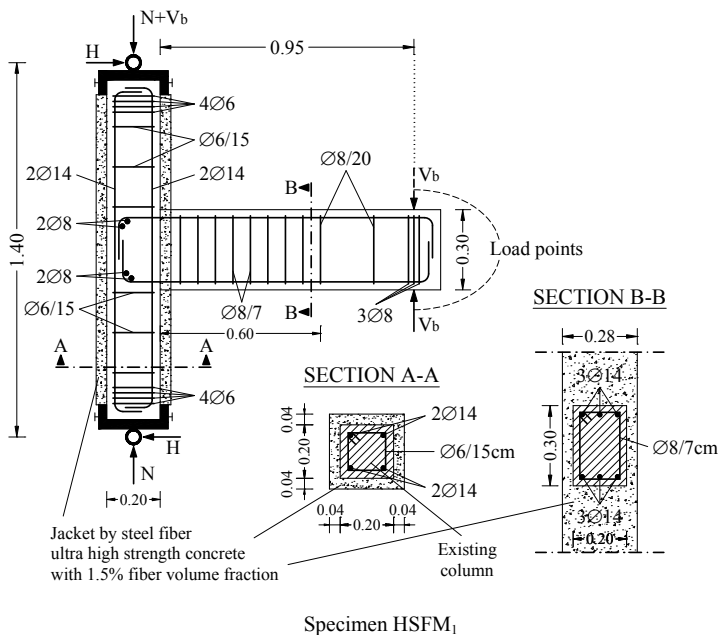


Figure 3: Continued.

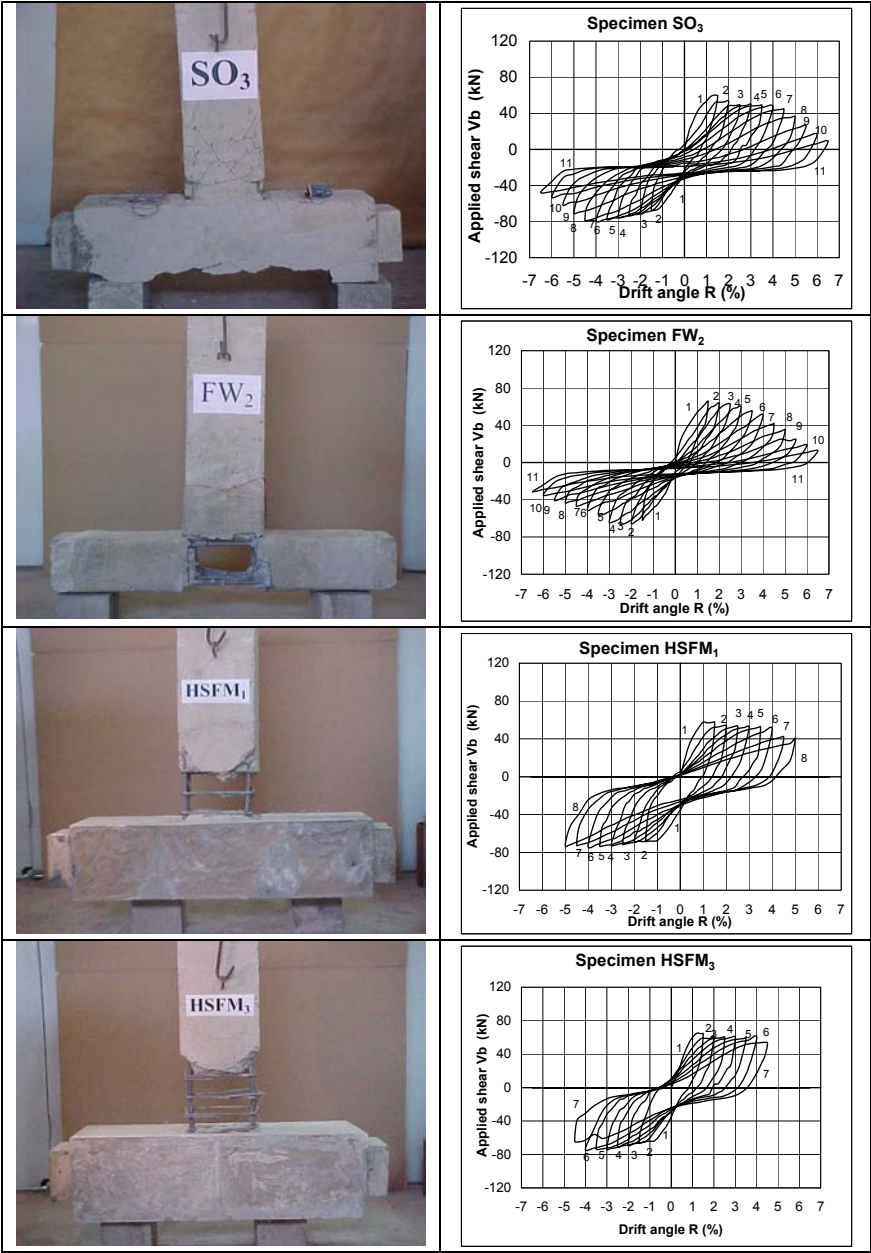


Figure 4: Plots of applied shear versus drift angle and failure mode of the strengthened subassemblages SO₃, FW₂, HSFM₁ and HSFM₃.



The seismic behavior of both these subassemblages was superior to those of specimens SO_3 and FW_2 retrofitted by reinforced concrete jackets and FRP-jackets.

A patent No 1005657 was awarded to Professor Tsonos [16] by the Greek Industrial Property Organization for the above invention.

3 An innovative new solution for improving the FRP strengthening method

An innovative solution is proposed also for the first time. This solution ensures a satisfactory and perhaps perfect seismic performance of existing old reinforced concrete buildings strengthened by using composite materials FRPs. The weak point in using such materials in repairing and strengthening reinforced concrete structures is the area of beam-column joints. Indeed, all the strengthened subassemblages in the beam-column region with composite materials FRPs of the literature demonstrated in the best case a mixed type failure during seismic type loading. Thus, during the first cycles of loading their beams yielded, however during the following cycles a large part of damage of these strengthened subassemblages was concentrated in their joint regions. Of course, this failure mode is highly dangerous for the people who live in old buildings which were retrofitted in post-earthquake or pre-earthquake cases. The representative failure mode of subassemblage FW_2 clearly demonstrates this critical situation, figure 4. The whole strengthened beam-column joint region of FW_2 not only failed but also was removed (i.e. leaving a hole in this position) during the last cycles of loading. This exactly is the reason why the Greek Code of the Repair and Strengthening of Reinforced Concrete Buildings [17] does not allow the use of composite materials for the strengthening of reinforced concrete beam-column joints.

The second innovative solution presented in this study consists of strengthening the joint regions of subassemblages with a local jacket of ultra-high-strength steel fiber concrete with 1.5% fiber volume fraction, while retrofitting the columns can be achieved by using composite materials FRPs. In order to investigate the effectiveness of the proposed solution of mixed type strengthening a new beam-column subassemblage W_3 identical with the other four (O_3 , W_2 , M_1 and M_3 , figure 1), was constructed and was imposed to seismic type loading as the other original subassemblages. The failure mode of W_3 was the same as that of O_3 previously described. The subassemblage was retrofitted by the new mixed type technique shown in figure 5. After the interventions this specimen was designated $FHSFW_3$. The columns of $FHSFW_3$ and FW_2 were retrofitted exactly in the same way with composite materials CFRPs, while the joint region was retrofitted with ultra high-strength steel fiber concrete with 1.5% fiber volume fraction. Specimen $FHSFW_3$ was imposed to the same type loading as that of the original specimen W_3 . The seismic performance of $FHSFW_3$ was optimal. The damage was concentrated only in the critical region of the beam, while the columns and the joint region were intact at the conclusion of the tests. This optimal performance was demonstrated also in the hysteresis loops of the subassemblage $FHSFW_3$. The hysteresis loops of $FHSFW_3$ were



much better than the loops of FW₂, figures 4 and 6. The latter indicate the serious and almost premature joint shear failure of the subassembly FW₂, (see fig. 4).

4 Conclusions

1. A new innovative technique for strengthening of poorly detailed structural members of old buildings is proposed for the first time. This method consists of jacketing the structural members with non-shrink, non-segregating steel fiber concrete of ultra high-strength, without the addition of conventional reinforcement in the jackets.
2. This new innovative method was found to be much more effective than the conventional reinforced concrete jackets and especially the FRP-jackets.
3. Beam-column subassemblies, which had failed in pure joint shear failure during seismic-type loading and upgraded in the columns and beam-column joint region by the new innovative technique (patent No 1005657/2007) demonstrated the optimal failure mode, with damage concentration only in the beam region during re-loading with the same loading.
4. A second innovative solution is presented in this study also for the first time. This mixed type technique, by using local jacketing with steel fiber ultra-high-strength concrete only in the joint region, while the columns were upgraded by composite materials, eliminated the disadvantages of the application of composite materials FRPs for the strengthening of old building structures, due to the ineffective strengthening of beam-column joints by FRPs.

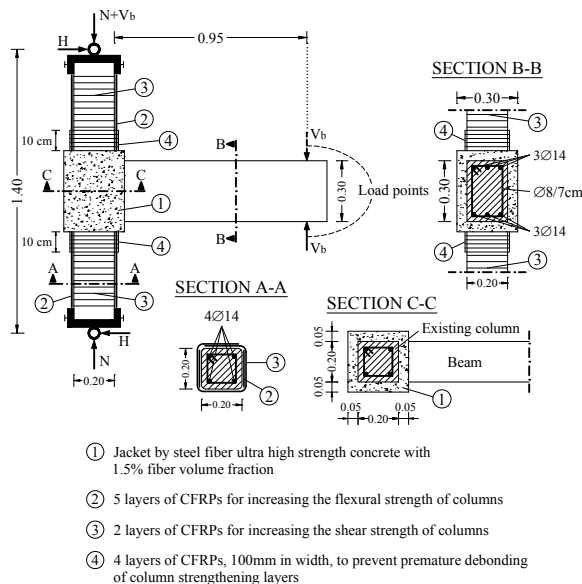


Figure 5: Strengthening of column and beam-column connection of subassembly FHSFW₃ by the new mixed type technique.





Figure 6: Plots of applied shear versus drift angle and failure mode of the strengthened subassembly FHSFW₃.

Acknowledgements

The experimental part of this research investigation was sponsored by the Greek General Secretariat of Research and Technology and by the Company ISOMAT S.A. The author gratefully acknowledges the financial support by the sponsors.

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Improvement in wear resistance of TiNi alloy processed by equal channel angular extrusion and annealing treatment

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Abstract

In the present paper, the equal channel angular extrusion (ECAE) and subsequent annealing treatment are applied to the Ti-50.6at.%Ni alloy. The microstructure and pseudo-elasticity of TiNi alloy after ECAE and annealing treatment are investigated, and the wear behavior of the alloy under dry sliding condition is studied. The results indicate that ECAE technique contributes to refine the microstructure and improve the pseudo-elasticity of the TiNi alloy. The wear of TiNi alloys increases with load. Moreover, the ECAE processed TiNi alloy exhibits higher resistance to wear compared with the as-received TiNi alloy. For as-received TiNi alloy, adhesion and delamination were main damage mode under low load, while deep plough tracks were observed under high load. The slight adhesive wear was primary wear mode for the ECAE processed TiNi alloy under both low and high loads.

Keywords: equal channel angular extrusion (ECAE), pseudo-elasticity, shape memory alloy, wear.

1 Introduction

Recently, a number of investigations have demonstrated that TiNi alloy has high resistance to wear in different wear conditions compared it to many conventional wear-resistant materials such as steels, Ni-based and Co-based tribo-alloys [1–5]. This makes TiNi alloy attractive for application in many environments. Extensive researches have confirmed that the high wear resistance of TiNi alloy



is mainly attributable to its special martensitic phase transformation [6-8] which is also called pseudo-elasticity. Liang et al. [9] has noticed strong correspondence between the wear behavior and the pseudo-elasticity. Specimens with pseudo-elasticity show higher wear resistance than those with little pseudo-elasticity.

Ultra-fine grained materials have attracted much attention from materials scientists owing to their better mechanical properties. Of several techniques developed for producing fine-grained materials by severe plastic deformation (SPD), the equal channel angular extrusion (ECAE) technique introduced by Segal et al. has been successfully applied to produce various fine-grained materials [10–14]. Many studies have confirmed that ECAE process can not only refine the microstructure, but also improve the mechanical properties of materials.

The microstructure of a material remarkably affects its mechanical properties and the wear behavior. Till now, some results on the microstructure and phase transformation behavior of TiNi alloy processed by ECAE have been reported [15,16]. However, the wear behavior of TiNi alloy processed by ECAE has not been well reported yet. The objective of this research is to understand the wear behavior of TiNi alloy processed by ECAE against GCr15 steel under dry sliding condition. The microstructure, pseudo-elasticity, and wear behavior of TiNi alloy processed by ECAE and annealing treatment are studied to evaluate the effects of ECAE and annealing treatment on the wear properties. The wear mechanisms of the TiNi alloy are discussed based on the SEM examination of the worn surfaces.

2 Experimental

Experimental materials were Ti-50.6at.% Ni alloy rod with a diameter of 25mm. The rod had been hot forged at 1123K and annealed at 773K for 2 hours. Billets for ECAE process were cut from the TiNi rod and had dimensions of 9.4 mm×9.4 mm×100 mm. The ECAE die was designed to yield an effective strain of ~ 1 by a single pass. The inner contact angle (Φ) and the arc of curvature (ψ) at the outer point of contact between channels of the die were both 90°, as shown in Fig. 1. Two ECAE processes were conducted at high temperature. Keeping the die at 823K, billets were preheated at 1123K for 20 min before the first extrusion, and at 1023K for 20 min before the second extrusion. During ECAE process, the billet was not rotated between passages. To obtain homogeneous and fine microstructure, the billets processed by ECAE were annealed at 500°C for an hour.

Specimens for microstructure observation, pseudo-elasticity and wear behavior measurements were cut along the extrusion direction from the TiNi billets processed by ECAE and subsequent annealing treatment. After mechanically polished and etched with a mixture solution of HF:HNO₃:H₂O with a ratio of 1:3:10, the microstructure of specimens was observed on a NEOPHOT-1 type optical microscope.

Tensile testing was done to investigate the effect of ECAE and annealing treatment on the pseudo-elasticity of TiNi alloy. Tensile test specimens with a reduced gage section of 1 mm thick, 2 mm wide and 20 mm long were machined



from as-received TiNi alloy and the ECAE processed TiNi alloy. Tensile tests were performed using an Instron Universal Testing machine at room temperature (24°C). The rate of extension was 0.1 mm/min.

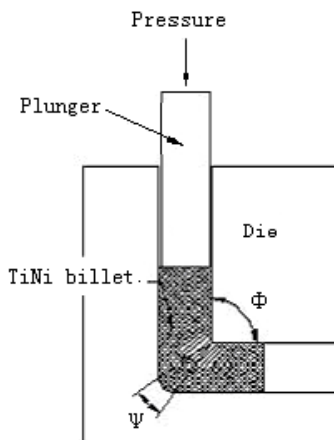


Figure 1: Schematic illustration of the ECAE process in the experiment.

The wear behavior of the Ti-50.6at.%Ni alloy sliding against a GCr15 steel ring under dry sliding condition was evaluated using a block-on-ring tribometer. The size of the TiNi block for wear tests was 20 mm×7 mm×8 mm. Wear tests were carried out at a sliding speed of 0.42 m/s and sliding time of 30 min. The applied load was ranged from 50 N to 100 N. A BP211D electron scale to evaluate the wear resistance was used to measure wear of TiNi specimens. The morphology of worn surfaces was observed using an OPTON CSM 950 scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy X-ray analysis system.

3 Results and discussion

3.1 Microstructure

For comparison, the as-received and the ECAE processed TiNi alloy were investigated. Fig. 2 shows the cross-section microstructure of the TiNi alloys. It can be seen that the microstructure of the as-received TiNi alloy (Fig. 2(a)) was coarse equiaxed structure with the mean grain size of 60 μm . After ECAE and subsequent annealing treatment, the microstructure of TiNi alloy was refined markedly, having an average grain size of approximately 5 μm .

3.2 Pseudo-elasticity

Results of the measurement demonstrated that the TiNi alloys showed pseudo-elastic characteristics, which was illustrated by $\sigma - \epsilon$ curve of the TiNi alloys



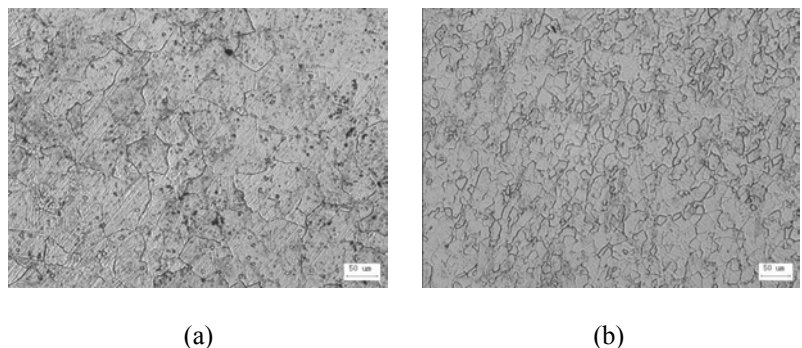


Figure 2: Microstructures of TiNi alloy: (a) as-received TiNi alloy; (b) the ECAE processed TiNi alloy.

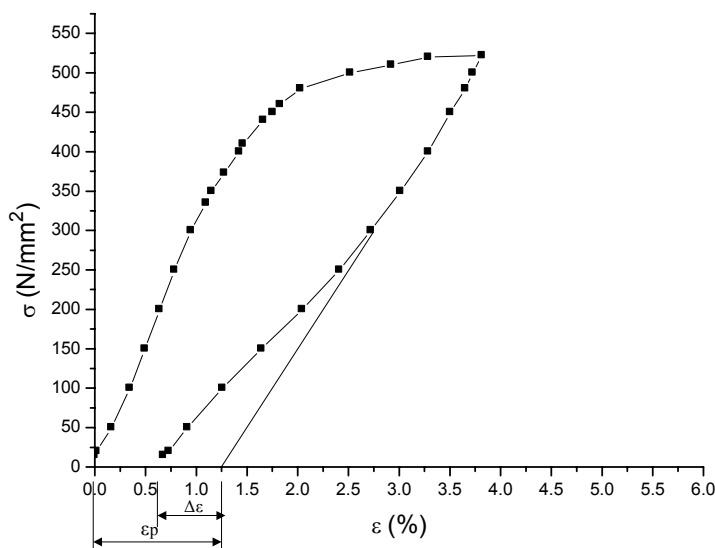


Figure 3: $\sigma - \epsilon$ curve of TiNi alloy.

Table 1: The γ value of TiNi alloy.

	As-received TiNi alloy	The ECAE processed TiNi alloy
γ value	40%	63%

(Fig. 3). The pseudo-elasticity was evaluated based on the value of $\gamma = \frac{\Delta\epsilon}{\epsilon_p}$, ϵ_p was the overall residual strain which was supposed to remain when the applied load was removed, and $\Delta\epsilon$ was the recoverable strain which was not



caused by the operation of slip systems but by stress-induced martensitic transformation. The permanent residual strain was, therefore, equal to $\varepsilon_p - \Delta\varepsilon$. The higher the γ value is, the greater the pseudo-elasticity. Table 1 showed γ value of the TiNi alloys. It can be seen that the γ value of the TiNi alloy after ECAE and annealing treatment increased obviously, which suggests that the TiNi alloy processed by ECAE and annealing treatment had better pseudo-elasticity than the as-received TiNi alloy.

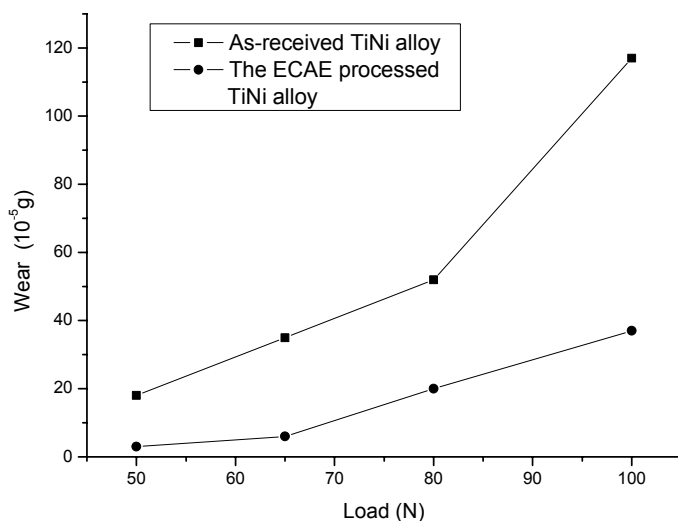


Figure 4: Variation of wear with applied load at a sliding speed of 0.42 m/s.

3.3 Wear behaviour

The effects of applied load on the wear resistance of TiNi alloys were investigated under dry sliding wear condition. The variation of wear of TiNi alloys with applied load was given in Fig. 4. It can be seen that the wear of both the as-received TiNi alloy and the ECAE processed TiNi alloy increased with applied load. This can be explained by the friction-induced thermal and mechanical effects which may increase the actual contact area and the adherence between the frictional pair as the load increased. Moreover, it was found that the ECAE processed TiNi alloy exhibited lower wear in the load range of 50 -100 N than the as-received one. This can be rationally explained by the following reasons. Firstly, the ECAE processed TiNi alloy had more fine grains than the as-received TiNi alloy, leading to the smaller stress concentration. Under the same external stress, the smaller stress concentration caused by fine grains made it difficult adjacent grains deform plastically, so the larger external stress was needed to make adjacent grains plastic deformation. It means that the plastic deformation resistance of the ECAE processed TiNi alloy is enhanced after the microstructure was refined, which reduces the initiation probability of crack and

decreases stress concentration, resulting in the increase of wear resistance of the alloy. Secondly, the ECAE processed TiNi alloy has better pseudo-elasticity than the as-received one, which was recorded in Table 1. Liang et al. [9] had demonstrated the strong correspondence between the wear resistance and the pseudo-elasticity. The greater the pseudo-elasticity is, the higher the wear resistance. ECAE and annealing treatment enhanced the pseudo-elasticity of TiNi alloy, which was certainly beneficial to the wear resistance of TiNi alloy.

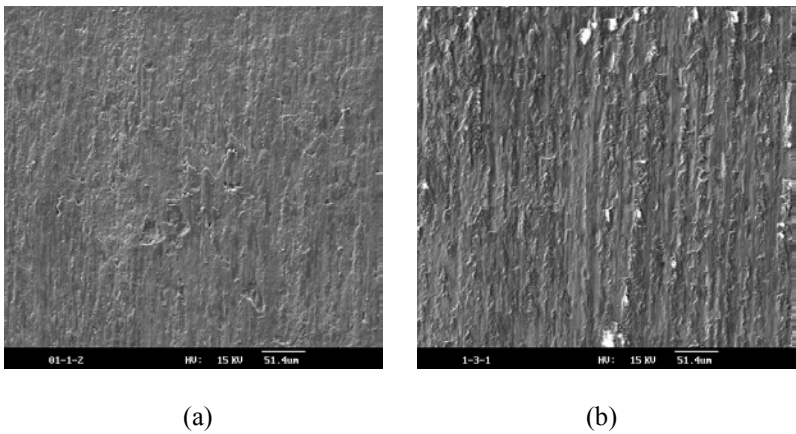


Figure 5: Worn surfaces of as-received TiNi alloy: (a) worn under a low load of 50 N; (b) worn under a high load of 100 N.

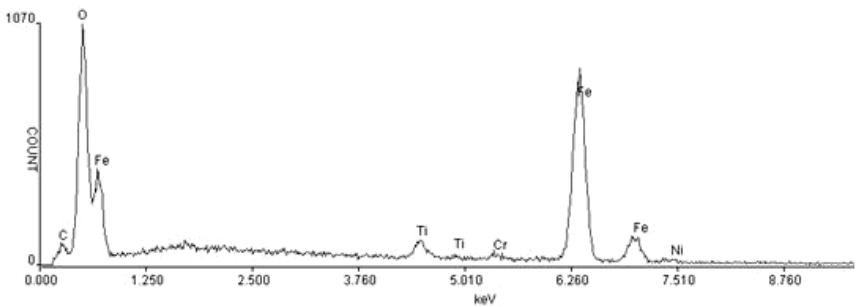


Figure 6: Results of the energy dispersive spectroscopy X-ray analysis performed on the wear tracks of the initial TiNi alloy after sliding against GCr15 steel under a load of 50 N and a sliding speed of 0.42 m/s.

The worn surfaces of as-received TiNi alloy under different applied loads were shown in Fig. 5, respectively. It can be seen that the worn surfaces of the as-received TiNi alloy had different morphologies under different applied loads. At the load of 50 N, the worn surface was smooth. However, a strong iron contamination transferred from the steel ring counterpart was observed by EDS analysis (as shown in Fig. 6), suggesting that adhesion occurred during friction.



At a higher load, deep plough tracks were observed on the worn surface of as-received alloy. Fig. 7 shows worn surfaces of the TiNi alloy with ECAE and annealing treatment. It can be seen that there is not significant difference in the worn surface between low applied load and high load. The surface scuffing was primary wear mechanism under both low and high loads. The morphological difference in worn surface of the ECAE processed TiNi alloy under different loads was not significant as that of the as-received TiNi alloy.

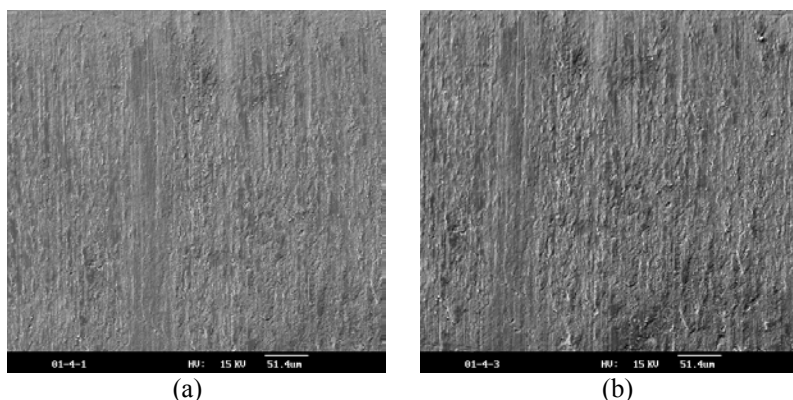


Figure 7: Worn surfaces of the ECAE processed TiNi alloy: (a) worn under a low load of 50 N; (b) worn under a high load of 100 N.

4 Conclusions

(a) After ECAE and annealing treatment, both the microstructure and the pseudo-elasticity of the TiNi alloy were improved markedly.

(b) The wear of the as-received TiNi alloy and the ECAE processed TiNi alloy both increased with load. When the load ranged from 50 to 100 N, the ECAE processed TiNi alloy exhibited higher wear resistance than the as-received alloy.

(c) The wear mechanism of as-received TiNi alloy was adhesion and delamination under low load; while under high load, deep plough tracks were observed. After ECAE and annealing treatment, the surface scuffing was primary wear mechanism of the TiNi alloy under both low and high loads.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 50071034) and State Key Laboratory of Tribology, Tsinghua University, Beijing, P.R. China.

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Tunnelling measurements as a new method of investigation of thin film superconducting cuprate junctions

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Abstract

Tunnelling measurements in thin film superconducting junctions involving cuprates (like $\text{YBa}_2\text{Cu}_3\text{O}_7$ or $\text{La}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$) are emerging as a unique tool of investigation. Thus, looking into tunnelling of Cooper pairs (the current that flows with no resistance) or quasiparticles in specially designed junctions is the most reliable method to investigate the symmetry of the superconducting order parameter in cuprates. This is crucial to establish a pairing mechanism for the electrons, i.e., the formation of Cooper pairs in these materials - one of the most important unsolved problems in modern solid state physics. Then, a detailed investigation of both dc and ac tunnelling of Cooper pairs in these junctions is essential to determine the current-phase relation (the relation between the current and the phase of the superconducting condensate). This represents a key element required in many applications like low-dissipative superconducting electronics or superconducting qubits in quantum computation. Also, tunnelling of quasiparticles in these junctions represent an accurate new method to determine the second critical field of cuprates. Here an overview on all these fundamental and applied aspects of this interesting class of nano materials will be given.

Keywords: unconventional superconductivity, thin film superconducting cuprate junctions, low temperature electric transport measurements.

1 Introduction

Understanding the mechanism responsible for superconductivity in unconventional superconductors, in particular in the high transition temperature superconductors (HTS), i.e., the cuprates discovered in 1986 [1] has been one of



the major goals of condensed-matter physicists. What we do know about these materials is that the mechanism for superconductivity is fundamentally different than for conventional BCS [2] superconductors. Essential to the successful development of a microscopic theory for unconventional superconductors is the knowledge of the symmetry of the superconducting order parameter (SOP) or condensate wave function that describes the pairing of electrons in the superconductive state. By unconventional, we mean a state with an SOP that has a symmetry in momentum space different from that of the isotropic *s*-wave Cooper pair state that is believed to describe the conventional superconductors. Much of the recent attention has been focused on particular states with $d_{x^2-y^2}$ (*d*)-wave [3], d_{xy} -wave, *p*-wave symmetry and also imaginary combinations like $s+id$, $d+id_{xy}$ [4] all being highly anisotropic and characterized by a sign change in the SOP. These types of symmetry are implied by a number of possible superconducting pairing mechanisms, particularly those involving magnetic interactions that are known to be important in the cuprates.

Whereas for hole doped cuprates the *d*-wave symmetry has been established, for electron doped cuprates $R_{2-x}Ce_xCuO_4$ (RCCO with $R = La, Nd, Pr, Sm, Eu$) where carriers are predominantly electrons the issue remains controversial. Another important issue is the determination of the SOP in other recently discovered presumably unconventional superconductors. One example is the natural superconductor/ferromagnet hybrid $RuSr_2GdCu_2O_8$, an exotic superconductor exhibiting the coexistence of superconductivity and ferromagnetism. The search for unconventional superconductivity received a significant boost from recent phase-sensitive experiments [5] that established *p*-wave symmetry in the Sr_2RuO_4 compound. In addition there is strong evidence that plutonium compound $PuCoGa_5$ [6] as well as heavy fermions $CeRhIn_5$ [7] are also unconventional superconductors. Thus, unconventional superconductivity appears to be a much more wide spread phenomenon among superconductors having very different crystal structure, as well as, chemical and physical properties, as previously believed. It should therefore not any more be exclusively related to the CuO planes that characterizes the structure of cuprates, but, to a somewhat more general common feature of various superconductors that has to be identified and understood. That appears to be one of the most challenging unsolved problems in condensed matter physics.

In this paper, I will review some of the most recent developments in the field of unconventional superconductivity in cuprates. Several topics will be covered:

section 2: the SOP in electron doped cuprates;

section 3: the current-phase relation in hole doped cuprate junctions;

section 4: the upper critical field in electron doped cuprates, i.e., the value of the applied external magnetic field that completely suppresses superconductivity.

2 Unconventional superconductivity in cuprates

There are several well established methods to determine the SOP in unconventional superconductors. Here we concentrate on one of the most powerful ones. It consists of looking into unconventional SOP-induced



anomalies in the electric transport measurements of superconducting interferometers. The basic concept of such experiments is to create an interferometer consisting of a closed superconducting ring incorporating two Josephson junctions connected in parallel. The interferometer is specially designed to probe the phase of the pair wave function in specific directions of interest. To test the pairing symmetry of the SOP of an electron doped cuprate, namely, the $\text{La}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$, in [8], such an interferometer has been fabricated and its electric transport properties have been measured. In particular, the Josephson junction critical current I_c as a function of a magnetic field B applied perpendicular to the planar thin film interferometers (see Fig. 1) has been measured. I_c is defined as the maximum value of the supercurrent in a Josephson junction, i.e., the maximum current that flows with no resistance. The interferometers were constructed as follow. A $0.5\text{ }\mu\text{m}$ thick c-axis oriented $\text{La}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ thin film was epitaxially grown on a tetracrystal SrTiO_3 substrate by molecular-beam epitaxy. The film was near optimal doping with $x = 0.105$ and a critical temperature of about $T_c = 29\text{ K}$. The tetracrystal SrTiO_3 substrate contains three identical 30° [001] tilt symmetric grain boundaries (denoted by 1, 2, and 3 in Fig. 1(a)) that make an angle of 120° with respect to each other. Grain boundary 3 is not optically visible so that it has been represented by red dotted line in Fig. 1(a). Subsequently the film was patterned by standard photolithography and Ar ion milling to form three interferometers photographed in Fig. 1(a). All three interferometers have two junctions of identical width $500\text{ }\mu\text{m}$ and a rectangular hole of width $160\text{ }\mu\text{m}$ and height $300\text{ }\mu\text{m}$. The hole of the central interferometer contains the “tetracrystal point”. The junctions of this interferometer are located at the grain boundaries labelled as “1” and “2”. In the measurements the interferometers are biased with a dc current I and the dc voltage U across the two junctions is recorded. The current has been swept from 0 up to a maximum positive value of about $10\text{ }\mu\text{A}$, then back to 0, then down to a minimum negative value of about $-10\text{ }\mu\text{A}$, and finally back up to 0 again. A family of several hundreds such $I(U)$ sweeps each recorded for different B values between $-0.8\text{ }\mu\text{T}$ and $0.8\text{ }\mu\text{T}$ were then used to extract the $I_c(B)$ characteristic. An anomalous $I_c(B)$ pattern with a central minimum has been measured for the central interferometer, called π -design. This highly unusual result is in high contrast with a Fraunhofer-like pattern, i.e., an $I_c(B)$ curve with a central maximum, that has been obtained for the other two interferometers that are conventional (i.e., they contain no π -junctions). Such a difference can only be explained if assuming that the superconducting order parameter in the optimally doped $\text{La}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ has a predominantly d -wave symmetry schematically represented in Fig. 1(a) with red and white lobes. Another important implication of such an anomalous $I_c(B)$ is that the interferometer measured consists of a so-called π -junction (i.e., a junction with a negative critical current I_c) connected in parallel to a conventional junction (i.e., a junction with a positive critical current I_c). Such π -junctions are ideal for implementation of complementary low dissipative superconducting digital electronics [9].



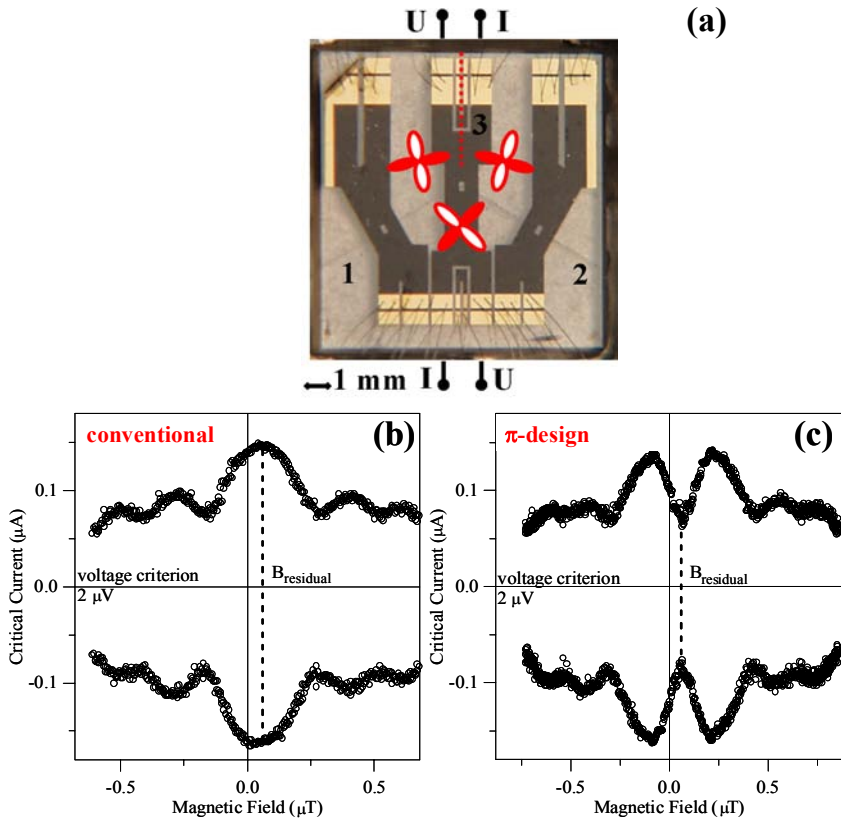


Figure 1: First realization of a π -junction (having a negative Josephson critical current) made of an electron doped cuprate. (a) the photograph of the three interferometers patterned. (b) The two side interferometers have a conventional Fraunhofer-like $I_c(B)$ pattern. (c) The central interferometer (π -design) consisting of a π -junction in parallel to a conventional one has an anomalous $I_c(B)$ with a central minimum.

3 Current-phase relation of thin film cuprate Josephson junctions

Josephson junctions formed between two superconductors of which at least one is an unconventional one, or so called, a d -wave superconductor are very attractive candidates for the implementation of superconducting qubits in quantum computation [10] or π -junctions in Josephson (low-dissipative) digital circuits [9]. In addition, arrays of such d -wave junctions are of interest as model systems for studying magnetic phenomena—including frustration effects—in Ising antiferromagnets [11]. Moreover, d -wave junctions are among the most



reliable tools to investigate the unconventional SOP in these materials [3]. The physics of *d*-wave junctions, however, is not fully understood. A key element, namely the knowledge of the current-phase relation (CPR) of the Josephson current remains unsettled [12]. It has been predicted [13–17] that zero-energy Andreev states (ZES) formed at the *d*-wave junctions interface are expected to induce a second harmonic Josephson current J_2 in the CPR. For various qubit concepts this J_2 is essential, as a superconducting qubit based on J_2 will have an operating point intrinsically stable and protected against the environmental noise, which will reduce decoherence [18]. Whereas it is now well understood that *d*-wave induces formation of ZES states [3] the existence of J_2 has been an intriguing unconfirmed prediction for a long time. Recently, this issue has been addressed [19] for Josephson junctions made between the *d*-wave $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and the conventional s-wave Nb. There the authors first provided evidence for the formation of ZES and, secondly they searched for the existence of J_2 . If it exists, this second harmonic component is expected [13–17] to be highly anisotropic as we change the tunneling orientation in the *ab* plane reaching its maximum for tunneling close to [110] direction and its minimum for the [100] or [010] directions.

J_2 is expected [7–11] to produce a deviation from the standard sinusoidal CPR ($J_c(\varphi) = J_{c1} \sin(\varphi)$) of the Josephson current density J_c [6]

$$J_c(\varphi) = J_1 + J_2 = J_{c1} \sin(\varphi) + J_{c2} \sin(2\varphi) \quad (1).$$

Here φ is the phase difference across the junction. For a purely *d*-wave order parameter as we increase θ (the angle in the *ab* plane between the normal to the junction interface and the [100] crystal axis) starting from 0, J_2 is expected to increase monotonically up to $\theta = 45^\circ$ which corresponds to tunneling into the [110] direction. It should then decrease monotonically as we further increase θ from 45° to 90° , corresponding to tunneling into the [010] direction. In particular, for tunneling close to the [110] direction, where J_1 vanishes due to the nodes of the *d*-wave order parameter, J_2 will dominate the CPR.

In [19] the authors prepared thin film ramp-edge junctions between 170-nm untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and 150-nm Nb using a 30-nm Au barrier. The use of untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films is especially important because otherwise J_2 may be strongly suppressed due to excessive diffusive scattering at the twin boundaries. Also, J_2 may be averaged out for a badly defined nodal orientation in a twinned film. The junctions are fabricated on the same chip, and the angle θ with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystal *b*-axis is varied in units of 5 degrees, so that tunnelling can be probed in $360^\circ/5^\circ = 72$ different directions in the *ab* plane (see Fig. 2). The growth of untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films [20], as well as detailed order parameter issues [21], and ZES-assisted quasiparticle tunneling [22] in these particular junctions were reported elsewhere. All 72 junctions were 4 μm wide. Quasiparticle conductance spectra $G(V)$ of all 72 junctions were measured for a wide range of temperatures T (4.2–77 K) and magnetic fields B (0–7 T). It was found that all observed features, in particular a well defined zero-bias conductance peak (ZBCP), were consistent with a convolution of density of states with broadened ZES formed at the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ /Au/Nb junction interfaces [19]. Here a summary will be given of some of the most important



findings from a qualitative point of view. The authors observed the same qualitative picture independent of the tunneling direction (see Fig. 3). At 4.2 K and a small B of 0.01 T, which is large enough to completely suppress the dc Josephson current well-defined Nb coherence peaks and a dip at the center of a broadened zero-bias conductance peak (ZBCP) were observed. As superconductivity is suppressed in Nb, by increasing T from 4.2 K up to slightly below the critical temperature of Nb ($T_{c,Nb} \approx 9.1$ K) or B from 0.1 T up to slightly below the second critical field of Nb ($B_{c2,Nb} \approx 1.15$ T) the Nb coherence peaks become suppressed and the ZBCP-presence gradually manifests. Close to the critical temperature $T_{c,Nb}$ (see Fig. 3(a)) or to 0.4 T (see Fig. 3(b)) no trace is left of the Nb coherence peaks, while the ZBCP is fully developed. That provides clear evidence for the formation of ZES. Increasing T or B even further (from $T_{c,Nb}$ up to 77 K, or B from 0.4 T to $B_{c2,Nb}$ and further to 7 T), however, a significant difference appears between the T and B dependence of $G(V)$. The ZBCP (its amplitude and width) is essentially not affected by an increase of B , while by increasing T the ZBCP becomes strongly suppressed and widens. In particular, we could not observe any trace of a ZBCP at 77 K. The remarkable insensitivity of $G(V)$ to the tunneling direction strongly suggests the existence of ZES in all tunneling orientations in the ab plane, including the $[100]$ and $[010]$ directions. The authors believe this is a signature of diffusive reflection or scattering, possibly due to microscopic interface roughness.

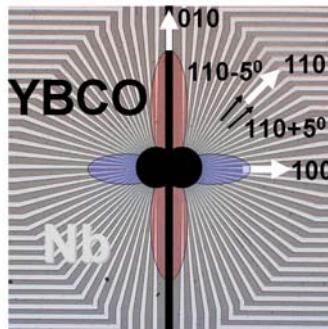


Figure 2: Topview photograph of the untwinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}/\text{Au}/\text{Nb}$ ramp-type junction layout. The YBCO base electrode (in black) is contacted by a Au barrier (not shown) and a Nb counterelectrode (light-gray). Tunneling is tested in 72 different directions in the ab plane. The arrows indicate some of those tunneling directions.

Now that there is solid evidence of ZES formation, then what about J_2 : does it exists, can it be measured? A powerful experiment on J_2 concerns Shapiro steps. It is well known that if the CPR is purely sinusoidal ($J_{c2} = 0$ in Eq. (1)) microwave radiation of frequency f will induce Shapiro steps at integer n multiples of the voltage V_0 , satisfying the Josephson voltage-frequency relation

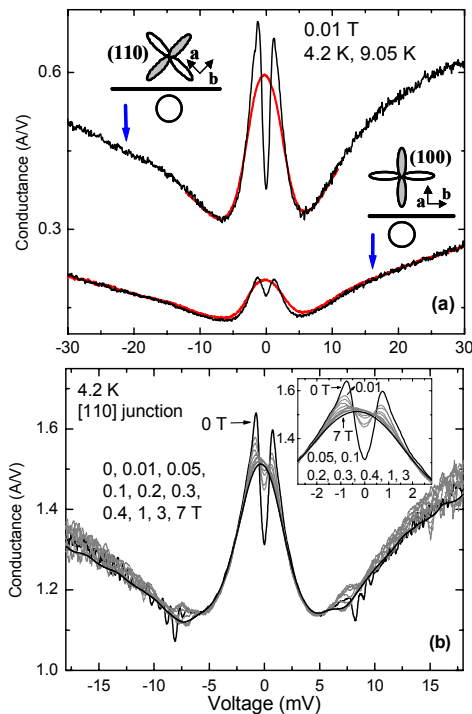


Figure 3: (a) Conductance spectra of 2 junctions with different tunneling directions (100 and 110) at 4.2 K (in red) and just below $T_{c,Nb}$. Insets show schematically the isotropic s-wave SOP in Nb and the highly anisotropic d-wave SOP in the cuprate, as well as, the orientation of the a and b axis of the unit cell. (b) Conductance spectra of a [110]-oriented junction for ten different magnetic field values from 0 T (in black) up to 7 T (in black). The inset shows details of the low voltage spectra.

$f/V_0=0.486$ GHz/ μ V. If J_{c2} is finite also *half-integer* Shapiro steps should appear at multiples of $V_0/2$ [23–25]. If half-integer Shapiro steps are not observed then the presence of a significant J_2 in the CPR can be ruled out. In [19] a very detailed search was performed in the entire frequency range where integer Shapiro steps could be observed. A carefully examination was done of every 10 MHz frequency interval within the 1-20 GHz region. Such an approach was repeated for all junctions investigated. Typical sets of current-voltage characteristics are shown in Figs.4(a)-4(c) for three junctions: [100], [110] and [110]-5°. Well-defined integer Shapiro steps in accordance with the theoretical expectations are clearly visible. Pronounced integer Shapiro steps up to $n=21$ (as

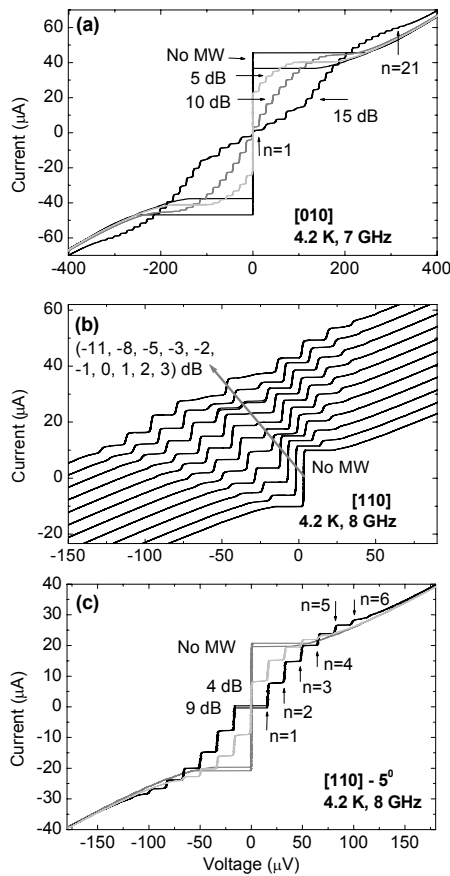


Figure 4: Integer Shapiro steps (indicated by vertical arrows) at 4.2 K of [010], [110], and [110]-5°-oriented junctions at different microwave amplitudes. For clarity, the current-voltage characteristics in (b) are shifted in diagonal direction shown by the gray line.

in Fig. 4(a)) or even higher in some cases were detected. However, no trace of half-integer Shapiro steps was found in any of the junctions, although particular attention was given to those microwave amplitudes where the integer Shapiro steps or the I_c vanishes and consequently the half-integer Shapiro steps are expected to be most pronounced. These observations strongly suggest that J_2 in these junctions is so small (if present at all !) that it cannot be measured. In conclusion J_2 should be completely ignored in Eq.(1) so that the junctions investigated have to be considered as having a pure sinusoidal CPR.



4 Second critical field of thin film cuprate superconductors

Mapping the magnetic field-temperature (B-T) phase diagram of cuprate superconductors is essential for their understanding. Unlike conventional type-II superconductors where the B-T phase diagram consists of the Meissner phase, the Shubnikov phase and the normal state, the phase diagram of cuprates superconductors is extremely complex, exhibiting a variety of vortex phases [26] and also an intriguing pseudogap region [27,28]. The transition between the superconducting state and the normal state, and thus the relation between the superconducting and the pseudogap states, is hard to determine, not only due to the large values of the second critical field B_{c2} in the case of hole-doped cuprates, but also because of the presence of vortex liquid phases as well as strong fluctuation effects, leading to nonzero resistance well below B_{c2} . For the electron-doped cuprates $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ resistive measurements [29] or the vortex Nernst signal [30–32] revealed B_{c2} (at temperature 0 K) values in the range of 7–10 T. For $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ an analysis of the vortex pinning strength yielded B_{c2} (at temperature 0 K) of about 9 T [33]. However, the various methods applied to determine B_{c2} often yield inconsistent results; see, e.g., the discussion in [29]. In [34] the authors showed that an analysis of ZES causing a zero bias conductance peak (ZBCP) – see Fig. 5 – in the conductance spectra of cuprate grain boundary junctions (GBJs) yields a new lower bound for B_{c2} which is at least a factor of 2.5 above previous estimates. ZES result from the constructive interference of Andreev reflected electron- and hole-like quasiparticles [35]. If the quasiparticles experience a sign change of the superconducting order parameter upon reflection, ZES appear at the Fermi energy, giving rise to the ZBCP [36]. A ZBCP caused by ABS relies on the phase coherence of the elementary excitations above the Cooper pairing ground state. It thus should vanish when the phase coherence is lost, i.e., at the transition between the superconducting state and the normal state. Such ZBCPs thus allow us to determine B_{c2} , or at least to give a reasonable lower bound. Indeed, in [34] it has been shown that in the electron-doped cuprate $\text{La}_{2-x}\text{Ce}_x\text{CuO}_4$ the superconducting state persists to substantially higher magnetic fields than reported previously. Thus, well defined ZBCP have been observed for B field direction both parallel to the c -axis or perpendicular to it (i.e., parallel to the *ab* plane) for a wide range of temperatures from 4.2 K close to the transition temperature from the superconducting state to the normal state [37]. Some typical ZBCP measurements are shown in Fig. 5. The integrated density of states DOS (i.e., the area of the ZBCP) normalized to its value at 0.1 T versus H is shown in the insets of Figs. 5(a) and 5(b). The observed *nonlinear* dependence strongly suggests that the measured ZBCP is due to the formation of ZES at the junction interface. The ZBCP persists for B fields as high as 16 T [34]. A zero temperature extrapolation suggests that B_{c2} (at temperature 0 K) is at least 25 T. Extending superconductivity to such high fields shrinks the region where a pseudogap phase may exist. Such a method allows the investigation of the B-T phase diagram via ZES. It should be applicable to any superconductor where the



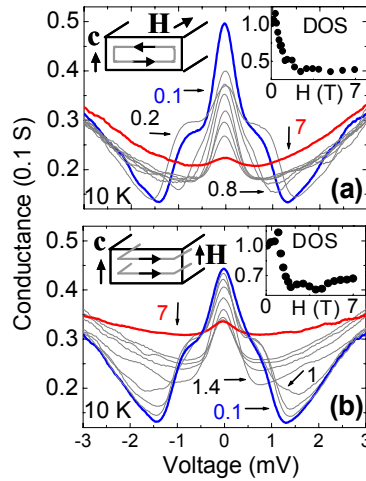


Figure 5: Variation of the $G(V)$ spectra of a junction with magnetic field H parallel to the ab plane (a) or H parallel to the c -axis (b) at a temperature $T = 10$ K. In the insets the junction cross section is shown schematically together with the direction of screening current flow (horizontal arrows). The unspecified values of $\mu_0 H$ are: (a) 1, 2, 2.5, 3 T (b) 0.2, 0.8, 2, 3, 4 T; the numbers labeling the $G(V)$ curves are field values in Tesla. In the insets the integrated density of states DOS normalized to its value at 0.1 T versus H are shown.

SOP changes sign (like for d-wave superconductivity), providing an effective additional tool to explore the superconducting state.

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Section 5

Advanced materials

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Synthesis, characterization and bioactivity evaluation of nano-structured hydroxyapatite

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Abstract

Due to its biocompatibility and bioactivity, hydroxyapatite (HA) has a wide range of applications in medical engineering cases, such as bone repair and bone tissue regeneration. The use of artificial HA with a similar structure and chemical composition to biological apatite could increase the durability of the HA inside the natural hard tissues. The aim of the present work was to synthesis nano-structured HA via different routs, the comparison of their characteristics and enhancement of the bioactivity of HA by controlling its crystallite size and chemical composition. Nano HA was prepared by mechanical activation and sol gel routs. The x-ray diffraction technique (XRD), Fourier transform infra red spectroscopy (FTIR) and transmission electron microscopy (TEM) were used to characterize the HA powder. The synthesized powder was soaked in simulated body fluid (SBF) for various periods of time in order to evaluate its bioresorbability and bioactivity after immersion in SBF. Atomic absorption spectroscopy (AAS) was used to determine the dissolution of calcium ions in the SBF media. Results showed that the prepared HA powder had a nanoscale structure with a size of 29 nm for the powder prepared by mechanical activation and 25 nm for the powder that was prepared by the sol gel method. The ionic dissolution rate of nano-structured powder was higher than conventional HA (with micro scale size) and was similar to biological apatite. It could be concluded that bioactivity behaviour of HA powder is affected by its crystallite size. Using the nano-structured HA powder with less than 50 nm crystallite size, the optimum bioactivity and bioresorbability would be achieved.

Keywords: *nano hydroxyapatite, mechanical activation, sol gel, bioactivity.*



1 Introduction

Bioactive materials, such as hydroxyapatite (HA), can integrate well with living bone tissues by forming spontaneously a biologically active bone-like apatite layer on their surfaces [1–4]. HA shows excellent biocompatibility with hard skin and muscle tissues and can directly bond to the bone [5].

Mechanical activation (MA) as a solid-state reaction has been widely studied as an appropriate technique to produce nano-structured HA [6–9] and carbonate substituted HA [10–12]. Solid-state reactions usually give a stoichiometric and well-crystallized product [6–12]. Sol-gel route, which is one of the wet chemical methods for the preparation of HA nanopowder, has a low fabrication rate but can produce products with high purity and nano-sized particles [13].

It is possible to improve the properties of HA by controlling the parameters of powder, such as particle size, distribution and agglomeration. Nano-structured HA shows suitable bioactivity. Using nano-structured HA can result in more reliable bonding with the host biological bone. Nano-structured HA powders exhibit a greater surface area and are expected to have better bioactivity than coarser crystals. Osteoconductivity, solubility, sinterability and mechanical reliability of the HA can be promoted by controlling its particle size and structural morphology in the order of nanoscale [14–17].

Biological HA contains substituted carbonate groups and presents a nanoscale structure of less than 50 nm in dimension. Based on these facts, artificial carbonated nano-structured HA has bioactivity, bioresorbability and biological properties, closer to biological apatite [18].

The aim of the present work was to produce nano-structured HA with less than 50 nm dimensions by solid state and wet chemically routes and to evaluate and compare their bioactivity with biological apatite.

2 Experimental procedure

The starting materials were dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, Merck >98%, average size: 10 micron) and calcium carbonate (CaCO_3 , Merck >98%, average size: 5 micron). Appropriate amounts of the two starting materials were mixed together at a molar ratio of 3:2. The mixture was loaded into a hardened steel bowl, together with stainless-steel balls of 20 mm in diameter. Mechanical activation (MA) reactions were performed in a planetary ball mill at a rotating speed of 530 rpm and the time in the period of 2–40 hours. The mass ratio of balls to reactants was 20, whereby the overall ball mass was 160 g.

Sol-gel derived HA powder was prepared based on the previous study by the authors [19], and in such a manner that was previously reported [19].

The phase composition of prepared HA powders was analyzed by the x-ray diffraction (XRD) technique using $\text{CuK}\alpha$ radiation generated at 40 kV and 100 mA, at a scan rate of $0.02^\circ/\text{s}$. The crystallite size of the HA powders was determined by using XRD patterns and the Williamson-Hall approach [20]. Fourier transform infrared (FTIR) spectroscopy analysis (Bomem, MB 100) was



carried out to identify the functional groups. The spectrum was recorded in the $4000\text{--}400\text{ cm}^{-1}$ region with 2 cm^{-1} resolution. The transmission electron microscopy (TEM) technique was utilized to evaluate the shape and size of the prepared HA powders.

In vitro bioactivity evaluation of the synthesized HA powders was performed in a simulated body fluid (SBF) media of pH 7.4 at a ratio of 1 mg/ml in a water bath at 37°C . The dissolution amount of calcium ions in the SBF medium were determined by atomic absorption spectrometer (AAS). The changes in the pH of the SBF medium were measured at pre-determined time intervals using a pH meter.

3 Results and discussion

Fig. 1 shows the XRD patterns of the powder mixtures of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 that were subjected to MA for various periods of time (2–40 hours). The 2 hours milled powder showed only the CaCO_3 and $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ phases. By increasing the milling time, the XRD peaks became broader and the intensities decreased. The peak broadening was attributed to crystallite size refinement. This trend continued for up to 12 hours. At this stage, no peak of starting materials could be observed and according to JCPDS No. 09-0432, the only present phase was HA. Further MA led to the formation and growth of nano-structured HA. However, no additional increase in intensity was observed after 12 hours of milling, suggesting that the synthesis reaction was completed.

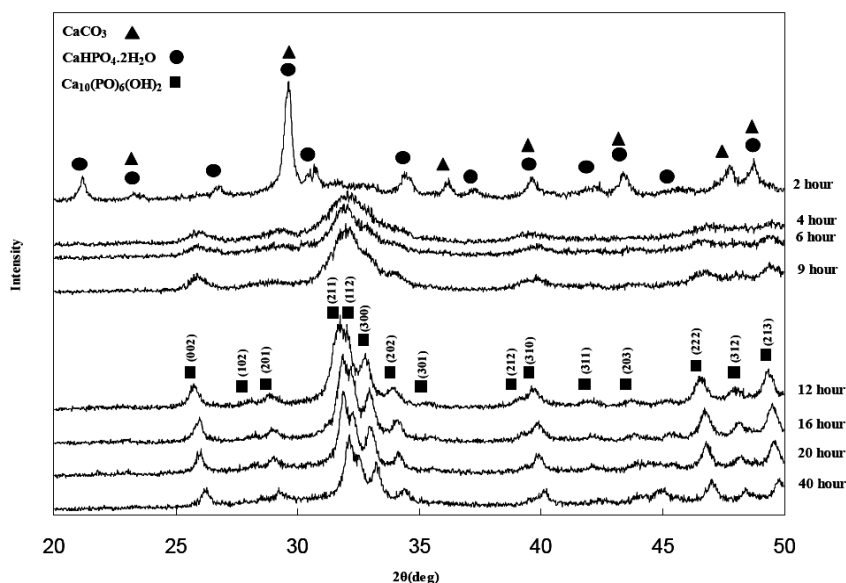


Figure 1: XRD patterns of powder mixtures of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 after ball milling for various periods of time.



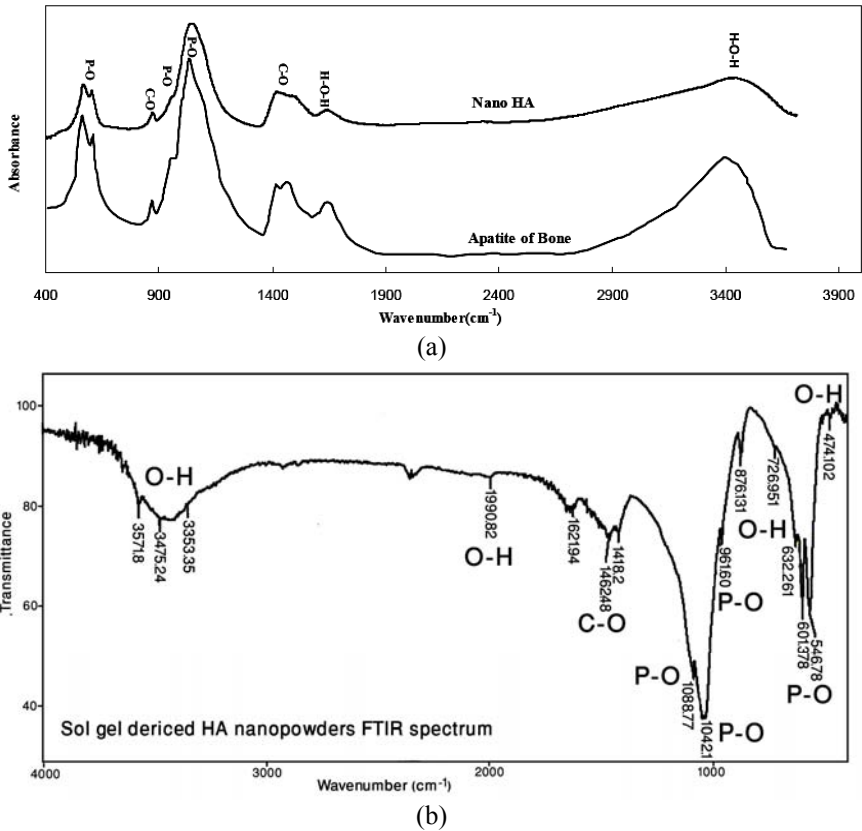


Figure 2: FTIR spectrum of (a) ball milled nano-structured HA and bone apatite; (b) sol-gel derived nano-structured HA.

The average crystallite size of the prepared HA after 12 hours of milling was about 29 nm according to the Williamson-Hall approach.

As was reported in the previous work by the authors, the XRD pattern of sol-gel derived HA indicated that a pure crystallite nature of typical apatite crystal structure with broad diffracted peaks could be obtained without any extraneous phases [19]. The average crystallite size of sol-gel derived HA was about 25 nm according to the Williamson-Hall approach. Controlling the process parameters could make the crystallite size of products in MA and sol-gel routs similar.

Fig. 2(a) shows the FTIR spectroscopy of nano-structured HA synthesized by 12 hours MA and also the biological apatite of bone. The FTIR spectrum showed all the characteristic peaks of pure HA and additionally the characteristic peak of the CO_3^{2-} group that appeared at 873 cm^{-1} , 1454 cm^{-1} and 1769 cm^{-1} . Bone apatite also contains substituted carbonate ions and has a similar FTIR pattern [21].



The FTIR spectrum of sol-gel derived HA is also shown in Fig. 2(b), indicating all characteristic peaks of pure and stoichiometric HA. The characteristic bands from inorganic carbonate ion ($1465\text{--}1415\text{ cm}^{-1}$ and 876 cm^{-1}) are also present.

The bone contains carbonated HA having 4–6% carbonate by weight [22]. A common method for determining the type of carbonate substitution is to examine the positions of carbonate bands observed in FTIR spectra. Fig. 2 shows that carbonated HA were achieved by using both sol-gel and MA processes. As indicated earlier by Emerson and Fischer [23] and Elliott et al. [24], the place of carbonate group in FTIR spectrum in Fig. 2 is located in B type carbonated HA. In B type carbonate HA, phosphate group is replaced by carbonate groups.

Fig. 3(a) shows TEM image of 12 hours ball milled powders. The prepared HA powder has average crystallite size close to the size determined by Williamson-Hall calculation. TEM image shows high agglomerated powder with less than 50 nm crystallite size. Agglomeration was occurred because of high surface energy of ball milled HA powder. The morphological shape and size of sol-gel derived HA is also shown in Fig. 3(b). The sizes of the particles are in the nano scale region with a mean crystallite size of 25 nm in diameter. Furthermore, HA particles are not agglomerated and are mono dispersive. These differences between two types of process were shown in other studies [25, 26]. However, nano-structured powder with particle size of less than 50 nm could be obtained by both processes.

Results showed that nano-structured carbonated HA was produced by MA and sol-gel processes. In comparison with other researches [25–27], nano-structured HA with crystallite size less than 50 nm could be prepared and the sol-gel process that was used in this study, did not need any catalyst and pH control.

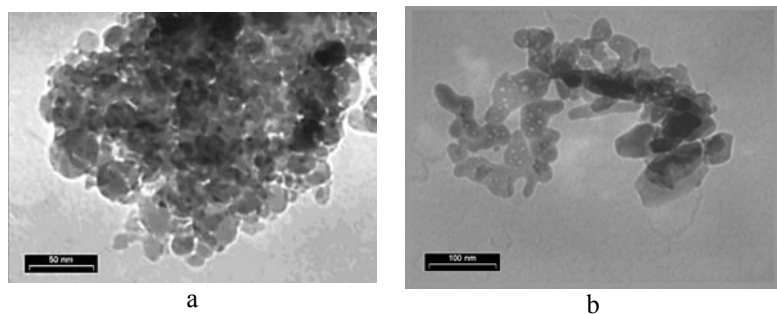


Figure 3: TEM micrograph of nano-structured HA powder produced by; (a) MA; and (b) sol-gel processes.

Fig. 4 (a) shows the trend of releasing of calcium ions from nano-structured HA into SBF. More calcium ions were released from the nano-structured HA as compared with conventional HA (Con. HA). The amount of calcium release from the nano-structured HA corroborated well with the calcium release pattern of biological apatite [28]. The ionic dissolution rate of ball milled nano-

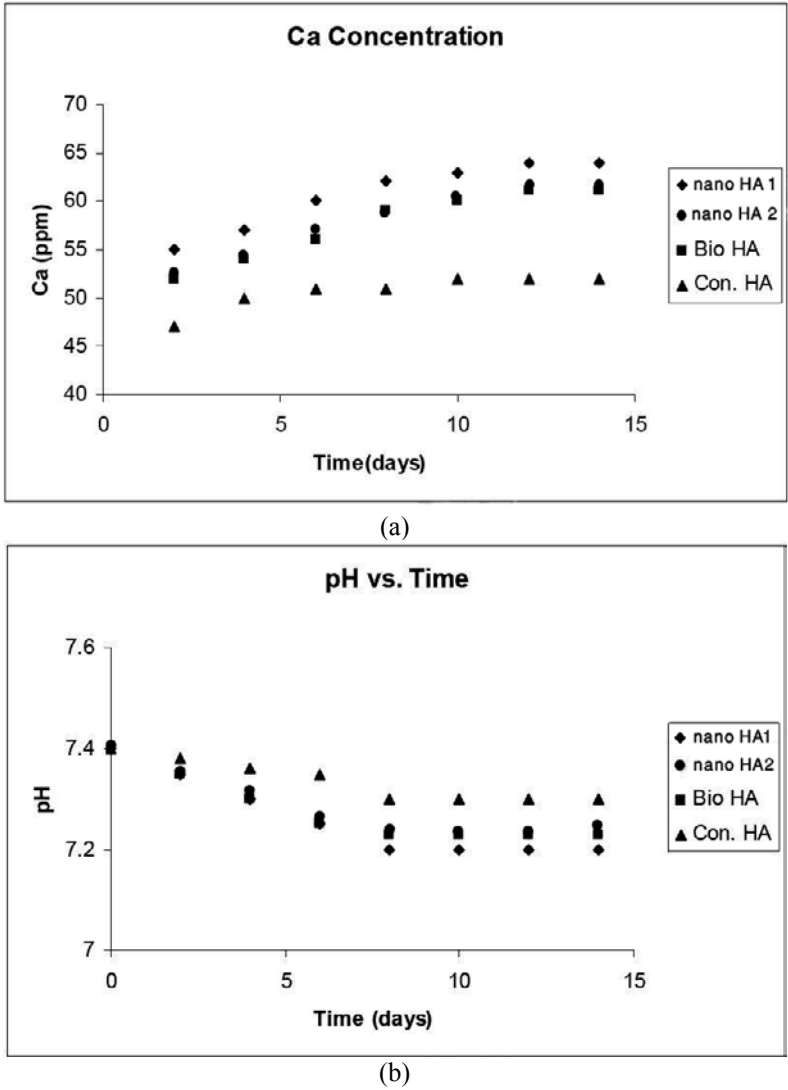


Figure 4: (a) Release of calcium ions from sol-gel derived nano-structured HA (nano HA1), ball milled nano-structured HA (nano HA2), biological HA (Bio HA) and conventional HA (Con. HA). (b) The changes of pH versus time for nano HA1, nano HA2, Bio HA, and Con. HA.

structured HA (nano HA 2) is much similar to that of sol-gel derived nano-structured HA (nano HA 1) and biological HA (Bio. HA). As the solubility is highly sensitive to the structural and chemical compositions of the apatite, the crystallite size is an essential key factor for in vitro behaviour of HA.



There is a little difference between the ionic dissolution rate of nano HA 1 and nano HA 2. This is because of agglomeration of ball milled powder. Surface area is one of the most effective factors on ion releasing. Sol-gel derived HA contains nano scale individual particles that make its surface area higher than ball milled HA.

Fig. 4 (b) shows a graph of the changes of pH versus time which illustrates the resorbability of nano HA 1 and nano HA 2. The graph also shows the variation of pH versus time for a Con. HA and, Bio. HA for comparison. The pH changes of the Con. HA were found to be insignificant variation trend as it was not resorbed in SBF medium which indicates its physiological stability during the period of study. The nano HA 1 showed drastic pH changes, suggesting that it dissolves much faster than Con. HA. The pH value depends on solubility or resorbability of the HA. As the pH decreases, the solubility increases. Accordingly, it is clear from the Fig. 4 (b) that the rate of bioresorbability of the prepared nano-structured HA is higher than the rate of bioresorbability of the Con. HA and is similar to Bio. HA.

Based on the type of medical application, bioactivity of the HA can be controlled by its crystallite size. Due to the presence of substituted carbonate groups and nanoscale structure, prepared HA powder shows the similar bioactivity and bioresorbability properties to biological apatite and could be used near the hard tissues [29–31]. Using such as nano-structured HA can improve the host/implant reactions in biomedical applications.

4 Conclusion

Carbonated nano-structured HA with crystallite size less than 50 nm was prepared by mechanical activation and sol-gel processes. Prepared carbonated nano-structured HA showed similar bioactivity properties to biological apatite. Bioactivity of nano-structured HA was affected by its crystallite size and was independent to the type of preparing routs. Controlling the crystallite size of HA is the most effective factor on bioactivity behaviour.

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Evaluation of ABS patterns produced from FDM for investment casting process

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Abstract

The paper presents the investigation of the Acrylonitrile Butadiene Styrene (ABS) pattern produced from Fused Deposition Modeling (FDM) for use as a pattern for an investment casting process. The investigations were carried out to establish the physical and collapsibility characteristics of an H-shape pattern produced from two different construction methods, i.e. hollow and solid, using rapid prototyping FDM2000 machine. Surface roughness, dimensional accuracy and distortion were evaluated to establish the physical characteristics of the pattern constructed. Results on surface roughness showed no significant variation between hollow and solid constructed patterns. As for dimensional accuracy, hollow patterns produced better accuracy compared to solid patterns. However, the result on distortion shows that hollow constructed patterns experienced 33.11% higher than solid constructed patterns. For collapsibility investigation, shell investment casting mould built from the two different pattern construction methods were fired to a temperature ranging from 300°C to 600°C. The moulds were weighted at a predetermine temperature intervals to establish the collapsibility characteristic of the patterns. ABS (P400) was found feasible to be used as an investment casting pattern material. Hollow pattern construction proved to be more viable than solid pattern construction in terms of dimensional accuracy, mould cleanliness, pattern collapsibility and no mould cracking at all temperatures.

Keywords: ABS, FDM, investment casting.



1 Introduction

Investment casting process (IC) is a metal casting technique capable of providing an economical means of mass production components with complex features such as thin walls, undercut contours and inaccessible spaces which are difficult or impossible to produce using other fabrication methods (Beeley [3]). Despite the wide range of applications in many industries, the standard (conventional) IC process practice in modern foundries has its drawbacks. High tooling costs and lengthy lead times are associated with the fabrication of metal moulds required for producing the sacrificial wax patterns used in IC (Sachs *et al.* [11]). The high tooling costs involved in conventional IC results in cost justification problems when small numbers of castings are required.

Rapid prototyping (RP) techniques are fast becoming standard tools in the product design and manufacturing industries. With the capability of rapidly fabricating 3D physical objects, RP has become an indispensable tool employed for shortening new product design and development time cycles (Hilton and Jacobs [7], Chua and Leong [5], Wohlers [13]). RP techniques are unlimited either by the geometry or by the complexity of the parts to be fabricated.

In addition, RP techniques involve no tooling or fixtures, resulting in simpler set up, lower overhead cost and shorter production lead times compared to other fabrication methods. With RP, parts that were previously impossible or extremely costly and time-consuming to fabricate can be built with ease.

The application of RP-fabricated patterns as substitutes for the traditional wax patterns employed in IC stems from the fact that RP materials can be melted and burned out from the ceramic shell (ceramic shell casting) without damaging it (Beaman *et al.* [2]). Most commercialized RP techniques are capable of producing such patterns that can be used directly in IC.

ABS plastics are a family of opaque thermoplastic resins formed by copolymerizing acrylonitrile, butadiene, and styrene (ABS) monomers. ABS plastics are primarily notable for especially high impact strengths coupled with high rigidity or modulus. Consisting of particles of a rubberlike toughener suspended in a continuous phase of styreneacrylonitrile (SAN) copolymer, ABS resins are hard, rigid, and tough, even at low temperatures. ABS parts are strong and able to withstand the rigors of transportation. In addition, the surface finish of ABS parts is proved to be far better than RP wax. On the contrary, the previous RP wax produced patterns are very fragile, thus transportation within foundry could yield multiple parts. Besides, the softening point of RP wax is as low as 77°C, which can be reached in the hot sun.

The study was aimed at evaluating the physical and collapsibility characteristics of the Acrylonitrile-butadiene-styrene (ABS) P400 produced from a commercial fused deposition modeling (FDM) model FDM2000. Surface quality, dimensional accuracy, distortion, and collapsibility characteristics were compared between solid and hollow constructed pattern.



1.1 Procedure

Four H-shape specimens from each construction method; solid and hollow, were produced using rapid prototyping FDM2000 machine. The specimens were designated as S and H for solid and hollow patterns respectively. The patterns were evaluated with respect to their dimensions, surface roughness and distortion. The patterns were then used to build ceramic shell moulds before being burned at temperatures between 300°C and 600°C.

1.1.1 Specimens preparation

The H-shape specimen (Figure 1) were designed taking into consideration the

- Complexity of the shape for the easy removal of the ABS pattern from the mould;
- Complexity of features, which can distort the shape easily; so that the variation between solid and hollow pattern can be compared.

AutoCAD 2005[®] software was used to produce a 3D CAD model for the H-shape specimen as shown in Figure 1. It was then transferred to the intermediate software (*QuickSlice*[®]) for process setting. From 3D CAD, the file was converted into Stereolithography (STL) file format before being sent to the FDM machine for fabrication.

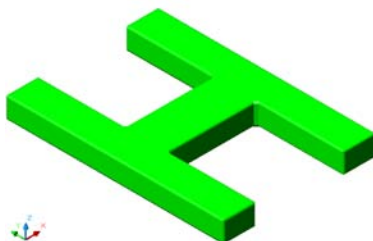


Figure 1: A 3D CAD H-shape specimen model produced from *AutoCAD 2005*[®] software.

In general the CAD parameters used to build the solid and hollow H-shape specimens were the same. However, modifications were made on the air gap and raster angle to create differences between solid and hollow internal feature. The internal feature of hollow specimen consists of large air gaps with 45°/-45° raster angle whilst 0 mm air gaps and 0° of raster angle for solid specimen (Lee *et al.* 2005). The option for producing hollow pattern can be set by applying a “Fast mode” option offered by *QuickSlice*[®] software. Similarly no “fast mode” option could be set for the solid specimen. Figures 2(a) and (b) show the H-shape solid and hollow specimens respectively. The FDM process parameters for both types of specimen are shown in Table 1.

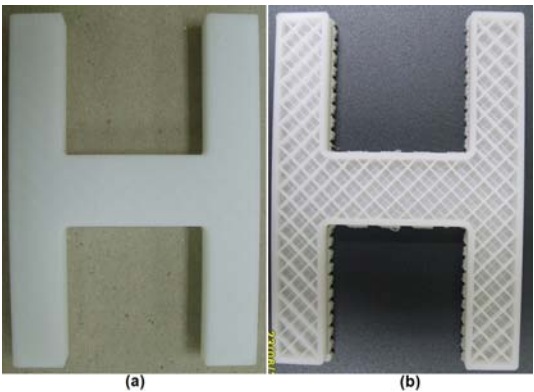


Figure 2: The H-shape specimens used in the investigation (a) solid construction (b) hollow construction.

Table 1: FDM2000 setting parameters.

Setting Parameters	Value
Nozzle tip size	0.0016 in
Raster Angle	45°/0°
Air gap	45/0 mm
Slice thickness	0.2540 mm
Wipe tip	All
Support thickness	10 layers
Support style	Sparse
Liquefier temperature	265°C
Envelope temperature	70°C

1.1.2 Measurement of surface roughness (SR)

The surface roughness measurement on the ABS patterns was made by using a Mitutoyo FORMTRACER CS-5000 with cut-off value (*Lc*) of 0.8 mm. The *FORTRACER*® software was directly connected to the machine that analyzes and provides the value of surface roughness measured. A total of 14 surfaces with three measurements on each surface were conducted for each pattern.

1.1.3 Dimensional accuracy (DA) measurement

A total of 26 dimensions were measured. The dimensions were measured using profile projector Mitutoyo PJ-3000 with the accuracy of 1µm.

1.1.4 Measurement of distortion (D)

The degree of distortion was determined by the difference between measurements A and B as shown in Figure 3.

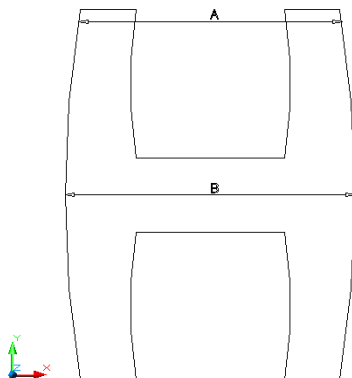


Figure 3: The dimensions measured to determine the degree of distortion in the ABS pattern.

Table 2: The setting condition with holding and cooling time is 1 hour and 12 hours each.

Solid		Hollow	
Specimen	Temp.	Specimen	Temp.
S1	300°C	H1	300°C
S2	400°C	H2	400°C
S3	450°C	H3	450°C
S4	500°C	H4	500°C
Extra S1	550°C	Extra H1	550°C
Extra S2	600°C	Extra H2	600°C

1.1.5 Collapsibility test of ABS H-shape patterns

The ceramic moulds that were built from both solid and hollow patterns were fired at the temperature between 300°C and 600°C (Stratasys Inc. [12]). A digital weighing machine (Precisa XT 6200C) was used to measure the weight loss of specimens as the temperature is increased. The reduction in weight indicates the decomposition or collapsibility volume/weight of the specimen. Prior to burning the moulds were weighed to establish the initial weight of the pattern. The mould was placed in the furnace in an inverted position to ease the flow of the molten pattern material from the mould. The furnace was heated at an average rate of between 2°C/min 10°C/min (British Standards Institution [4]). When the required temperature is attained, the shell moulds; hollow and solid, were placed inside the furnace and left for 1 hour. The moulds were then left to cool for 12 hours inside the furnace before it is weighed. The same procedure was repeated for the other temperatures. Table 2 shows the summarized procedure for the



burning process. The weight difference between before and after the burning process indicates the collapsibility characteristic of the pattern for a particular temperature.

2 Results and discussion

2.1 Surface roughness (SR)

The surface B (interface between ABS and its support material) recorded the highest Ra value for all pattern compared to other surfaces. Solid pattern, S4, recorded the highest Ra value of $32.13\mu\text{m}$. Similar trend was observed on surface A (top surface of ABS pattern), where it recorded comparatively low value of Ra for all pattern. Hollow specimen, H2, was found to record the lowest Ra value of $6.17\mu\text{m}$. The rest of the studied surfaces recorded almost a constant trend for both solid and hollow patterns with Ra values ranges between $17.00\mu\text{m}$ to $19.00\mu\text{m}$. The extreme values were only observed for surface A and B. It is observed that surface A is the final finishing horizontal surface whilst surface B is the surface which is in contact with the support materials whilst other surfaces are side surfaces developed as a result of layer building. The value of these surfaces will depend on the slice thickness which is in this case 0.254mm . Thinner slice layer may reduce the surface Ra value. This is in line with the finding of the previous researcher (Azanizawati [1]) where better surface finish was found to mainly due to the low layer thickness. Surface finish for rapid prototyping pattern was found to be dependent on the lower degrees of the build orientation) and pattern air gap (Pandey *et al.* [9]).

2.2 Dimensional accuracy (DA)

The bar chart in Figure 4 shows the relationship of percentages deviation versus dimensional location for both types of specimen. It can be seen that, there is no sign of typical distribution trend of the measured specimens. In other word, the recorded data revealed that inconsistency of deviation's phenomena had occurred at difference locations. Among the 208 of the dimensional locations, the highest percentage of deviation was found at location 22 on solid specimen S4 with deviation value of 1.23%. Follow by 1.14%, which occurred at location 2 on solid specimen S3. Hollow specimens recorded lower deviation value than solid. It is suggested that the higher percentage of deviations occurred on solid patterns as compared to hollow pattern. The mean average deviation value of hollow patterns was 26.40% lower than the solid patterns. The average deviation value of solid patterns was within $0.356 \pm 0.56\%$ while for hollow pattern was $0.262 \pm 0.33\%$. These phenomena occurred due to internal structures of the patterns. During cooling, the pattern experienced internal stresses in the interior structures which may cause the pattern to shrink. The solid structures experienced higher internal stresses than hollow structures because of the higher density of the internal structure. As a result the final accuracy of the solid patterns was significantly affected as compared to hollow pattern.



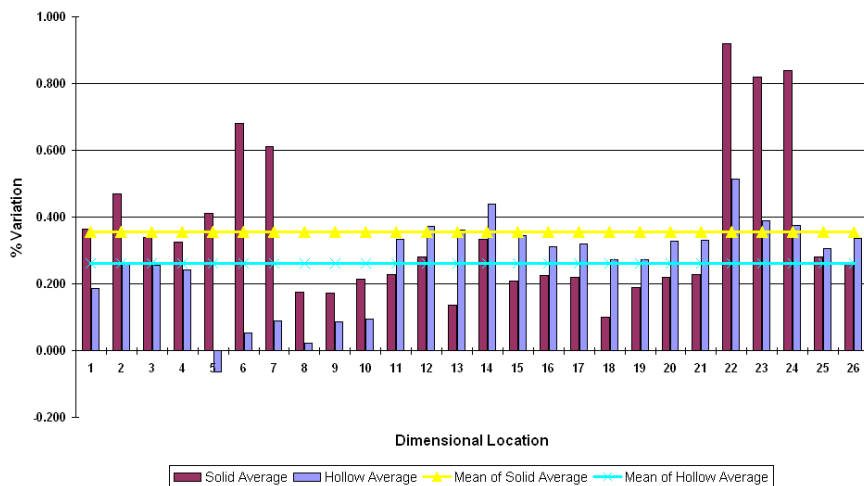


Figure 4: Average value of DA for solid and hollow pattern construction.

2.3 Distortion (D)

The distortions of the ABS patterns obtained from both solid and hollow construction patterns were plotted as shown in Figure 5. Results show that the ABS patterns of hollow construction distorted 33.11% more than solid construction patterns. The variations of hollow patterns were within 0.148 ± 0.108 mm, while those of solid patterns were within 0.099 ± 0.032 mm. It was also observed that the distortion of the ABS (P400) from the current study is less than wax pattern of similar shape reported by other researcher (Prasad *et al.* 2003).

2.4 ABS collapsibility

From the graph plotted in Figure 6, it is observed that 90% of the patterns from both construction types both were burned-off between the temperature of 300°C and 400°C. The patterns were completely burned-off at the temperature of 500°C. However, at that temperature a small amount of ash was observed at the internal wall of the empty shell mould. No ash was visible when the temperature was increased to the temperature above 550°C.

During burning process, cracks were observed on the shell of the solid construction pattern at the burning temperatures of 300°C, 400°C, 450°C, and 500°C. This may be due to the expansion of the ABS pattern when subjected to heating conditions. It is an establish fact that in burning of shell investment casting mould, the different in thermal expansion between the pattern wax and shell would cause the shell to crack. The wax pattern expands and exerts force on the shell which resulted in cracking of the shell mould. The same phenomenon may have happened with ABS pattern under study. Cracks may also develop if

pattern wax is not fully melted and left inside the mould. This may explain why the shell burned at the temperature of 500°C cracks.

On the contrary, at temperatures 550°C and 600°C no crack was observed. Theoretically, at high temperature, pattern material at the interface melted and provides a thin gap at the interface between the pattern material and the shell before the bulk pattern material expands. This will ‘reduce’ the force exerted directly onto the shell, thus avoiding the shell from cracking. For moulds developed from hollow construction pattern, no crack was observed at all temperatures. The thin internal 45° hatching constructions may have melted first compared to the solid surface/interface. This allows the pattern to collapse inwards before the bulk of the material expands, thus avoiding the shell from cracking.

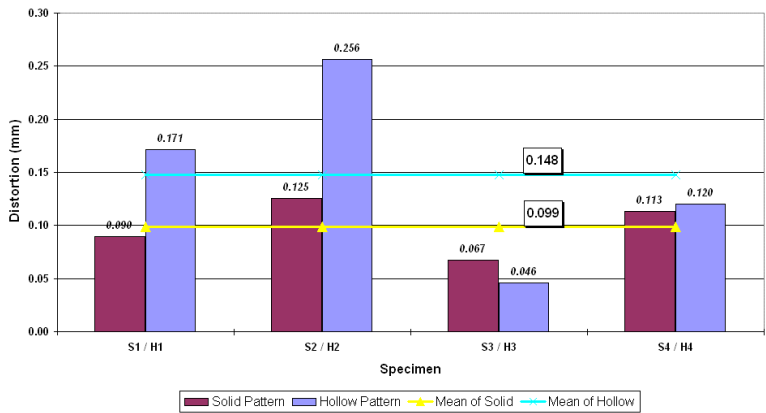


Figure 5: Distortion of solid and hollow construction ABS patterns.

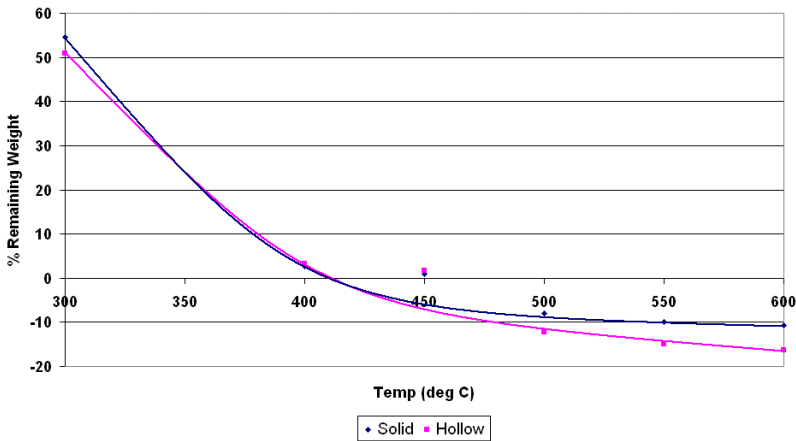


Figure 6: Graph plotted for pattern collapsibility analysis.



3 Conclusion

Based on the investigations conducted, several conclusions can be made:

- i Both hollow and solid pattern constructions produced the same surface roughness at the determine location measured. For both pattern constructions, the upper surface was found to be better in surface quality when compared to the bottom surface which was supported by the support materials. The surface roughness of the side surfaces depend on the slice thickness of each deposited layer.
- ii The hollow pattern proved to have better dimensional accuracy compared to solid pattern construction.
- iii The hollow pattern construction distorted 33.11% more than the solid pattern construction.
- iv Both pattern constructions show similar collapsibility pattern. However, the hollow pattern shows no mould cracking at all burning temperatures.

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Thermoelectric effect in quantum wells and hetero-structure

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Abstract

Thermoelectric effect has attracted much attention recently due to its potential application in cooling and power generation. The related theory (for bulk materials) is not new and the key parameter of interest, i.e., the thermoelectric power TEP or the Seebeck coefficient S can be derived based on charge transport and energy/heat transfer. Over the years, many thermoelectric materials have been identified and exhibited high conversion efficiency. Recent studies on thermoelectric effect in hetero-structures and delta-doped layers have also reported large thermoelectric power and it is of interest to find out if these selectively doped and/or interface layers (sometimes down to 1-2 unit cells) will exhibit the same thermoelectric properties as found in bulk materials. From the perspective of maximizing the thermoelectric power, the question would be whether one ought to favour the use of a quantum well structure or a hetero-structure. This work provides a comparative study on the performance of thermoelectric materials built on these layered structures. Analyses suggest that for a moderately doped surface layer, there is little difference between the 2-dimensional model and the 3-dimensional model. The difference occurs at high doping when a 'metallic' model has to be used. For the quantum wells and the hetero-structure our results indicate that there will be charge migration into the substrate, which may complicate the analyses. In our opinion, this can be the reason for the observed "giant" thermoelectric power found in the $\text{TiO}_2\text{-SrTiO}_3$ hetero-structure.

Keywords: hetero-structure interface, quantum well, sheet charge density, thermoelectric power, charge migration.



1 Introduction

Thermoelectric effect has been studied for a long time and the physics in bulk materials are well established [1, 2]. Because of its potential importance to power generation and cooling, there is much incentive to look for thermoelectric materials that offer higher figure-of-merit. As far as applications are concerned, the key interest has been to find a material with a large thermoelectric power S ; a low thermal conductivity κ , and a large electrical conductivity σ . Most known thermoelectric materials offer limited advantages in one or more aspects of these properties and recently there has been motivation [3–5] to look into materials with novel structures, such as those involving quantum wells and 2-dimensional electron gas layers. In these layered structures, both the charge density and the thermoelectric power are known to be affected by the charge density distribution and careful analyses are needed to better understand how the measured data may be related to the materials properties in the different layers. In this work, we examined the $\text{TiO}_2\text{-SrTiO}_3$ hetero-structure and the $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3/\text{SrTiO}_3$ multiple quantum well structure and developed analytical equations for the thermoelectric power S based on interface properties. Our observations suggest that for the samples under consideration there is little difference in the computed thermoelectric power S between the 2-dimensional and the 3-dimensional model as long as the charge density distribution is properly accounted for. Based on the data analyzed, there is convincing evidence that a ‘metallic’ model will better explain the reported data. In the case of the hetero-structure, extensive charge migration into the substrate appears to be the reason for the observed increase in the thermoelectric power.

2 Theory

The calculations of the average carrier density n_{avg} and the average thermoelectric power S_{avg} in inhomogeneous thermoelectric materials have previously been reported [6]. In essence, the average carrier density n_{avg} and the average thermoelectric power S_{avg} can be evaluated using a lumped circuit model consisting of thin thermoelectric layers of different carrier densities. Analytical expressions for instance have been derived even though some of the integrals cannot be expressed in simple form. For an n-type sample in 1-dimension:

$$n_{\text{avg}} = 1/t \int_0^t n(x) dx \quad (1a)$$

$$S_{\text{avg}} = k/q [(B' - 1/(n_{\text{avg}}t)) \int_0^t n(x) \ln(n(x)) dx] \quad (1b)$$

where t is the sample thickness, $n(x)$ is the charge density, k is the Boltzmann constant, q is the electron charge, and B' is a thermoelectric constant. In principle, Eqn.(1b) may be used to compute S_{avg} with any arbitrary distribution of the charge density provided that the profile is known.

Such an approach, however, will not be appropriate in the case of a hetero-structure with ‘metallic’ properties at the interface and complicated by potential



charge migration into the substrate. A more pragmatic approach is to compute S based on the sheet charge density n_s which can be readily measured. To generate a working model, we consider a rectangular sample under longitudinal thermal stress ΔT in the x -direction. The increase in charge flow due to the temperature difference results in a diffusion current density of the form: $J_D = q \, d(n_s D')/dx$, where q is the electron charge, n_s is the density of the charge sheet, D' is the diffusivity, and dx is incremental position. This will be balanced by a current density of the form: $J_T = n_s q \mu E'$, where μ is the charge mobility, and E' is the electric field due to the thermoelectric voltage ΔV_T . As a result, $d(D' n_s)dx = -q E' (D' n_s)/kT$. Since $dV_T = -E' dx + \Delta(E_C - E_F)$ where $\Delta(E_C - E_F)$ is the positional variation of the Fermi level with respect to the energy band (see for example reference [7] p.248), it can be shown that:

$$S = k/q [\ln(N_C) - \ln(n_s) + (q' + 1) + p'] \quad (2)$$

where N_C is the effective density of states (in 2 dimensions), q' is a scattering parameter and p' is a constant. Since $N_C = m^* kT/\pi \hbar^2$ and $p' = 1$, eqn.(2) leads to:

$$S' = \ln(m^* k/\pi \hbar^2) + \ln(T) - \ln(n_s) + (q' + 2) \quad (3)$$

where $S' = qS/k$, m^* is the density of states effective mass, and $\hbar$ is the reduced Planck constant. For the TiO_2 - SrTiO_3 hetero-structure, we assume $q' = -2.83$ according to [8].

In 3 dimensions, $N_C = 2(2\pi m^* kT/\hbar^2)^{3/2}$ and $p = 3/2$ where $\hbar$ is the Planck constant. In this case, we replace n_s by n_s/x_j , where x_j is the “effective” thickness of the charge sheet and this leads to:

$$S' = \ln(2) + 1.5 \ln(2\pi m_0 k/\hbar^2) + 1.5 \ln(T) - \ln(n_s) + \ln(x_j) + (q' + 5/2) \quad (4)$$

For the quantum well structure made up of $\text{SrTiO}_3/\text{SrTiNbO}_3/\text{SrTiO}_3$ layers for instance, $q' = -2.11$ according to [9].

At high doping, the sample becomes ‘metal-like’ with the Fermi energy $\varepsilon_F = \hbar^2(3\pi^2 n)^{2/3}/2m^*$. S is then given by:

$$S = (\pi k)^2 (1 + r) T / (3q \varepsilon_F) \quad (5)$$

where r is a scattering parameter normally equal to 2.

3 Results

We first examined the validity of the different models through simulations using eqns.(3), (4) and (5). Assuming a charge sheet of thickness 1 nm [10], we plotted in Fig.1 the computed thermoelectric power S as a function of the charge density. As expected, there was little difference between the 2-dimensional model and the 3-dimensional model at the low charge densities. These models however would not be valid at the higher charge densities when the Fermi statistics broke down. To cover this higher charge density range, we included in the figure the values of



S computed using the ‘metallic’ model of eqn.(5). When compared to the thermoelectric data taken from $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ samples [11], our results clearly indicated that the ‘metallic’ model was more accurate in the higher charge density range.

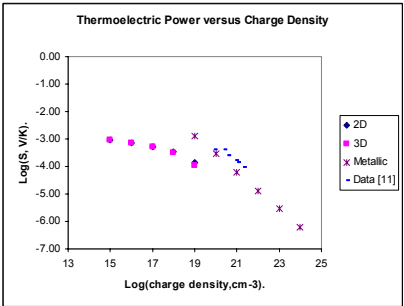


Figure 1: A plot of the computed thermoelectric power S as a function of the charge density.

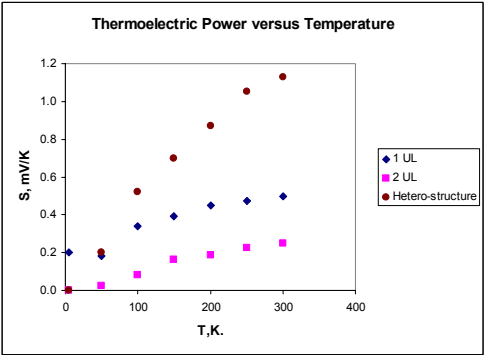
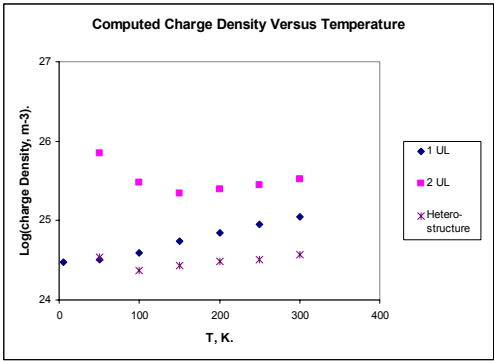


Figure 2: Measured values of S as a function of temperature for the quantum wells and the hetero-structure as reported in [12].

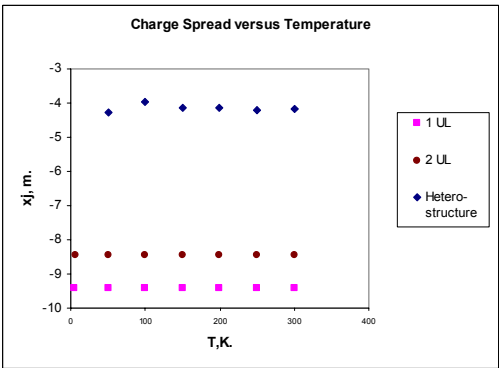
Our next task was to examine the thermoelectric power of quantum wells and hetero-structure as reported in [12]. These quantum wells were sandwiched structures consisting of alternating layers of $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ and SrTiO_3 in the ratio of 1 or 2 ULs (unit layers) of $\text{SrTi}_{0.8}\text{Nb}_{0.2}\text{O}_3$ for every 9 ULs of “intrinsic” SrTiO_3 . The Sr dopant density was $\sim 2.4 \times 10^{27} \text{ m}^{-3}$ and the atoms were reported to be fully ionized. For the quantum wells, our initial calculations of the charge density based on the reported values of S had suggested that the expected charge spread x_j ought to cover the entire SrTiO_3 (barrier) layers. Assuming this to be the case and the charge densities were essentially uniform in these thin charge layers, we used the values of S in Fig.2 to compute the charge density n as a function of temperature. The results are shown in Fig.3(a). As observed, the extent of charge build up increased with increasing temperature suggesting any



charge migration would be diffusion related. The computation of the charge density and charge spread in the $\text{TiO}_2\text{-SrTiO}_3$ hetero-structure was more straightforward as the SrTiO_3 thickness had been known to be 0.5 mm (and this ought to be much larger than x_j). In addition, the sheet resistivity was also available. Using these data together with the known estimates of the mobility values reported in [9], we computed the sheet charge density (from the sheet resistivity data) as well as the “composite” charge densities (computed from the values of S). The ratio of these values would be the estimated charge spread. The results are shown in Fig.3(b).



(a)



(b)

Figure 3: Computed values of (a) charge density and (b) charge spread as a function of temperature in the quantum wells and the hetero-structure as a function of temperature.

As observed, there was major charge spread into the neighbouring layers for all of the samples. For the quantum well sample with 2 ULs and the hetero-



structure sample, there was a dip in the charge density between 100K and 200K. We were unsure if this dip could be due to the “phonon drag” effect commonly observed in samples within this temperature range, or possibly charge re-distribution at the lower temperature. In Fig.3b, we showed the charge spread for the hetero-structure at different temperatures (also shown in the figure are the thickness values of 1 UL and 9 ULs). Charge spread in the hetero-structure was rather intriguing as it extended for tens of microns over a broad temperature range. If this observation turned out to be genuine, then the enhancement in the measured thermoelectric power as reported in [12] could well be explained by such charge spread. The actual spatial re-distribution of charge in the hetero-structure would be of significant interest and had been investigated separately [13].

4 Conclusions

In this work, we have found that the thermoelectric power data reported in [11] for highly doped SrLaTiO_3 samples can be best explained using an equation (eqn.(5)) applicable to metals. Such a finding encouraged us to use the same equation to analyze the thermoelectric power data in quantum wells and hetero-structure as reported in [12]. Our results suggested that for the quantum well samples, there was charge migration from the quantum wells into the neighbouring (barrier) layers resulting in thermoelectric power higher than the case when charge spread was absent. The extent of charge spread was immense in the hetero-structure which could reach a depth of tens of microns. In our opinion, this might be the reason for the observed “giant” thermoelectric power found in the $\text{TiO}_2\text{-SrTiO}_3$ hetero-structure reported in [12].

Acknowledgement

HLK would like to express his appreciation to NSERC Canada for partial financial support.

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Investigation of performance properties of novel composite fire-extinguishing powders based on mineral raw materials

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Abstract

At present the most efficient fire extinguishers are power ones. Fire-extinguishing powders of serial production do not fulfill modern requirements, primarily from the viewpoint of their universal and practical use. It must be noted that most of them contain halogen, and it is established that penetration of halogens into the atmosphere causes a breaking of the ozone layer. The main goal of investigation presented in this paper is development of non-halogen, non toxic, environmentally-friendly, highly-efficient, inexpensive, universal, composite fire-extinguish powders based on domestic mineral raw materials such as clay shale, zeolite and perlite. The proposed method of obtaining composite powders does not require the following expensive chemical processing and modification with halogen-inclusive hydrofobizative additives. Hence, these composite powders will be cheaper (1,5-2 times) than powders of serial production. The raw materials: clay shale, zeolite, perlite were selected according to high operating properties, which are indicative of a reduction of burning processes. The powders must not only be effective during the fire extinguish, but also they must maintain those properties, which decrease the extinguishing effect after small changes in properties. The effectiveness of powders is defined not only according to their dispersity and inhibition ability, but also according to their storage and transportation conditions. These conditions are defined by the exploitation properties of powders. The most important among them are: consolidation and caking, dispersity, tendency of humidity, flow and storage duration. We studied the performance properties of zeolite, perlite and clay shale and composite powders based on such materials and established dependence of tendency to consolidation and caking on dispersity. Accordingly, the dispersity of composite powders was selected in such a way that the tendency of consolidation and caking was minimal. At the same time particle size should be relevant towards the rapid head and destruction, so that we have a homogenous effect and heterogeneous inhibition.

Keywords: environmentally friendly, composite fire extinguishing powders, performance properties, tendency of consolidation and caking, dispersity, tendency of humidity.



1 Introduction

In order to receive composite fire-extinguishing powders the following raw materials are chosen: zeolite, clay shale and perlite. Their mineralogical composition presented in table 1 shows that they generally are of silicate origin and contain alkali and alkali-earth metal silicates, carbonates, oxalates; they contain Fe, Al and alkali metal hydroxides as admixtures, crystallization water which causes the reduction of burning processes.

Table 1: Chemical containing of mineral materials.

Materials	Main components (%)										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	CO ₂	SO ₃	Na ₂ O	K ₂ O	H ₂ O
Clay shale	51.2	13.60	7.40	-	8.06	3.02	10.62	0.9	3.02	2.1	-
Zeolite	62.9	14.45	2.32	0.51	5.67	1.32	-	-	3.73	0.42	2.16
Perlite	73.7	12.5	6.2	-	1.3	-	-	-	1.1	0.6	3.8

On the basis of thermo-gravimetric analysis it has been proved that zeolite, perlite and clay shale are characterized with the extraction of adsorptive and crystallization water and non-burning airs, creation of metal oxides protective film and coke layer. The extracted non-inflammable airs, water vapor and metal oxides in flame zone perform the role of flegmatizator, while in surface zone they cause the production of swelled up layer. The swelled up layer, metal oxides protective film and coke layer create “fire limit” effect, [1].

Fire-extinguishing powders should effectively extinguish fire and for a long time maintain their properties the change of which decreases powder effectiveness. The effectiveness of powder depends not only on inhibition ability but also on the conditions of their storage and transportation. These conditions are determined with powder performance properties the most important being: dispersity, consolidation and caking tendency, moisture content and moistening tendency, fluidity and storage time, [2, 3].

The most unfavorable properties of powder are moistening, consolidation and caking which complicate and cause the powder to lose fire-extinguishing ability. There are several methods of reduction of consolidation and caking but all of them are reduced to the decrease of moisture content in powder or the decrease of dispersive particles amount in powder and of contact surface area. Powder drying at high temperature or using of water adsorption admixtures causing powder hydrofobization belong to these methods. For hydrofobization of fire-extinguishing powders silicate and fluorine silicate compounds, high dispersive SiO₂ modified with chlorsilanes – “aerosile” – are used in serial production powders but it is not universal and its use in most cases is possible in complex with surface active matters, [4–6]. This stipulates that most extinguishing powders of serial production are halogen containing. It is known that penetration



of halogens into the atmosphere causes a breaking of the ozone layer. Therefore, at present, an elaboration of non-halogen, ecologically friendly fire-extinguishing powders is a most important problem. This paper is dedicated mainly to this problem. Proceeding from that requirement we refuse to use the halogen containing additives and selected mineral raw materials: zeolite, perlite and clay shale, which are generally of silicate origin. At the same time, it must be noted that zeolite is characterized with high adsorptive properties and low caking ability; thus zeolite itself acts in composite powders hydrofobizator.

2 Experimental procedure

In order to study performance properties of powders laboratory methods are used:

- powder dispersity, x (%) - granulometric composition, mass concentration of powder remains left on the sieve

$$x = \frac{m_1}{m} \cdot 100$$

where: m_1 - mass of powder remains on the sieve, kg;

m - total mass of remains, kg.

- area of powder specific surface S (sm²/g) is determined with the method of air permeability (a standard device "АДП-3" is used) and is calculated with formula;

$$S = k_{i-j} \frac{A\sqrt{\tau_{i-j}}}{m}$$

where: k_{i-j} - device constant;

A - the parameter which depends on the height of powder layer (h) and temperature of test (t) ($A = A(h;t)$);

τ_{i-j} - time of powder runoff in device column between i and j notches, sec;

m - powder weight mass equal to

$$m = 3.33p$$

where: ρ - powder material density, g/sm³.

- powder fluidity, Q (kg/s) - powder mass consumption in time necessary for its dispersion from test fire extinguisher



$$Q = \frac{m - m_{\tau}}{\tau}$$

where: m - mass of extinguisher before testing, kg;

m_{τ} - mass of extinguisher after testing, kg.

- moisture content and tendency to humidity, W (%) - the ratio of moist absorbed with powder to powder mass

$$W = \frac{m_1 - m}{m} \cdot 100$$

where: m_1 - mass of powder remains after moistening, kg;

m - total mass of remains, kg.

- tendency to consolidation and caking, C (%) - caked mass ratio to powder mass:

$$C = \frac{m_c}{m} \cdot 100$$

where: m_c - mass of formed cakes, kg;

m - powder mass, kg.

It is known the main reason of consolidation and caking is environment humidity and temperature. Powder adsorbs moisture from air, i.e. there happens solid particles solution in condensed water and creation of solid phase saturated solution. With further increase of humidity the solution becomes supersaturated and on contact surface with solid particles there happens solid phase crystallization. Elemental contacts average strength of separate particles depends on structural strength of powder (consolidation and caking), which, in its part, depends on dispersity, setting and consolidation quality of particles, [7, 8]. Thus, for production of fire-extinguishing powders the selection of powder dispersity is to happen with consideration of their performance characteristics.

3 Results and discussion

We studied the dependence of consolidation and caking ability on powder dispersity.

Test researches proved that for different powders even in the case of similar dispersity the areas of specific surfaces are distinctly different. As powder caking is caused with solid phase crystallization on contact surfaces of particles, therefore their caking will also differ. With consideration of this we determined specific surface areas for powders of different dispersity and stated the relation of powder caking and specific surface areas, as shown in table 2 and Fig.1.



Table 2: Performance properties of mineral materials.

Materials	Powder dispersity range, mm	Area of powder specific surface, S (sm ² /g)	Powder fluidity, Q (kg/s)	Moisture content and tendency to humidity, W (%)	Tendency to consolidation and caking, C (%)
Clay shale	N 0.1	7270	-	0.17	50
	N 0.1-0.2	5530	0.17	0.18	7.5
	N 0.2-0.3	4530	0.17	1.2	2.0
Zeolite	N 0.1	5530	-	3.6	25
	N 0.1-0.2	4640	0.16	4.6	0.5
	N 0.2-0.3	4280	0.16	4.6	0
Perlite	N 0.1	2540	-	0.7	18
	N 0.1-0.2	1295	0.14	0.7	0.3
	N 0.2-0.3	1093	0.14	0.8	0

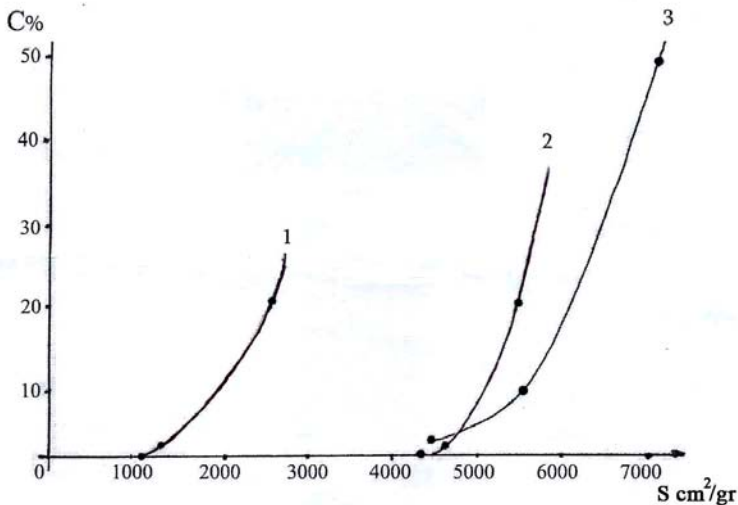


Figure 1: The relation of powder caking and specific surface areas: 1 – zeolite; 2 – perlite; 3– clay shale.

The analysis of the table and graph data proved that at increase of dispersion in highly dispersive powders caking is distinctly increasing while in lower dispersive powder (200μ-300μ) at variation of dispersion caking changes negligibly. Thus, for example, in powders dispersed to 100μ caking is 25-50%. In powders dispersed within 100μ-200μ caking decreases to 1.5-2%, while within 200μ-300μ it drops to 0-0.3%.

Therefore for production of fire-extinguishing powders we chose dispersity 200μ-250μ, when the powder will have high performance characteristics:



(consolidation and caking ability 0.03%), powder will be conveniently supplied to the fire site which is indicated powder runoff characteristics (Table 2). At the same time, size of particles will be convenient for their heating and destruction, or homogenic, as well as, heretogenic effect of fire-extinguishing will take place.

We studied test data of exploitation characteristics of clay shale, zeolite, perlite and their composite powders of 200μ-250μ dispersity. Test results are given in table 3.

Table 3: Performance properties of powders and composite powders.

Powders	Powder dispersity, X (%)	Powder fluidity, Q (kg/s)	Moisture content and tendency to humidity, W (%)	Tendency to consolidation and caking, C (%)
Clay shale	N 0.1–5 N 0.2–80 N 0.3–12	0.17	1.02	2.03
Zeolite	N 0.1–10 N 0.2–75 N 0.3–15	0.16	4.5	0.3
Perlite	N 0.1–10 N 0.2–75 N 0.3–15	0.14	0.7	0
Zeolite + Clay shale	N 0.1–7 N 0.2–75 N 0.3–12	0.16	3.5	1.5
Zeolite + Perlite	N 0.1–10 N 0.2–75 N 0.3–15	0.15	2.2	0.1
Zeolite+ Clay shale + Perlite	N 0.1–7.5 N 0.2–78 N 0.3–14	0.16	1.3	0

The data of the table show that zeolite is characterized with lower ability of consolidation and caking but with comparatively high moisture adsorption compared to perlite and clay shale, while after mixing of clay shale, zeolite and perlite the moisture adsorption ability increases noticeably.

4 Conclusions

Thus, composite powders of zeolite, perlite and clay shale the dispersity of which is 200-250μ are characterized with low moisture adsorption ability, as well as, low consolidation and caking ability or with high performance properties.



Thermogravimetric analysis and pilot tests carried out by us for determination of fire-extinguishing ability of such powders proved that they are characterized with high fire-extinguishing ability.

Thus, on the basis of the researches carried out by us we can conclude that zeolite, perlite and clay shale can be used for production of non-halogen, ecologically clean, composite fire-extinguishing powders, which does not require the following expensive chemical processing and modification with halogen-inclusive hydrofobizative additives and are characterized with high performance properties, as well as, high fire-extinguishing ability.

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Section 6

Cements

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Experimental confirmation of some aspects of the microstructural model of the impedance spectra of porous materials

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Abstract

The use of impedance spectroscopy, IS, has become a useful technique for the microstructural characterisation of cement pastes and mortars. The main advantage is that it is non destructive, but in the other hand the interpretation of the results obtained is not straightforward. A model has been proposed that gives microstructural interpretation of the electrical parameters obtainable from the impedance data. Here is presented a validation of that model, using a model material, which allows controlled changes in the electrolyte conductivity to be monitored by IS. The conductivity of pore solution cannot be controlled in cementitious materials, which makes very difficult to differentiate between changes of pore structure and changes in conductivity. The results presented here show good agreement between predictions of the model, and experimental results.

Keywords: microstructure, impedance spectroscopy, conductivity, modelling.

1 Introduction

The study of the microstructure of concrete and mortar is of great interest for civil engineers because the pore network is directly related to the mechanical properties of this material, and also to the durability.

There are several techniques for determining the pore structure of a material [1], but most of them are destructive and cannot be used in situ. In the 90s



impedance spectroscopy was used to study in a non destructive way the microstructure of cementitious materials [2,3]. This technique can also be used in situ in real structures, and the measurements are fast and easy to perform. The main drawback is the accurate interpretation of the measurements obtained. Nowadays it is well established that in each impedance spectra of cement pastes, mortars and concrete two time constants are present [4]. Proper equivalent electrical circuits involving two time constants have been proposed for the interpretation of the impedance spectra. Those models have been tested in different experimental conditions, with good agreement with the hypothesis established [4]. The relationship between the electrical parameters (resistances and capacitances) and the microstructure of the system (solid paste and aggregates, electrolyte, conductivity, pore dimensions and pore surface) was established in a recent model [5]. That work states that the unreacted solid phase is the responsible of the high frequency capacitance in the impedance spectra, while the low frequency capacitance accounts for the solid-electrolyte interface in the filled pores. The equivalent resistance is dependent on the geometry of pores and also on the conductivity of the inner electrolyte. The model was checked, with good results, with the impedance spectra of different ordinary Portland cement pastes and mortars.

For those materials it is not possible to split the effects of conductivity and pore dimensions. In ordinary Portland cement paste the value of electrolyte conductivity can be assumed to be constant, but in the case of cements with pozzolanic activity the value of the conductivity may vary because of the pozzolanic reactions that consume portlandite to form new C-S-H phases, with the consequent changes in the composition of the electrolyte. Obviously, changes in the pore dimensions also occur because of those new solids formed at pore walls.

The model has already been used to interpret microstructural modifications in pozzolanic cement mortars [5], but the conductivity was supposed to remain constant in the interpretation of those results. So, it seems to be very important to be able to study the influence of the conductivity by itself on the dielectric response with no variation of the pore structure, as a first step.

One of the objectives of this work is to set an experimental procedure involving samples of controlled electrolyte conductivity inside the pores. The second step is to study the influence of just electrolyte conductivity on the impedance spectra of a porous material.

The experimental section is devoted to describe the procedure followed to have a sample with known and controlled conductivity in the pores, and in the results section the impedance data and the simulations are compared.

2 Experimental setup

2.1 Sample preparation

In order to validate the electrical equivalent model taking into account the contribution of the conductivity of pore solution, a commercial ceramic material was chosen. The mineralogical composition of the material was determined to be



cordierite, and the pore structure was also very simple, as will be shown later. The thickness of the sample was of 0.5 cm.

This material mainly was chosen because no leaching of ions from the matrix is expected. All the pores of the material were first saturated with distilled water, using the saturation procedure described in the ASTM standard 1202-97 [7]. After saturation the sample was boiled for 4 hours in distilled water and the conductivity was measured before and at the end of the experiment, with no significant changes in the conductivity, meaning no leaching from the ceramic.

This result meant that the conductivity can be controlled by preparing solutions of different salt concentration, and saturating the empty pores with the chosen solution. The solutions were prepared using KCl (because of the equal mobility of both ions) to get 0.01, 0.05, 0.1 and 0.5 M KCl solutions. The conductivity of each solution was measured, and the results are shown in Figure 1.

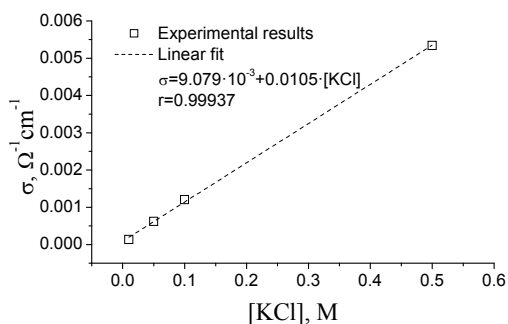


Figure 1: Values of conductivity for the different solutions of KCl used to fill the pores of the ceramic material. Conductivity values were taken at a temperature of 25°C.

The procedure for having the sample with all the pores saturated with a solution of known conductivity is the same procedure as that for saturating the pores with distilled water. The sample used was initially vacuum-dried, to ensure that all the pores are empty. After the time necessary for drying the sample, it was saturated by immersion in the corresponding solution and keeping it in vacuum (about 1mmHg) for 24 hours, so that the solution will fill the pores and remaining air will be released. Impedance spectra were recorded on saturated samples.

After the impedance spectroscopy measurement, and in order to remove the filling solution, the sample was boiled again in distilled water for three hours. The saturation procedure was then restarted using fresh solution. The saturation was made with the solutions in order of increasing concentration, or increasing conductivity. This fact is important because, for a given experiment, even though not all the ions of the preceding experiment were removed, their influence in the current conductivity measurement is negligible.



2.2 Mercury intrusion porosimetry measurement

The pore structure of the material is also a key parameter into the model because the total porosity and the pore size distribution are employed in simulations.

Mercury intrusion porosimetry was used to characterise the pore structure of the material. The equipment employed was an AUTOPORE IV 9500 from Micromeritics. This porosimeter allows pore diameter determination in the range from 5 nm to 0.9 mm. The total porosity measured was 22% in volume, and the pore size distribution is shown in Figure 2. Only one pore family, with centre at about 3900 nm, was found.

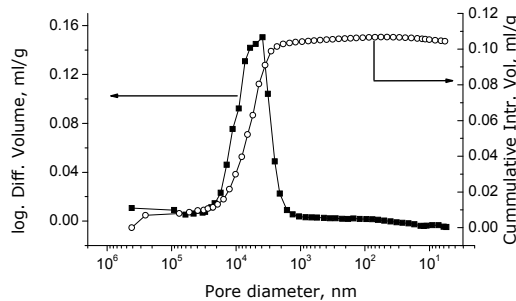


Figure 2: Pore size distribution of the ceramic material used.

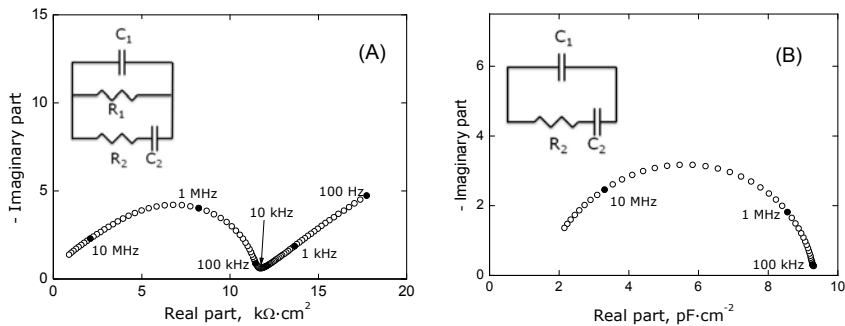


Figure 3: Impedance spectra of the ceramic material used with a solution 0.01M of KCl filling the pores. (A) corresponds to the contacting method, and (B) corresponds to the Cole-Cole representation, using the non contacting method. The equivalent circuits used for the fitting of the impedance spectra are also shown on each figure.

It is well known that only the pore diameter at the open surface of the sample is measured using this technique, as described in the literature [8]. This fact is not important at all. The model includes a major simplification of the pore structure, but it represents in an appropriate way the reality of complex materials [5].



2.3 Impedance spectroscopy measurements

The impedance spectra were obtained in a frequency range from 40 MHz down to 100 Hz. The impedance analyzer used was a HP4194A, which allows measurements in capacitance range from 10^{-14} F to 0.1 F, with a maximum resolution of 10^{-15} F. The electrodes were of flexible graphite, attached to copper plates of 4 cm diameter. Measurements were made both with contact between electrode and sample, and with a foil of polymer interposed between the graphite sheet and the sample, to minimise double layer effects, as explained in previous works [3,4].

The recorded impedance spectra are very similar to those obtained for cementitious materials, and hence the equivalent circuits used for the interpretation are the same. Figure 3 depicts an example of the impedance spectra measured, together with the corresponding equivalent circuit.

The equation corresponding to that circuit is the Havriliak-Negami equation and includes all the electric elements present in the circuit, and the symmetric and asymmetric dispersion factors, α and β .

$$C(f) = C_1 + \frac{C_1}{\left(1 + (2\pi f \cdot R_2 \cdot C_2)^\alpha\right)^\beta} \quad (1)$$

2.4 Simulations

The simulations were performed using MATLAB[®]. The model proposed and the calculations have been reported elsewhere [5]. The model is based in the transmission line model proposed by Park and McDonald [9]. The simulations were performed considering only one pore family, with dispersion around a central value of 4 μ m, approximately the central pore value obtained from MIP for the material employed. The values for the conductivity of the electrolyte were different but within the same range of variation. The total porosity used in the simulations was of 22%, in coincidence with the total porosity of the material. The spectra were obtained under the hypothesis of no contact among electrode and sample. The spectra obtained of the simulations were fitted using the same equivalent circuit. The results of the fitting of the simulations will be compared with the experimental results as a function of the electrolyte conductivity. The scheme of the model proposed for the calculations is shown in [5].

3 Results and discussion

The impedance spectroscopy data were fitted using the equivalent circuits above presented. The results of the fitting as a function of the conductivity are presented here. Initially the results presented correspond to the non contacting method, with the plastic foil between electrode and sample.

The value of the capacitance C_1 remains essentially constant for the experimental results, as expected, and is defined as constant for the simulations. The results for the capacitance associated to the solid phase are shown in Figure 4.



Figure 5 depicts the best fitting values obtained for the low frequency parameters, R_2 and C_2 . In that figure the results predicted by the model are also presented. The measurements were made with four different values of conductivity in the pore network of the material, and the simulations were made using 5 different points in the same range of variation of conductivity. As it can be seen in these figures, for both real measurements and simulations the behaviour of the parameters is the same. The capacitance C_2 has no clear tendency and remains almost constant while the resistance decreases in a double logarithmic way as the conductivity of the solution inside the pores increases.

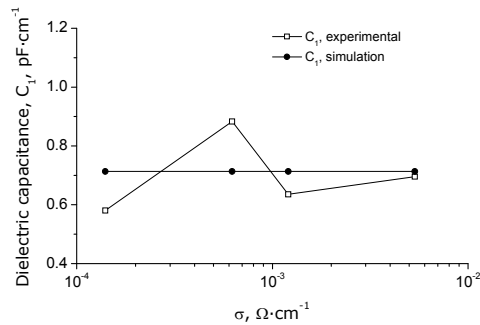


Figure 4: Dielectric capacitance, calculated using the model (solid circles) and obtained from the impedance measurements in the ceramic material, for different values of electrolyte conductivity.

As it can be seen in Figure 6, at low conductivity of the electrolyte the symmetric dispersion factor α is close to 1, while the dominant is the asymmetric dispersion factor β , whose value is about 0.7, meaning asymmetry in the impedance spectra. When the conductivity is increased, the value of the asymmetric dispersion factor tends to 1 (meaning no asymmetry in the impedance spectra) and the value of the symmetric dispersion factor decreases, meaning a more significant symmetrical dispersion in the impedance spectra.

The values of the capacitances C_1 and C_2 remain almost constant with conductivity changes. This result is in agreement with the model predictions. The capacitance C_1 is associated to the solid phase fraction in the material. Changes in the conductivity of the electrolyte do not involve any change in the solid phase. The experimental results as shown in Figure 4 do not show a clear tendency and only show not important changes around a central value. This central value, as expected is the prediction of the model for the capacitance C_1 .

The value of the low frequency capacitance C_2 is associated with the solid-electrolyte interface inside pores. Changes in the surface (due, i.e. to new solids formed at the pore walls) will be clearly reflected by this capacitance [6]. As stated before, no solids were formed in our system, and no part of the ceramic matrix was destroyed, hence no changes are expected in the surface of pore walls and thus C_2 shall remain constant.

One reason that could imply a change in the solid-electrolyte contact surface is salt precipitation at the pore walls during the drying period. The experimental procedure, involving boiling in distilled water for about 3 hours, seems to be good enough to remove every rest of possible salt precipitate inside the pores. Both experimental and simulation data show negligible fluctuations on C_2 capacitance values. These results agree with the physical meaning of this parameter previously stated.

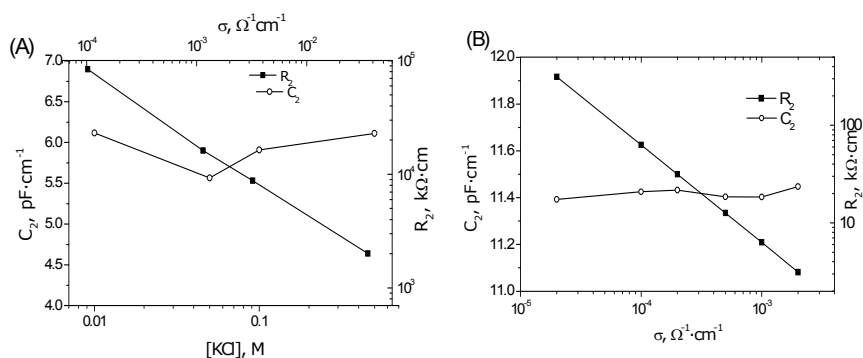


Figure 5: Dependence of the parameters R_2 and C_2 with the conductivity of the electrolyte in the experimental measurements (A) and in the impedance spectra obtained using the theoretical model (B).

The model also could be used to explain the dispersion factors in the dielectric response of the materials. The evolution of these factors with the conductivity value is shown in Figure 6.

The value of the pore resistance changes with the electrolyte conductivity, as expected. This result is obvious because of the inverse relationship between conductivity and resistivity, but it also confirms that the association of this resistance with the electrolyte in the pores is right. The value of the resistance decreases as the value of the conductivity of the electrolyte (or ionic concentration) increases, as depicted in Figure 7. This factor has to be taken into account when dealing with cements with pozzolanic activity, especially when a high portion of clinker is substituted by a material with pozzolanic activity. The pozzolanic reactions may change the conductivity of the electrolyte, and these possible variations should be taken into account in the interpretation of the impedance spectra. The changes in the resistance maybe only attributed to the changes in pore size and this interpretation can be erroneous.

According to the model, R_1 accounts for the connectivity of percolating pores while R_2 non-percolating pores. The interesting point here is the dissimilar dependence with electrolyte concentration between R_1 and R_2 depicted in Figure 7. While R_2 varies in agreement with the conductivity data reported in Figure 5 the slope for R_1 dependence is higher, which suggest the formation of new percolating paths as the electrolyte concentration increases. The associated mechanism can be additional ionic flux due to osmotic pressure.

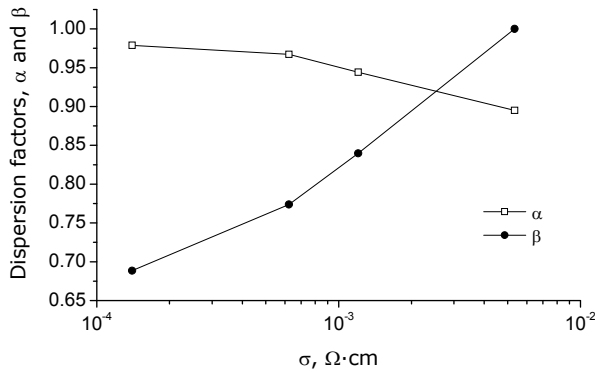


Figure 6: Evolution with conductivity of the symmetric and asymmetric dispersion factors in the impedance spectra of the ceramic material (Eq. 1).

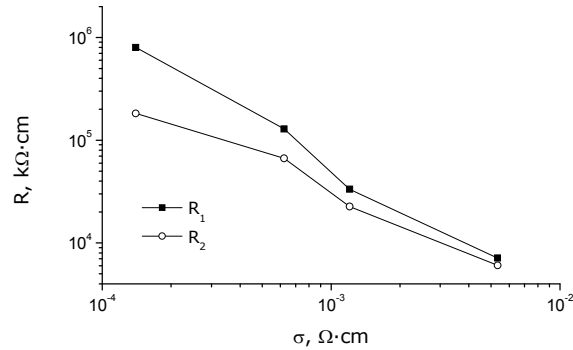


Figure 7: Evolution for different values of conductivity of the resistances R_1 and R_2 in the measurements made with contact between the electrodes and the sample.

Finally the values of the dispersion factors need some discussion. Under the experimental procedure followed, with the pores of the material saturated with the electrolyte, all the pores contribute to the measurement, and there is only one pore family present. Under those conditions, as it has been demonstrated in [5] only the symmetric dispersion factor will have a value lower than 1, and the asymmetric dispersion factor should be constant and equal to 1. Figure 6 shows a behaviour different than predicted taking into account the pore dimensions and structure. To understand the behaviour of these parameters, the penetration depth of an AC signal into a pore has to be taken into account. The penetration depth can be written as

$$\delta = \left(\frac{Z_1 + Z_2}{Z_3} \right)^{1/2} \quad (2)$$



for a transmission line as shown in Figure 8; used for the modelling of the dielectric response of porous materials [5].

The value of the penetration depth depends, among other factors, on the conductivity of the electrolyte included in Z_2 in the model. The influence of the conductivity is shown in Figure 9. It can be seen that, at a given frequency, the value of the penetration depth increases significantly as conductivity does. This result is predicted by the model. Thus, the frequency range at which the AC signal penetrates the sample is increased when the conductivity of the electrolyte increases. According to Figure 9, at 10^4 Hz the electric signal is not able to penetrate the sample for $\sigma_0=1 \cdot 10^{-4} \Omega^{-1} \text{cm}^{-1}$, but it penetrates up to 0.9 cm when the conductivity is increased by 100 times.

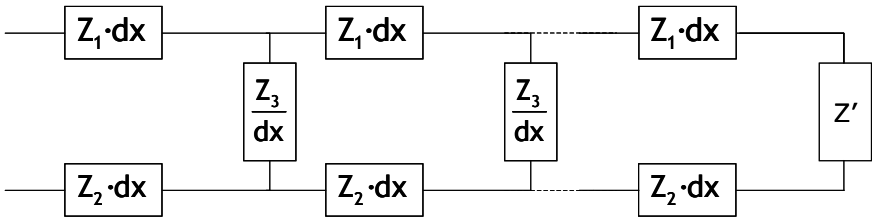


Figure 8: Transmission line model used as a base of the model, and also used to compute the penetration depth.

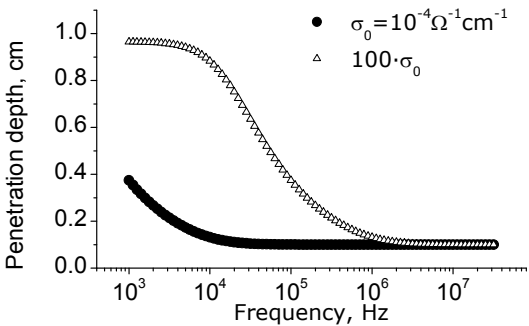


Figure 9: Changes in penetration depth (numerical calculations) for different values of electrolyte conductivity. Sample thickness was of 0.5 cm.

The low penetration of the signal due to low conductivity of the electrolyte causes asymmetric dispersion in the time constant [5], and justifies that with the solution of lower content in KCl the dielectric response is asymmetrically shaped, with a β value about 0.7. When de conductivity increases the effect of the penetration depth disappears, and symmetrical distribution of pore sizes is reflected by the impedance spectra with a factor α close to 0.85, as it could be expected for a pore size distribution such as that present in this material.

This fact of the asymmetrical dispersion due to the conductivity is not so clear in materials with a more complex pore size distribution such as cement pastes or mortars. In those materials the differences in pore size can also be responsible of the asymmetry of the time constant, and will not clearly reflect a lower value of conductivity due to portlandite consumption in the possible pozzolanic reactions.

4 Conclusions

From the study presented we can conclude that an experimental procedure has been established for the saturation of the pores of a material with different electrolytes, in order to control the conductivity. The model previously proposed is accurate for the study of the dielectric response of porous materials. Results are in good agreement for materials with a complex pore network and also for much simpler materials.

The effect of the electrolyte conductivity has to be taken into account because it has a huge influence on the resistance associated to the pores. This factor also affects the symmetry of the dispersion in time constants present, but this effect will not be so clear in materials with a great range of pore diameters.

Acknowledgements

Authors would like to thank by the financial supported the Ministerio de Educación y Ciencia of Spain and Fondo Europeo de Desarrollo Regional (FEDER) through project BIA2006-05961.

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Modelling of the elastic parameters development of an oilwell cement paste at a very early age under downhole conditions

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Abstract

The characterisation and modelling of the mechanical behaviour of an oilwell cement paste at a very early age (≤ 24 h) under high pressure and elevated temperature are studied. A multiscale homogenization approach is adopted. For this purpose, the evolution of the volume fractions of the different phases of the cement was determined by means of a kinetics model for the four main hydration reactions of a class G oilwell cement. Calorimetric experiments were performed in order to be compared with the results of the used kinetics model, on the one hand, and to study pressure and temperature effect on the hydration kinetics, on the other hand. A homogenization model is presented in order to predict the bulk and shear moduli evolutions. The model-based results are in agreement with dynamic moduli measurements data from ultrasonic propagation.

Keywords: cement paste, hydration, multiscale homogenization.

1 Introduction

In constructing oil and gas wells, primary cementing technique is used for placing cement slurries in the annular space between the drilled rock formation and the steel casing. The cement then hardens to form a hydraulic seal preventing the migration of formation fluids in the annulus. This later has to be especially well cemented because the cement sheath is submitted to various thermal and mechanical loadings from the drilling phase to the abandon phase. Over the past ten years, several papers concerned with the long-term mechanical durability of the cement sheath. However, until now there are no physical and mechanical inputs that permit to evaluate the development of stresses and strains at a very



early age during cement paste hydration in oil or gas wells [1–4]. The monitoring of the mechanical properties measurements of the cement paste at a very early age under downhole conditions (elevated temperature (HT) and high pressure (HP)) is not trivial due to the lack of instrumentation that can cure and maintain the cement paste under HTHP conditions while testing for mechanical properties. The present work aims to characterise and model the mechanical behaviour of a class G oilwell cement paste at a very early age curing under downhole conditions.

The first part of this paper concerns the homogenization of the mechanical behaviour of the cement paste at a very early age. The volume fractions evolution of the different phases of the cement paste are determined from a cement hydration kinetics model for the four anhydrous cement components. The evolution of the elastic properties at a very early age can be estimated by using an upscaling approach that provides access to the macroscopic behaviour from the intrinsic behaviour of the components at the first scale and their volume fractions.

The second part deals with the experimental characterisation of the oilwell cement paste. Semi-adiabatic calorimetric measurement is presented in order to be compared with the used kinetics model. Isotherm calorimetric measurements under HP were also conducted to study downhole conditions effect on hydration kinetics. Dynamic moduli obtained by ultrasonic propagation are finally compared with the homogenization model-based results.

2 Homogenization model

Several homogenization modelling approaches of the elastic behaviour of concrete were proposed [5–7] based on the knowledge of the elastic properties and volume fractions of its constituents (fig. 1) either during the hydration or in post-hydration phase. The predictive capabilities of these upscaling approaches to determine the macroscopic elastic properties seem to be well-established [5, 6].

The extension of such approaches to the prediction of the isothermal and no ageing viscoelastic behaviour of concrete to estimate its creep in post-hydration was also proposed from the use of the correspondence principle based on the Laplace-Carson transformation (Le *et al.* [7]). But this principle cannot be applied on the hydrating cement paste because of the evolving hydrate phase viscoelasticity and exothermic reactions in progress. The approach is consequently limited to the instantaneous elastic properties of the cement paste. However in this work, in contrast to previous studies [5, 6], the aqueous phase is taken into account to predict these properties. At a very early age, this phase has an important role and it cannot be occulted. This analysis appears to be essential from the beginning of the hydration and until the solid skeleton becomes sufficiently rigid to induce a cavitation of the aqueous phase in the capillary porosity.



In this contribution, the study is particularly focused on the instantaneous properties of the cement paste during hydration by the choice of a microstructure model and a given homogenization schema.

2.1 Schematization of the cement paste microstructure during hydration

When anhydrous cement is mixed with water, the cement paste can be regarded at a very early age as a suspension with a geometrical percolation (existence of a non-cohesive solid skeleton) of the anhydrous cement grains due to their sedimentation. Thereafter, the hydration leads to the nucleation and the growth of a multi-components and porous hydrate phase, which involves a gradual increase of the mechanical properties of the hardening cement paste (a mechanical percolation due to the development of a cohesive solid skeleton). The progressive development of the hydrated compounds induces a gradual decrease of the aqueous and anhydrous phases (fig. 2). After a certain time, the aqueous phase is mainly present in a filled or partially filled (due to water cavitation) porosity, drowned in the hydrate phase.

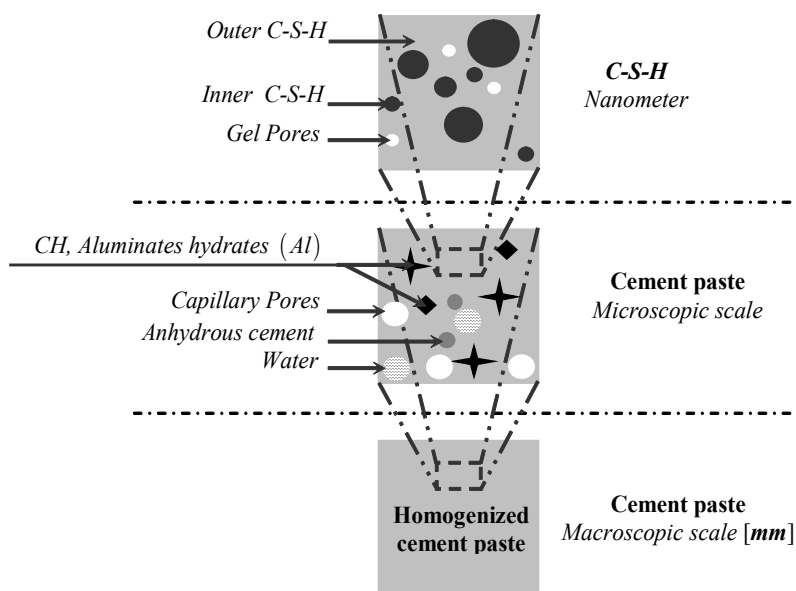


Figure 1: Upscaling method applied to cement paste.

Accordingly, the schematization of the evolutionary microstructure of the cement paste during hydration is not trivial. Nevertheless, the representation of this microstructure is necessary to estimate the homogenized mechanical properties. In this work, the adopted microstructure schematization is given in fig. 3 with the three main involved phases: anhydrous grains, aqueous phase and developed hydrates with an embedded gel porosity. The aqueous phase is assumed to initially surround the anhydrous phase (suspension) and

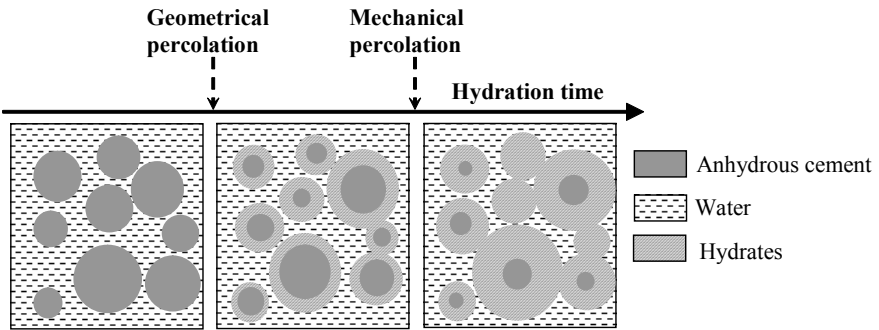


Figure 2: Cement paste phases evolution during early age hydration.

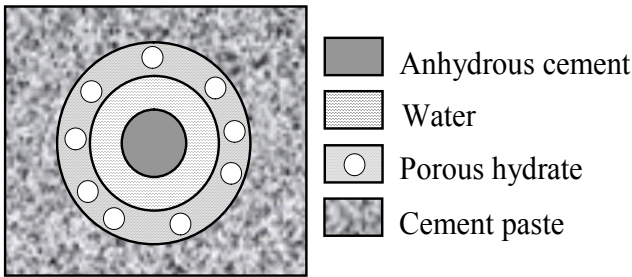


Figure 3: Schematization of the cement paste microstructure at a very early age after the mechanical percolation threshold.

progressively to be coated by the formed hydrate, this latter giving rise to a connected cohesive skeleton (fig. 2). Therefore, this schematic representation of the cement paste can cover all the hydration process (from suspension to mechanical percolation).

2.2 Retained homogenization schema

To determine the macroscopic elastic properties (bulk and shear moduli) of the adopted microstructure, a suitable homogenization schema is needed. For this purpose, Mori-Tanaka or the classic self-consistent schema do not seem to be adapted for the evolutionary microstructure of cement paste. The first one requires that one phase remains a dominant connected matrix, whereas none of the cement paste phases keeps this property during hydration. The second schema is more adapted to describe the percolation of one phase from an initial medium where all phases are equi-present. The initial phase concentrations show that the initial state is beyond the threshold of percolation. Accordingly, the generalised self-consistent schema is adopted here which ensures a continuous description of the evolution of the microstructure during hydration. For this purpose (fig. 4), n isotropic elastic phases are represented by concentric inclusions embedded in the effective medium ($n+1$). Each phase i is

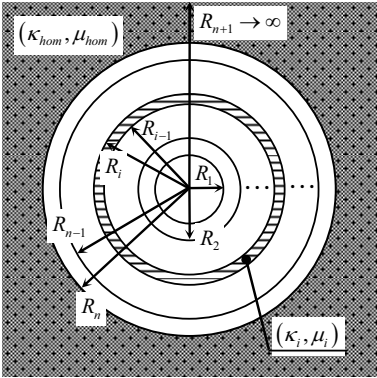


Figure 4: Generalized schema of a multiphase medium according to [8].

characterised by its bulk and shear moduli (κ_i, μ_i) and its volume fraction $f_i = (R_i^3 - R_{i-1}^3)/R_n^3$. This representation corresponds to a medium where the phases are distributed in a completely isotropic and random way.

For this schema, the homogenized bulk and shear moduli κ_{hom} and μ_{hom} are respectively given by [8]:

$$\kappa_{hom} = \kappa_n - \frac{(3\kappa_n + 4\mu_n)Q_{2l}^{(n-1)}}{3(Q_{1l}^{(n-1)}R_n^3 + Q_{2l}^{(n-1)})} \tag{1}$$

$$\mu_{hom} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \mu_n \tag{2}$$

where the matrix $Q^{(n-1)}$ and the terms coefficients A , B , and C are given in [8]. Eqns (1) and (2) are then applied to the retained microstructure with $n = 3$. Consequently, the three phases contribute in the estimation of the homogenized bulk modulus κ_{hom} through their volume fractions and their elastic properties except the shear modulus of the anhydrous cement phase μ_a :

$$\kappa_{hom} = \kappa_{hom}(f_w, \kappa_w, f_a, \kappa_a, \bar{\kappa}_h, \bar{\mu}_h) \tag{3}$$

where $\kappa_w, \kappa_a, \bar{\kappa}_h, \bar{\mu}_h$ are respectively the elastic properties of the aqueous phase, the anhydrous grains and the formed porous hydrate and $f_w, f_a, \bar{f}_h = 1 - f_w - f_a$ denote the corresponding volume fractions. As concerns the homogenized shear modulus μ_{hom} , the aqueous and anhydrous cement phase contribute only by their volume fractions and act as a void. Indeed, hydrate-water interface withstands no tangential stress when sheared [8].

3 Material input parameters

The homogenized bulk and shear moduli $(\kappa_{hom}, \mu_{hom})$ for the cement paste during hydration require to know the intrinsic elastic moduli of the cement paste components at the first scale and their volume fractions evolution during hydration. The mechanical and chemical inputs are detailed below.

3.1 Mechanical data

The hydrate phase illustrated in fig. 2 represents all forming hydrates which are first homogenized. Indeed the elastic properties of this hydrate phase (κ_h, μ_h) are determined by a mixture law of the elastic properties of each hydrate component (κ_y, μ_y) with $y = C-S-H, CH$ and *Aluminates hydrates* (*Al*).

The same approach is adopted to determine the elastic properties of the anhydrous cement (κ_a, μ_a) from the elastic properties of each anhydrous component (κ_x, μ_x) with $x = C_3S, C_2S, C_3A$ and C_4AF .

(\kappa_h, \mu_h) = \sum_y \hat{f}_y(t) (\kappa_y, \mu_y) (4)

(\kappa_a, \mu_a) = \sum_x \hat{f}_x(t) (\kappa_x, \mu_x) (5)

where $\hat{f}_y$ is the volume fraction of each hydrated component in the hydrate phase and $\hat{f}_x$ is the volume fraction of each anhydrous component in the anhydrous cement phase.

The bulk modulus of the aqueous phase is considered equal to $\kappa_w = 2,2\text{ GPa}$.

The intrinsic elastic properties $(\kappa_x, \mu_x, \kappa_y, \mu_y)$ are calculated using the following expressions:

\kappa = \frac{E}{3(1-2\nu)}; \mu = \frac{E}{2(1+\nu)} (6)

the Young modulus E and the Poisson's ratio ν values for the cement paste components are presented in table 1.

Table 1: Intrinsic elastic properties of the cement paste components [5].

	Anhydrous cement components: x				Hydrates: y		
	C3S	C2S	C3A	C4AF	C-S-H	CH	Al
E[GPa]	135	140	145	125	24	38	24
\nu[-]	0.3	0.3	0.3	0.3	0.24	0.3	0.24

Then the generalized self-consistent schema is first used for two phases ($n = 2$) to estimate the elastic properties of the hydrate taking into account the gel porosity created during hydration $(\bar{\kappa}_h, \bar{\mu}_h)$. Then the outputs $(\kappa_a, \kappa_w, \bar{\kappa}_h, \bar{\mu}_h)$ become inputs in the cement paste homogenization schema as illustrated in fig. 3.



3.2 Chemical data

The second set of inputs concerns the determination of the volume fractions evolution occupied by the different phases in the hydrating cement paste.

This requires two steps: (1) the description of the hydration degree evolution of each chemical reaction from kinetic laws and (2) the determination of the volume fractions evolution of each phase of the cement paste during hydration.

3.2.1 Hydration model

In this subsection, the kinetic laws using chemical affinity are used for the description of cement hydration kinetics [5]. These kinetic laws were found useful for the prediction of the cement hydration during all hydration stages and easily incorporated within the framework of the porous medium chemically reactive (Ulm *et al.* [9]). Therefore, the cement hydration kinetic reads:

$$\frac{d\xi_x}{dt} = \frac{1}{\tau_x(T, \phi)} \tilde{A}(\xi_x) \quad (7)$$

where $\tilde{A}[-]$ is the normalized chemical affinity, $\tau_x[h]$ denotes the characteristic time of the chemical reaction, which depends on temperature $T[K]$, blaine fineness $\phi [cm^2.g^{-1}]$, the type of clinker mineral and water/cement (w/c) ratio.

The concept of reaction dependence on temperature is well described by the Arrhenius equation (Pichler and Coussy [10]):

$$\tau_x(T, \phi) = \tau_x(T_0) \frac{\phi_0}{\phi} \exp\left(\frac{E_a^x}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (8)$$

where $\tau_x(T_0)$ is the characteristic time of the chemical reaction [5] with $T_0 = 293 K$, $\phi_0 = 3602 cm^2.g^{-1}$ is the reference fineness and ϕ is the fineness of the used cement.

As illustrated in fig. 6a, three stages are observed during cement hydration: (1) dissolution of clinker (induction stage), (2) nucleation accompanied by reactions acceleration and formation of hydration products (growth stage) and (3) finally hydration controlled by dissolved ions diffusion through a thickening layer of hydration products to the anhydrous cement grain (diffusion stage).

The normalized affinity consequently takes a particular expression according to the stage similarly to [5].

Finally the overall hydration degree $\xi(t)$ is obtained from the values of the partial hydration degree $\xi_x(t)$ of each anhydrous cement component x determined from the kinetic laws as follows:

$$\xi(t) = \frac{\sum_x m_x^0 \xi_x(t)}{m_a^0} = \sum_x f_x^m \xi_x(t) \quad (9)$$



where m_x^0 is the initial mass of the anhydrous cement component x , $m_a^0 = \sum_x m_x^0$ is the initial total mass of the anhydrous cement and f_x^m is the initial mass fraction of the anhydrous components.

As $\zeta(t)$ will be obtained by calorimetric measurement (semi-adiabatic), an alternative relation to eqn (9) is proposed in eqn (10):

$$\zeta(t) = \frac{Q(t)}{Q^\infty} = \frac{\sum_x f_x^m q_x^\infty \zeta_x(t)}{\sum_x f_x^m q_x^\infty} \tag{10}$$

where $Q(t)$ is the heat of hydration, Q^∞ is the asymptotic hydration heat ($\zeta=1$) and q_x^∞ is the asymptotic heat hydration of each component x .

Note that $Q(t)$ depends on the used q_x^∞ values taken into account (table 2).

Table 2: Values of hydration heat for each component x at $\zeta=1$.

	The Heat of hydration ($J.g^{-1}$)			
	$q_{C_3S}^\infty$	$q_{C_2S}^\infty$	$q_{C_3A}^\infty$	$q_{C_4AF}^\infty$
Taylor [11]	517	262	1144	418
Chouguet [12]	520	70	1670	725

3.2.2 Volume fractions evolution during hydration

The hydration kinetics for each anhydrous cement component is used to determine the volume fractions evolution of the different phases of the cement paste during hydration.

At each time t , the volumes of remaining anhydrous cement V_a and water V_w and the formed volumes of hydrates V_h and gel porosity V_p are determined. The volume of the cement paste V_c is then given by:

$$V_c(t) = V_a(t) + V_w(t) + V_h(t) + V_p(t) \tag{11}$$

In this work, the cement paste volume is assumed constant during hydration:

$$V_c(t) = V_c^0 = V_a^0 + V_w^0 \tag{12}$$

where V_a^0 and V_w^0 are the initial volumes of anhydrous cement and water in the mix.

The volume fractions for each phase of the cement paste can be formulated as:

$$f_a(t) = \frac{V_a(t)}{V_c^0} ; f_w(t) = \frac{V_w(t)}{V_c^0} ; f_h(t) = \frac{V_h(t)}{V_c^0} ; f_p(t) = \frac{V_p(t)}{V_c^0} \tag{13}$$

with:

$$f_a(t) + f_w(t) + f_h(t) + f_p(t) = 1 \tag{14}$$

Then, based on the stoichiometric ratio of the chemical reactions (θ) for the four main components of the cement, the molar masses (M) and densities (ρ) of



the different phases, the volume fractions of the different phases $f_a(t)$, $f_w(t)$, $f_p(t)$ and $f_h(t)$ can be determined according to [5] versus the hydration degree $\xi_x(t)$.

The volume fractions of the different phases of the cement paste are then formulated as:

$$f_a(t) = f_a^0 \sum_x (1 - \xi_x(t)) f_x^0 \frac{\rho_x}{\rho_a} \quad (15)$$

$$f_w(t) = f_w^0 - f_a^0 \sum_x \left(\theta_w^x f_x^0 \frac{\rho_x}{\rho_w} \frac{M_w}{M_x} \xi_x(t) \right) \quad (16)$$

$$f_p(t) = f_a^0 \sum_x \theta_p^x \frac{\rho_x}{\rho_a} f_x^0 \xi_x(t) \quad (17)$$

$$f_h(t) \left[\begin{array}{l} f_{C-S-H; CH}(t) = f_a^0 \sum_y \left(\sum_x \theta_y^x \frac{M_y}{M_x} \frac{\rho_x}{\rho_h} f_x^0 \xi_x(t) \right) \\ f_{AI}(t) = 1 - f_a(t) - f_e(t) - f_p(t) - f_{C-S-H; CH}(t) \end{array} \right] \quad (18)$$

Fig. 5 shows the volume fractions evolution during the first 24 hours of the class G cement paste hydration. The volume fractions linearly evolve versus the overall hydration degree $\xi(t)$ determined from eqn (9). The consumption of the anhydrous cement and water during the hydration reactions results in the formation of hydrates and gel porosity which is estimated to be about 2% after 24 hours of hydration when the curing temperature is equal to 60°C (fig. 5b).

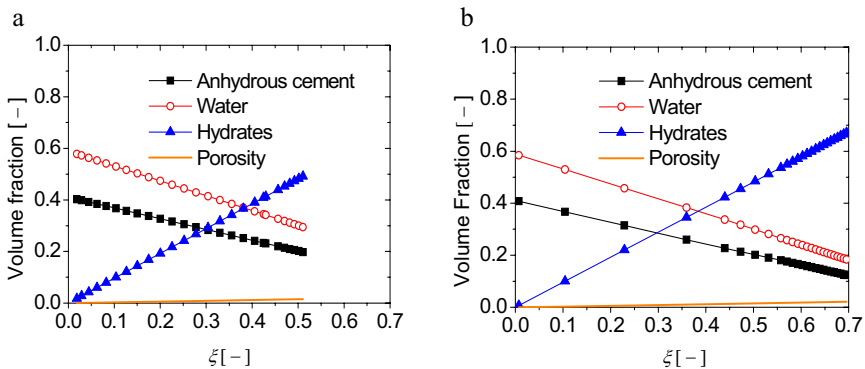


Figure 5: Volume fractions evolution of a class G cement paste components of $w/c = 0.44$ vs. the overall hydration degree at 23°C (a) and 60°C (b).

4 Cement paste characterisation

Experimental characterisation aims to provide data in order to be compared with the model-based results. Class G cement produced by Dyckerhoff which is considered a representative oilwell cement is used in this work. Its physical

Table 3: Physical properties and mineral compositions of the class G cement.

Physical properties	fineness ($cm^2.g^{-1}$)	3160
	grains average radium (cm)	9.4×10^{-4}
Mineral compositions	C_3S (% mass)	56
	C_2S (% mass)	25.7
	C_3A (% mass)	2
	C_4AF (% mass)	16.3

properties and mineral composition are given in table 3. The anhydrous cement was mixed with deionised water to prepare cement paste with $w/c = 0.44$.

4.1 Hydration characterisation

4.1.1 Isotherm calorimeter DSC

Calorimetric measurements were performed using isotherm calorimeter (HP micro DSC VII). Such calorimeter permits to study the temperature (T) and the pressure (P) effect on the hydration kinetics by following the heat flow emitted during cement paste hydration under downhole conditions. The tests conditions are summarized in table 4.

Table 4: Experimental conditions of DSC tests.

	Test 1	Test 2	Test 3	Test 4
T (°C)	23	23	60	60
P (Pa)	10^5	200×10^5	10^5	200×10^5

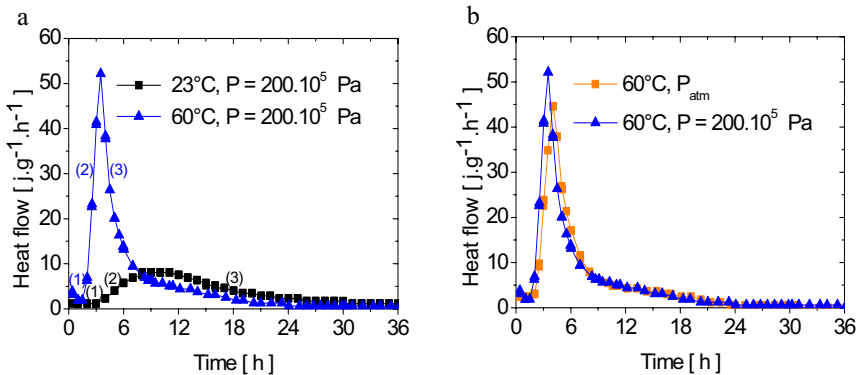


Figure 6: Heat flow per gram vs. the used cement paste ($w/c=0.44$) hydration time. Curing conditions: a. 23°C and 60°C under Nitrogen pressure equal to 200×10^5 Pa. b. 60°C under two different pressures: P_{atm} and 200×10^5 Pa.

Fig. 6a shows that when curing temperature is elevated (60°C), the three main phases of hydration duration are significantly reduced and the exothermic heat



flow peak is higher than the heat flow evolution at 23°C. Indeed, it is well known that the increase of curing temperature accelerates the hydration reactions of the cement paste [13, 14]. However, the effect of (P) on the hydration kinetics is by far less remarkable than the one of (T) (fig. 6b). The (P) effect is consequently assumed negligible in this work. For this reason, the pressure effect was not taken into account in the homogenization model.

4.1.2 Semi-adiabatic calorimeter

The Langavant semi-adiabatic calorimeter was used to quantify the heat emitted $Q(t)$ during the exothermic chemical reactions between anhydrous cement and water. Such calorimeter works only at atmospheric (P) and (T). The overall hydration degree is then calculated by using eqn (10) where $Q(t)$ is the measured hydration heat. The overall hydration degree obtained from semi-adiabatic measurement is in good agreement with the results of the used hydration model (fig. 7) obtained either from eqn (9) or from eqn (10).

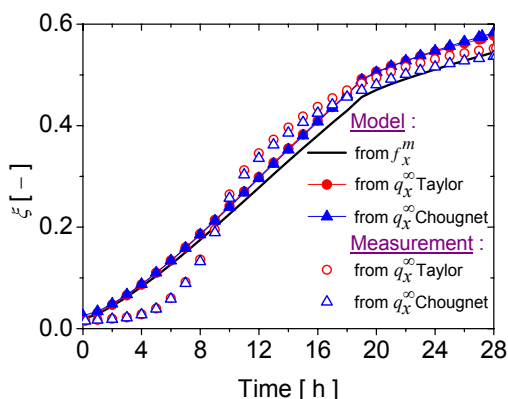


Figure 7: The overall hydration degree obtained from semi-adiabatic measurement compared with the used hydration model results at 23°C.

5 Modelling and experiment comparison

Fig. 8 shows that the homogenized elastic properties first gradually increase during the hydration of the class G oilwell cement paste then tend to stabilize from 20 hours at 23°C, and earlier from 8 hours at 60°C.

The comparison in fig. 6a between the model-based results and the dynamic elastic moduli measurements obtained by ultrasonic propagation at atmospheric conditions carried out on a white cement paste (PCCB9402) of $w/c=0.4$ [15] shows that the used model qualitatively describe the elastic mechanical properties evolution of the used cement paste.

Ultrasonic measurements and unconfined uniaxial compression tests are in progress on the studied cement paste curing at 23°C and 60°C in order to be compared with the homogenization model-based results.



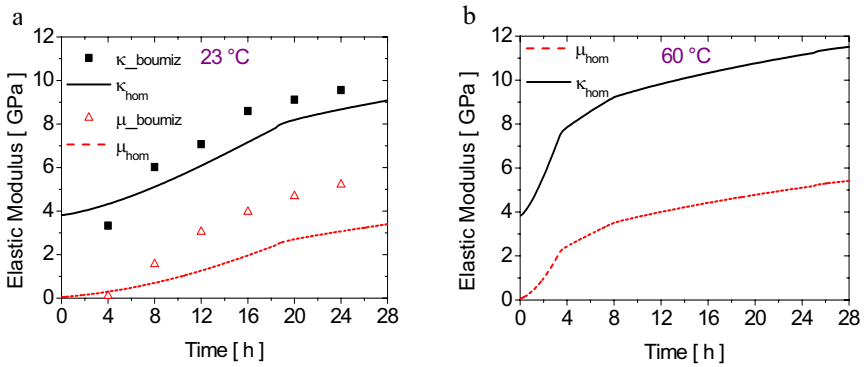


Figure 8: Elastic moduli evolution during cement paste hydration. a. Homogenized elastic moduli evolution compared with dynamic elastic moduli from ultrasonic measurements at atmospheric pressure [15]. b. Homogenized elastic moduli evolution at 60°C.

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Performance of concrete containing high volume coal fly ash - green concrete

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Abstract

Concrete is usually the most common element in a building and over the years, many solutions were developed in order to improve its qualities. We conducted a comparison between ordinary Portland cement concrete and high volume coal fly ash concrete, with the fly ash used as a substitute for the cement. Generally accepted, the total binder in a green concrete is composed of 50% cement and 50% fly ash, which is less than 200 kg/m^3 in our case (P. Kumar Mehta – High Performance, high-volume fly ash concrete for sustainable development. University of California, Berkeley, USA). We investigated concrete mixes containing 40% and 50% fly ash as partial replacements of the cement. A C20/25 class concrete was tested at 7, 28, 90 and 365 days of age for: compressive and tensile strength, modulus of elasticity, freeze thaw resistance, water permeability, and shrinkage and bond strength. We found that concrete made with fly ash is a good choice for a medium concrete class with increased durability properties.

Keywords: fly ash, compression, splitting, modulus, bond, freeze thaw, permeability, shrinkage.

1 Introduction

Concrete, usually composed of gravel, sand, water and Portland cement, is an extremely versatile building material. Unfortunately, significant environmental problems result from the production of the Portland cement, which is responsible for 6–7% of the total carbon dioxide (CO_2) produced by humans [1]. A waste product can be used as a substitute for large portions of the Portland cement, significantly improving concrete's environmental characteristics, as shown in previous research [2–5]. When mixed with lime and water, fly ash forms a



compound very similar to Portland cement. If high volumes of fly ash are used in concrete, displacing more than 20% of the cement content, the environmental impact will be reduced and the durability of the concrete will be improved [1]. Furthermore, a more dense concrete, with smaller capillary pores would be obtained [6]. The addition of pozzolanic materials, such as fly ash, influences the concrete durability and also the mechanical properties, especially the compressive and tensile strength and the modulus of elasticity [3]. These properties are very important for structural design. The objective of this paper is to evaluate the effect of pozzolanic materials, especially fly ash, on the mechanical properties of the concrete.

2 Experimental program

Four concrete mixes were prepared and tested to evaluate the influence of the fly ash on the mechanical properties [2–5]. Experimental investigations were performed to assess the influence of the fly ash on the concrete. The cement was partially replaced by fly ash (40–50%). A superplasticiser MAPEI (1.3% of the cement mass) was combined with the mixing water, in order to obtain a normal consistency of the cement paste. Tests were performed to obtain the concrete density and strength and the water absorbing kinetics.

It was established from the tests that when replacing the cement with a major amount of fly ash, the water requirement increases, because of a large porosity and because of the specific surface of the fly ash.

Table 1: Mix proportions.

Mix	1		2	
	a	b	a	b
Cement type CEM I -52.5R (kg/m ³)	352	176	-	-
Cement type CEM II/B–M(S-V) 42.5N (kg/m ³)	-	-	361	216
Gravel (kg/m ³)	1025	1025	1096	1096
Sand (kg/m ³)	723	723	916	916
Fly ash (kg/m ³) (%)	-	176 (50%)	-	145 (40%)
Water (l/m ³)	167	167	217	217
W/B	0.47	0.47	0.60	0.60
Superplasticiser (ml/m ³)	4600	4600	5200	5200

2.1 Material properties

The cement used was Portland cement CEM I -52.5R and CEM II/B – M(S-V) 42.5 N. River gravel (Aghires) with a maximum size of 16mm was used as a coarse aggregate and river sand as the fine aggregate. The pozzolanic material was fly ash with the specific gravity of 2.5 and the size of the particles ranging



from 1 to 100 microns. The fly ash was also characterized by a high silica and high alumina content. Other admixtures consisted of water-reducing agents. The mix proportions are presented in Table 1.

The aggregates were added in the mixer with one half of the water requirement. The cement came next (after 90 seconds) and was followed by the pozzolanic materials. The concrete was mixed in the mixer with all the ingredients for 6 minutes. Later, the rest of the water and the superplasticiser were added and the mix was allowed to homogenize for 3 to 4 minutes. The batch was placed in cubes and prisms and vibrated to homogenize. The cubes and prisms were removed from the formwork after 24 hours and the specimens were cured in water until the age of seven days. For each mix, approximately 30 specimens were prepared and tested.

2.2 Experimental methods

The compressive strength tests were made in accordance to RILEM. Six cubes of 150x150x150 mm were tested for strength, f_c at 7, 28 and 90 days and another six cubes were tested for splitting tensile strength $f_{ct,sp}$ at 7, 28 and 90 days. Also, six prisms were tested for the modulus of elasticity at 7, 28 and 90 days.

The tests for the strengths and the modulus of elasticity were performed on the same day, using Advantest testing machine. The strain was measured using two digital dial gages attached on opposite sides, around the perimeter of the specimen. The prisms were loaded to a maximum stress equal to 40% of the maximum compressive strength, according to RILEM. The loading rate was constant at 0.2-0.25 MPa/s. The compressive strength was also tested on cubes of 100x100x100 mm, subjected to 100 cycles of freezing and thawing.

The water permeability was determined on cubes of 200x200x200 mm, after being subjected to an increasing pressure up to 8 atmospheres.

The shrinkage was monitored on prisms of 100x100x550 and cylinders of $\Phi 90 \times 300$ mm. The specimens were kept in constant conditions of $60 \pm 5\%$ relative humidity and $20 \pm 2^\circ$ temperature. The deformations were measured with the Huggenberger device, with the precision of $0.0001''/10''$, starting from first day after casting and up to 90 days.

3 Test results

3.1 Mechanical properties

The investigation results are shown in Table 2.

The investigation results show that the compressive and tensile strengths are decreasing when a high percentage (40–50%) of the cement is replaced by thermal-electrical fly ash (Table 2). However, the strengths are sufficient for a medium class of concrete. One can observe that the compressive strength decreases with 30% and the modulus of elasticity decreases with 10–15% for the concrete mix that contains 40% and 50% fly ash replacement. A decrease of



Table 2: Properties of concrete with and without fly ash.

Properties of concrete	Age (days)	Mix					
		1			2		
		a	b	b/a	a	b	b/a
Compressive strength – f_{cm} (MPa)	7	55.30	40.40	0.73	43.12	25.10	0.58
	28	64.90	50.60	0.78	54.70	35.50	0.65
	90	67.59	62.40	0.92	64.80	46.70	0.72
Splitting tensile strength – $f_{ct,sp}$ (MPa)	7	4.60	3.10	0.70	3.00	2.00	0.67
	28	5.50	3.30	0.60	3.50	3.10	0.88
	90	5.70	3.70	0.65	3.90	3.50	0.90
Modulus of elasticity - E_{cm} (GPa)	7	42.05	34.09	0.81	37.33	32.72	0.87
	28	43.35	40.13	0.92	40.80	34.17	0.84
	90	44.55	41.11	0.92	42.29	35.63	0.84
Freeze-thaw f_{cm} (MPa)	Witness f_{cm}^m	59.35	52.60	0.88	58.25	44.75	0.78
	After 100 cycles f_{cm}^{100}	66.42	54.10	0.82	54.57	40.90	0.75
	f_{cm}^{100}/f_{cm}^m	1.12	1.03	-	0.937	0.914	-

3–5% in compression strength is also observed after 100 cycles of freezing and thawing, compared to the witness specimens (Table 2).

3.2 Water permeability results

The concrete containing fly ash (mix 1b and 2b, Table 3) proved a higher permeability to water under pressure than ordinary cement based concrete (mix 1a and 2a, Table 3).

Table 3: Water permeability.

Mix		Water penetration depth (mm)	$f_{ct,sp}$ (MPa)
1	a	0	3.39
	b	40	3.20
2	a	0	3.48
	b	30	2.30

3.3 Shrinkage

The shrinkage of the concrete is directly influenced by the presence of the fly ash in the mix. One can notice a more significant shrinkage in the mixes with zero content of fly ash (Figure 1).



3.4 Bond strength

Previous research [7] shows that a friction bond between fibers and concrete is improved by the presence of fly ash.

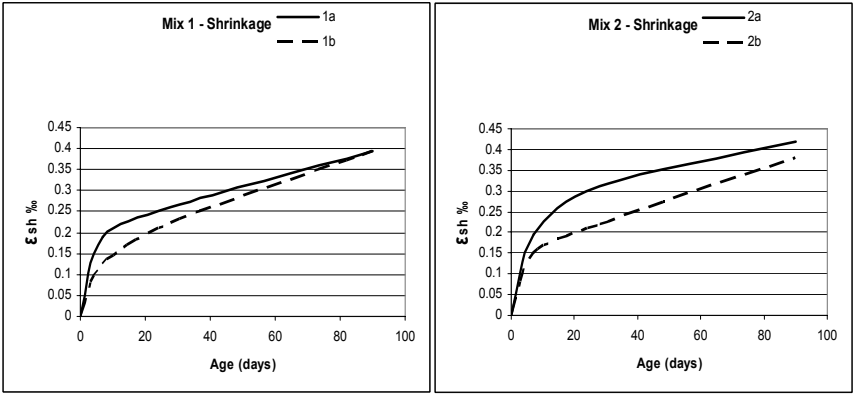


Figure 1: Influence of fly ash on the shrinkage of mix 1 and mix 2.

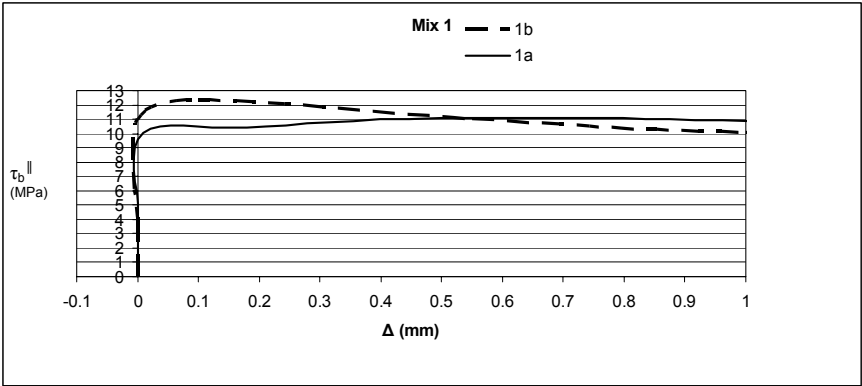


Figure 2: Bond strength $\tau_{||}$ and Δ at 28 days.

Figures 2 to 5 illustrate the influence of the fly ash on the bond strength of the concrete on mix 1 and 2. The presence of the fly ash improves the quality of the concrete in terms of bond strength between the concrete and a round steel bar, as the fine particles fill the pores of the concrete, creating a denser microstructure. Furthermore, the mix with 50% replacement of the cement by fly ash (mix 1) developed higher bond strength than the one containing 40% fly ash (mix 2). Mix 1 performed better than mix 2 by 24% for parallel bond (Figures 2 and 4) and 7% for perpendicular bond (Figures 3 and 5).



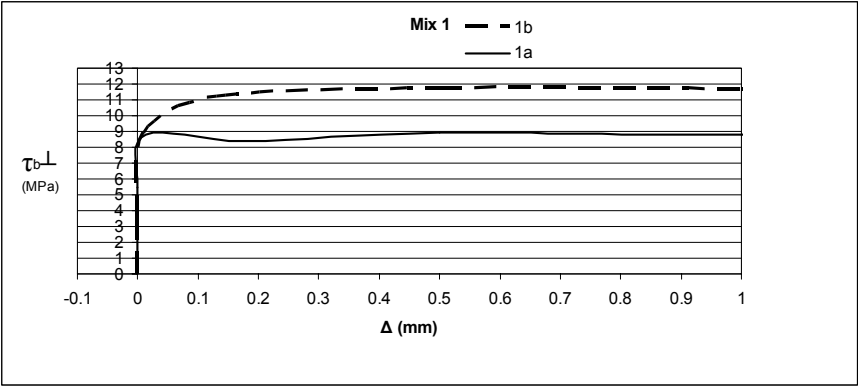


Figure 3: Bond strength $\tau_{\perp}$ and Δ at 28 days.

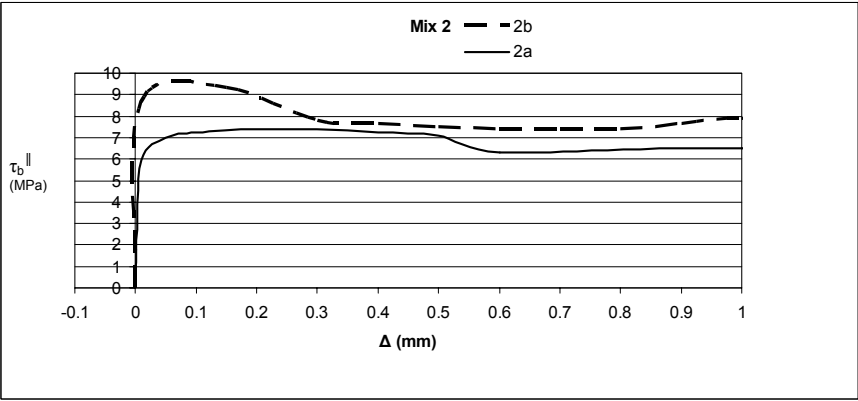


Figure 4: Bond strength $\tau_{\parallel}$ and Δ at 28 days.

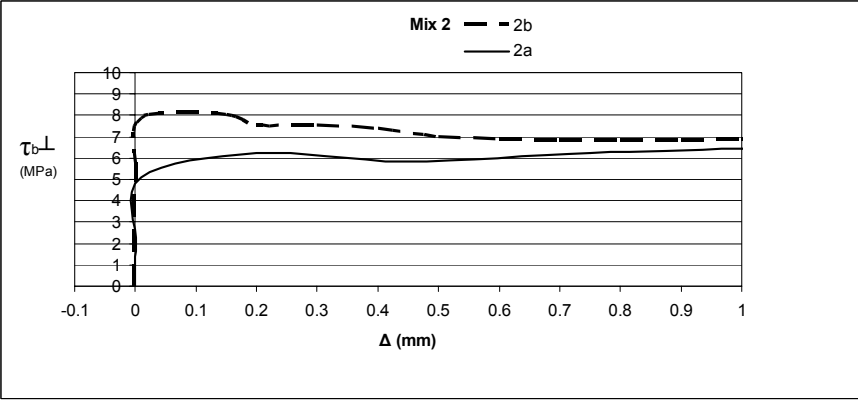


Figure 5: Bond strength $\tau_{\perp}$ and Δ at 28 days.



4 Conclusions

Fly ash increases the workability of the concrete. Used as a partial binder, fly ash leads to sufficiently high properties for small and medium compressive strength classes of concrete in respect to compressive strength and tensile strength, although the strengths decrease by approximately 30%. A smaller percentage of 15% represents the influence of the fly ash on the modulus of elasticity (Table 2).

When subjected to harsh environmental condition as freeze-thaw cycles, high volume fly ash concrete (Table 2) will not significantly diminish its properties.

The shrinkage (Figure 1) and the bond strength (Figures 2 to 5) prove a good behavior of the green concrete, compared to the ordinary concrete, which is consistent with previous studies.

However, water permeability is higher in the green concrete than in ordinary concrete and the concrete mixes will be revised on that matter.

Our results show that the use of fly ash as a cement replacement in certain quantities will produce a green concrete of medium class, less precarious for the environment than ordinary concrete, with good durability properties.

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Influence of curing conditions on the mechanical properties and durability of cement mortars

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Abstract

Real structures are hardened in conditions different from the optimum laboratory conditions, where materials are usually tested. The different temperature, and especially the different relative humidity present in the environment, may cause a different microstructure and, as a consequence, different service properties. In this work mortars made with two different cement types are tested in laboratory conditions and at a lower relative humidity. These new environmental conditions cause a slower microstructural development and different durability and mechanical properties at early hardening ages.

Keywords: microstructure, environmental conditions, mechanical strength, durability.

1 Introduction

Durability and mechanical properties of cementitious materials are directly related to the microstructure of these materials [1]. In recent years the use of active additions in concrete has become quite popular. The particular case of ground granulated blast-furnace slag, and the effect on the properties of the cementitious materials is a topic of study [2]. They are known to reduce the diffusion coefficient of chlorides in concrete [3].



The different temperature [4], and especially the different relative humidity [5] present in the environment, may cause a different microstructure [6] and, as a consequence, different service properties, such as compressive strength [7] and the diffusion coefficient of chlorides [8] in concrete.

In this work mortars made with two different cement types, an ordinary Portland cement and ground granulated blast-furnace slag cement, were tested in laboratory conditions and at a lower relative humidity. The development of their microstructure, durability and mechanical properties were studied at early hardening ages, as a function of the relative humidity of the environment.

2 Experimental setup

2.1 Sample preparation

Mortar samples were prepared using an ordinary Portland cement (OPC), CEM I 42.5 R (CEM I from now on), and a ground granulated blast-furnace slag (GGBS) cement (with a content of GGBS between 66-80% of total binder), CEM III/B 42.5 N/SR (CEM III from now on), according to the Spanish standard UNE EN 197-1. Two different water:cement ratios, 0.4 and 0.5, were employed. Fine aggregate was used according to the Spanish standard UNE EN 196-1. The aggregate to cement ratio was 3:1 for all the mortars.

Two kinds of specimens were prepared. Ones were cast in cylindrical moulds of 10 cm diameter and 15 cm height, while the rest were cast in prismatic moulds of dimensions 4 cm x 4 cm x 16 cm according to the standard UNE EN 197-1. Samples were kept in 95% RH chamber and 20°C for 24 hours. After that time they were demoulded and cylindrical samples were cut into cylinders of 5 cm thick.

Curing conditions (RH and temperature) were managed with glycerol solutions introduced in hermetically sealed containers. Solutions were prepared according to the German standard DIN 50 008 part 1. Containers were introduced into a chamber with controlled temperature. There were two environmental conditions: curing condition A (100% RH and 20°C, optimum laboratory condition) and curing condition B (65% RH and 20°C). The tests were performed at 7, 28 and 90 days of age.

2.2 Mercury intrusion porosimetry

In order to study the microstructure of mortar samples, a classical and well-known technique, such as mercury intrusion porosimetry, was used. Samples were oven dried for 24 hours at 105°C, even though this fact could change the contact angle between mercury and cement [9]. Two measurements were made on each sample. The porosimeter employed was an Autopore IV 9500 from Micromeritics. This porosimeter allows pore diameter determination in the range from 5 nm to 0.9 mm.

It has to be considered, that as reported by Diamond [10, 11], only the dimensions of the pore superficial structure can be detected by MIP, and the irregularities in pore shape cannot be determined. However, information on the



possible tortuosity of pore network can be obtained from the mercury retained in the sample after the end of the experiment. The analysis of the curve plotting the logarithmic differential intrusion volume vs. pore size, or applied pressure, shows the size where pores appear. The numerical analysis will be done calculating the volume of pores at different pore diameter intervals.

2.3 Capillary absorption test

The capillary absorption test was performed according to prUNE 83.982. This test is based in the Fargelund method to determine the capillarity of concrete. Samples of 10 cm diameter and 5 cm height were used. According to the Rilem recommendation TC 116-PCD [12], the circumferential surface was sealed using self-adhesive tape.

Samples were completely dried for 24 hours in an oven at 105°C. The Rilem recommendation [12] suggests a saturation degree of 70% on samples. The election of complete drying was made in order to accelerate the test. Especially at early ages, the hardening of samples has not been completed, and the contact with water for a long period may cause changes in the microstructure, and these changes are not a result of the hardening environment. According to the prUNE 83.982, the samples were introduced in a container with a flat base. The container was filled with distilled water until 5 ± 1 mm on the lateral surface and more than a 95% of the base of the sample was in contact with water. During the test, water level was kept constant and the container was hermetically closed. Samples were weighed at different times set in the standard. The test finished when the difference between two consecutive weights, with 24 hours difference, was lower than 0.1%, in mass. The capillary suction coefficient and effective porosity were calculated according to the expressions:

$$\varepsilon_e = \frac{Q_n - Q_0}{A \cdot h \cdot \delta_a} \quad (1)$$

$$K = \frac{\delta_a \cdot \varepsilon_e}{10 \cdot \sqrt{m}} \text{ with } m = \frac{t_n}{h^2} \quad (2)$$

where ε_e is the effective porosity. Q_n is the weight of the sample at the end of the test, g. Q_0 is the weight of the sample before starting the test, g. A is the surface of the sample in contact with water, cm^2 . h is the thickness of the sample, cm. δ_a is the density of water, 1 g/cm^3 . K is the capillary suction coefficient, $\text{kg/m}^2 \text{min}^{0.5}$. m is the resistance to water penetration by capillary suction, min/cm^2 . t_n is the time necessary to reach the saturation, minutes.

For each cement type, curing condition and w:c ratio three different samples were tested.

2.4 Forced migration test

The forced migration test was performed according to NT Build 492. The result of the test is the non-steady-state chloride migration coefficient. The method required cylindrical samples with a diameter of 10 cm and a thickness of 5 cm. Samples were saturated for 24 hours according to ASTM Standard C1202-97



[13]. The specimens, introduced in rubber sleeves, were placed in the catholyte reservoir, filled with a 10% NaCl solution. The reservoir above the specimen was filled with a 0.3 N NaOH solution. The anode was immersed in the anodic solution.

An external electrical potential was applied across the specimens to force the chlorides to migrate into the specimen. The electrical potential and test duration was chosen according to the measured current applying an initial voltage of 30 V. The value of the initial and final currents and temperatures were noted.

After the test, the specimen is axially split and sprayed with a silver nitrate solution (0.1 N). Chloride penetration depth was measured from the visible white silver chloride precipitate. The migration coefficient (D_{nssm}) can be calculated from this average penetration depth (x_d) according to the expression:

$$D_{nssm} = \frac{0,0239 \cdot (273 + T) \cdot L}{(U - 2) \cdot t} \cdot \left(x_d - 0,0238 \cdot \sqrt{\frac{(273 + T) \cdot L \cdot x_d}{U - 2}} \right) \quad (3)$$

where: D_{nssm} is the non-steady-state migration coefficient, $\times 10^{-12} \text{ m}^2/\text{s}$, U is the absolute value of the applied voltage, V. T is the average value of the initial and final temperatures in the anodic solution, °C. L is the thickness of the specimen, mm, and t is the test duration, hours.

For each cement type, curing condition and w:c ratio three different samples were tested.

2.5 Mechanical strength test

The strength was measured according to the Spanish standard UNE EN 196-1. Samples of dimensions 4 cm x 4 cm x 16 cm were tested. Compressive and flexural strength were studied. For each cement type, curing condition and w:c ratio three different samples were tested.

3 Results and discussion

3.1 Mercury intrusion porosimetry results

Total porosity, Hg retained and pore size distribution of the samples were studied. The results of total porosity are depicted in Figure 1(A). Samples with w:c ratio 0.5 presented higher total porosity than with w:c ratio 0.4.

For curing conditions A, total porosity kept constant between 7 and 90 days in specimens prepared with CEM I. Only samples with w:c ratio of 0.4 have an important porosity decrease between 28 and 90 hardening days. Total porosity of samples of CEM III showed a high decrease between 7 and 28 days. This decrease only continued between 28 and 90 days for w:c ratio 0.5 specimens.

These results could mean that a higher RH accelerates the development of the hydration and pozzolanic reactions. With these reactions, new solids appear and total porosity decreases at early ages.

For curing conditions B, total porosity of CEM I samples and w:c ratio 0.5 kept constant until 28 days and decreased between 28 and 90 days. Total



porosity in CEM III samples remained constant between 7 and 28 days, and decreased between 28 and 90 days. It can be thought that the lower RH slows down hydration and pozzolanic reactions, and the decrease of total porosity happens later.

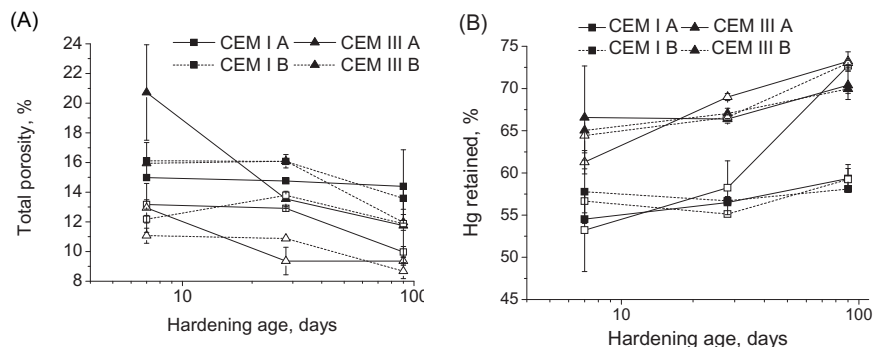


Figure 1: (A) Evolution with time of total porosity for both cement types and hardening conditions. (B) Results of mercury retained for specimens studied. Full symbols are for w:c ratio=0.5 while open symbols are for w:c ratio=0.4.

The study of the mercury retained in the sample after the end of the experiment enables to obtain information of the possible tortuosity of pore network. The results of total porosity are depicted in Figure 1(B). The percentage of mercury retained increased in most of the samples studied. For samples cured under conditions A, this increase of mercury retained is higher than specimens under conditions B. These results could mean that a higher RH helps the hydration and pozzolanic reactions. Then new solids are quickly made and tortuosity of pore network increases.

The study of pore size distribution of samples was done considering the following diameter ranges: < 10nm, 10-100 nm, 100 nm-1 μ m, 1-10 μ m, 10 μ m-0.1 mm and > 0.1 mm.

For all the samples studied, the majority ranges were 10-100 nm and 100 nm-1 μ m. Values of the contributions to total porosity are shown in Figure 2(A) for samples prepared with CEM I. The intrusion volume decreased with age in these mortars. At 7 days of age, the intrusion volume is higher for CEM I samples under curing conditions B. However, this volume is similar for the majority of the specimens at 90 days of age, independently of curing conditions. The pores volume of majority ranges decreased with time. From these results, it can be said that the higher RH accelerates the hydration reactions of CEM I specimens, and then, the pores volume of majority ranges decreases mainly at early ages.

For specimens prepared with CEM III, the pore size distribution is shown in Figure 2(B). The intrusion volume decreased quickly for samples under curing conditions A. For curing conditions B, the intrusion volume decreased at 90 days of age. These results show that a high RH in the environment makes easier the

development of pozzolanic and hydration reactions, and then, the intrusion volume decreases quickly. Nevertheless, if RH is lower, intrusion volume decreases later in the case of the cement type III that contains ground granulated blast-furnace slag cement.

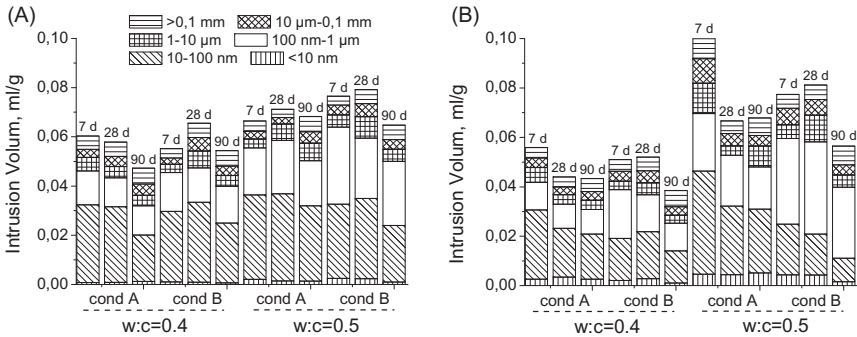


Figure 2: (A) Pore size distribution for CEM I specimens under curing conditions A and B. (B) Pore size distribution for CEM III specimens under curing conditions A and B.

3.2 Capillary absorption test results

The capillary suction coefficient (K) and effective porosity of samples are obtained from the test. The results of capillary suction coefficient are shown in Figure 3(A). CEM I samples show a smaller coefficient K than the CEM III samples. For the curing conditions A, samples prepared with CEM III and w:c ratio 0.4 had the highest coefficient K and it kept practically constant. Specimens with same type of cement and w:c ratio 0.5 presented lower coefficient K at the age of 7 days, but it increased with time. For both w:c ratios, the coefficient K for samples prepared with CEM III under curing conditions A was very similar at the age of 90 days.

The CEM I samples under curing conditions A had a small rise of coefficient K between 7 and 90 days of age. Specimens with w:c ratio 0.5 presented lower coefficient K than with w:c ratio 0.4.

For the curing conditions B, samples with CEM III and w:c ratio 0.4 had higher coefficient K than w:c ratio 0.5 at the age of 7 and 28 days. The coefficient K at the age of 90 days presented a very important increase and had a very similar value for both w:c ratios. Specimens with CEM I and w:c ratio 0.5 had a smaller coefficient K than w:c ratio 0.4 at the age of 7 days. The coefficient K of w:c ratio 0.5 samples decreased with the age and it increased for the samples with w:c ratio 0.4. At the age of 90 days the coefficient K was very similar for both w:c ratios.

The effective porosity of samples cured in conditions A was lower than the porosity of samples cured in conditions B. For both curing conditions, samples prepared with w:c ratio 0.5 had higher effective porosity than with w:c ratio 0.4.



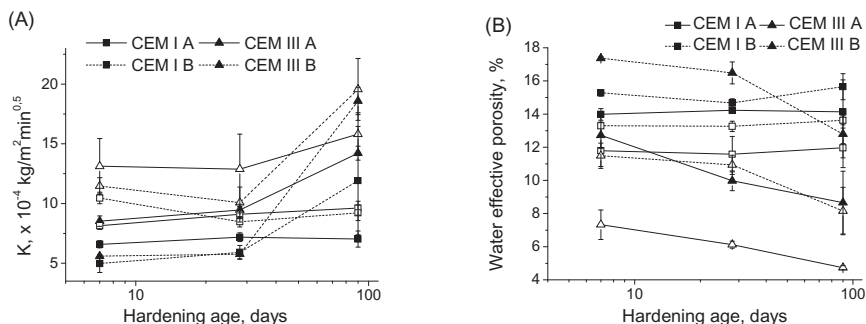


Figure 3: Results of capillary suction test. (A) Depicts the variation of the capillary suction coefficient with time for both cement types and hardening conditions. (B) Shows the water effective porosity also obtained from the test. Full symbols are for w:c ratio=0.5 while white symbols are for w:c ratio=0.4.

For curing conditions A, specimens with CEM III showed a lower effective porosity than with CEM I for the same w:c ratio.

As it can be seen in Figure 3(B) for each cement type, and w:c ratio the values of the water porosity are greater always under the curing conditions named B. This parameter has the physical meaning of the volume fraction accessible by water, and as a consequence by aggressive (i.e. chloride). This result proves that the laboratory conditions are optimal, and give a greater durability, from this point of view. This behaviour can be explained in terms of the higher RH present in the curing environment A. The unrestricted presence of water in the environment makes easier the development of the hydration and pozzolanic reactions. The products of these reactions are solid phases that cause a more compact structure of the materials.

When the RH is smaller than 100% (65% condition B) these reactions are slower, specially the pozzolanic reactions. This fact is reflected in the results of the effective porosity. As it can be seen, the influence of the relative humidity has a greater importance for CEM III. Samples hardened at 100% RH show a decreasing tendency from the beginning of the study, while samples hardened at 65% RH show an important decrease of the effective porosity between 28 and 90 days. From these results it can be said that the lower relative humidity causes a slower development of the hydration and pozzolanic reactions, meaning that until 90 days a worse behaviour can be expected from the point of view of the aggressive ingress in concrete. The high decrease of the effective porosity from 28 to 90 days for the CEM III suggests a study at later ages, where the behaviour of cement with slag can be similar in both environments.

The behaviour of CEM III is always better than CEM I, and even in the hardening condition with less water, the difference in the effective porosity increases with time, which means a big improvement with time of the durability of mortars containing CEM III.



3.3 Forced migration results

The results of the non-steady-state migration coefficient (D_{NTB}) are depicted in Figure 4.

The migration coefficient has smaller values for samples prepared using CEM III than using CEM I. This result could be expected from the results obtained for the total, and water effective porosities. For mortar specimens with CEM I under curing condition A (100% RH), the samples with w:c ratio 0.4 had the highest migration coefficient at 7 days age. The chloride migration coefficient obtained with these samples decreases with the hardening age, and at the age of 90 days their migration coefficient is the lower of all the CEM I samples.

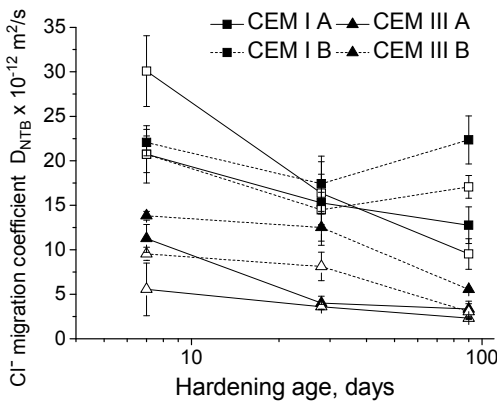


Figure 4: Results of the non-steady-state migration coefficient (D_{NTB}) for both types of cements studied. Full symbols are for w:c ratio=0.5 while white symbols are for w:c ratio=0.4.

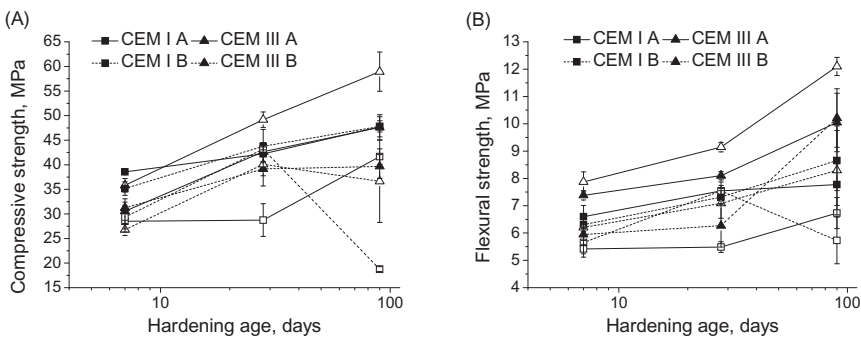


Figure 5: (A) Evolution of the compressive strength with the age of mortar samples. (B) Results of the flexural strength for specimens studied. Full symbols are for w:c ratio=0.5 while white symbols are for w:c ratio=0.4.



For the curing conditions B (65% RH), samples of OPC and w:c ratio 0.5 had higher D_{NTB} than samples with w:c ratio 0.4 and both presented a similar decreasing tendency of D_{NTB} between 7 and 28 days age. As should be expected from previous results, samples prepared with CEM III in curing conditions A had an important decrease of D_{NTB} with special importance between 7 and 28 days. In curing conditions B, the biggest decrease of the migration coefficient happened between 28 and 90 days. At the age of 90 days, D_{NTB} was very similar for all the samples of CEM III.

Again, it is shown that a high RH in the environment makes easier the development of hydration and pozzolanic reactions, and then, the non-steady-state migration coefficient decreases quickly. Nevertheless, if RH is lower, the pozzolanic reactions develop slower and the non-steady-state migration coefficient decreases later, but also reaches good values for CEM III.

3.4 Strength results

Compressive and flexural strengths were studied. Compressive strength results are depicted in Figure 5(A). Flexural strength results are shown in Figure 5(B).

Both strengths increased in the majority of studied samples. For samples cured under conditions A, this increase is higher than that obtained under conditions B. These results could mean that a higher RH accelerates the hydration and pozzolanic reactions. Then new solids are quickly formed and the gain of strength is faster in this case, in coincidence with all the results already discussed.

4 Conclusions

The main conclusions that can be obtained from the results previously discussed can be summarized as follows:

Relative humidity has an influence on materials properties. This influence is higher in cements containing ground granulated blast furnace slag (CEM III).

Hg retained is greater in CEM III mortar samples. This shows that the tortuosity of pore network increases due to the formation of new solids, by the hydration and also the pozzolanic reactions.

In general, CEM III samples show better properties of durability at 90 days of age.

High relative humidity improves slightly the durability properties of CEM I mortars. The presence of water favours hydration reactions of CEM I components.

The development of pozzolanic reactions and the formation of new solids, cause an important improvement of durability properties of CEM III mortars.

The improvement of the durability is delayed in environments with relative humidity lower than 100%, but after 90 days hardening these properties have reasonable good values.

Compressive and flexural strength increased with the age in the majority of samples studied.



Acknowledgements

This work has been financially supported by the Ministerio de Educación y Ciencia of Spain and Fondo Europeo de Desarrollo Regional (FEDER) through project BIA2006-05961. J.M Ortega is indebted to the abovementioned Spanish Ministry for a fellowship of the “Formación Personal Investigador (FPI)” programme (reference BES-2008-002650). Authors would like to thank Cementos Portland Valderribas, S.A. and Holcim España, S.A. for providing the cements studied in this work.

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Section 7
Porous construction materials
Special session organised
by A. J. Klemm

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Microstructural characterisation of porous construction materials – major challenges

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Abstract

This paper focuses on the microstructural characterisation of porous construction materials. The attempt was made here to assess the existing methods of analysis of pore structure in cementitious materials, such as Mercury Intrusion Porosimetry (MIP) and Differential Scanning Calorimetry (DSC). Due to a number of simplifying assumptions and limitations on the use of individual methods, it is not possible to describe in a qualitative, reliable way the microstructure of porous construction materials. The way to achieve this goal is to employ a wide range of complementary techniques.

Keywords: cementitious materials, microstructural characterisation, MIP, DSC, limitation of methods.

1 Introduction

The majority of materials in practice are or may be porous to a greater or lesser extent. Pores taking up the same relative volume in material may be characterised by a completely different structure (Fig. 1). They may exist in the form of closed pores, i.e. not connected with each other and not connected with the surface of material (for example some insulation materials made of foamed polymers) or in the form of less or more developed canals and gaps connected with each other and forming a network, penetrating the whole material evenly.

As the porosity structure greatly affects physical properties, strength characteristics and durability in general, a clear need is perceived to measure it.

Unfortunately, due to a number of simplifying assumptions and limitations on the use of individual methods, it is not possible to describe in a qualitative, reliable way the microstructure of porous construction materials. Although the Mercury Intrusion method is commonly regarded as the most convenient



technique, mainly because it may be applied to moderately large samples (1 - 3g) and covers a very wide range of pore sizes (100 μm - 3nm), its ability to yield accurate information about the size of the pores and their shape is very questionable. It is necessary to employ other techniques to assess errors in porosity analysis. Differential Scanning Calorimetry may become very useful here. This method allows detection of physical and chemical changes that are accompanied by a gain or loss of heat in a material as its temperature is increased or decreased. Characteristics of the phase transition process “water to ice” in porous materials may provide very important information.

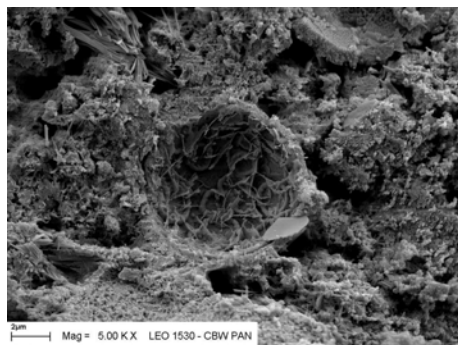


Figure 1: Microstructure of cement-based mortar.

2 Differential Scanning Calorimetry

Variations in the microstructure and chemical composition of materials result in substantial differences in the characteristics of phase transition in pores and capillaries. Generally capillaries, having the highest diameters, create the largest possibilities of spontaneous nucleus creation and then growth. The values of the supercooling, necessary to be reached in order to initiate the transition, are lower here. A more complex character of transition can be expected in smaller capillaries where the condition of ice penetration is the higher difference of the pressures between ice and water. This is again associated with the creation of internal forces acting on the composite matrix.

The Differential Scanning Calorimetry (DSC) technique can provide quantitative information about these changes by measuring the amount of heat that is involved as a material undergoes either an endothermic or exothermic transition. The gain (exothermic process) and loss (endothermic process) in the enthalpy of the material can be related to physical and chemical changes in the material during the heating or cooling.

Figure 2 shows an example of a DSC trace with three stages of phase transition clearly marked: “water to ice” - nucleus creation, spontaneous growth of nuclei and ice crystal growth.

As the temperature increases during heating, the ‘onset’, ‘peak’ and ‘end’ of any temperature endotherm are clearly distinguished so the heat of fusion in

consequence can be calculated from the area encompassed. A similar procedure can be applied during cooling to obtain the location and magnitude of the temperature exotherm and again the heat of crystallization can be calculated from the area encompassed. Latent heats may be obtained by numerical integration of the area between the heat flow curve and the extrapolated base line. Melting and freezing points are taken at the intersection of the extrapolated base line and the tangent to the heat flow curve at the inflection point of the appropriate side of the peak. Melting and freezing 'peak' temperatures can be defined as the temperatures of the points that are located farthest from the base line in a heating or cooling cycle.

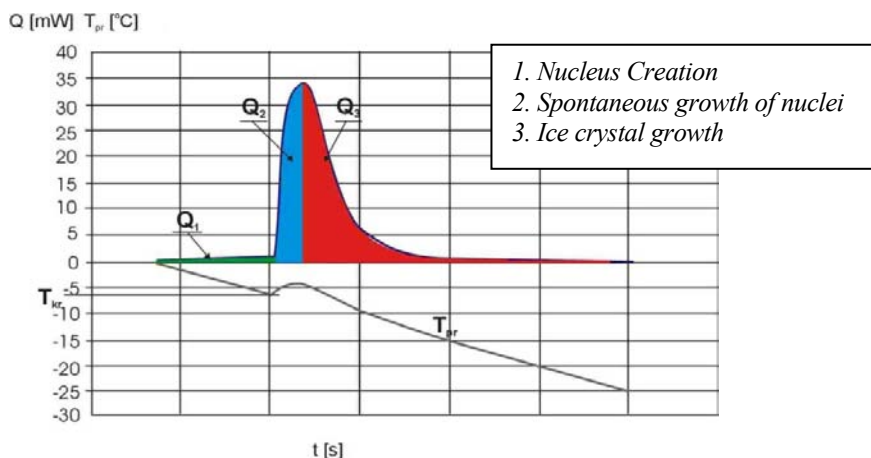


Figure 2: An example of a DSC trace.

Various environments (vacuum, inert atmosphere or controlled gas composition) and heating rates (from 0.1 K/min to 320 K/min) can be employed for temperatures ranging from -150°C to 2400°C , depending upon the equipment used.

Considerable attention has been paid in the past to the influence of a number of factors - such as sample weight, particle size, heating and cooling rate, atmospheric conditions surrounding the sample - on the results obtained from DSC instruments. Whilst the influence of these should not be underestimated, the present design using milligram samples makes it relatively straightforward to obtain good results and reduces the effects of most of these factors.

Good technique is very necessary, and points such as possible misplacing of specimen dishes on the thermocouple platforms, inadequate drying of the sample or reference, selection of the wrong reference material, should not be overlooked.

3 Mercury intrusion porosimetry

Mercury porosimetry is the measuring method of open porosity. It allows not only determination of the total volume of open pores but also gives an



information of the volume of pores having the specified sizes (pore size distribution). The Mercury Intrusion Porosimetry technique together with microscopic examinations and density measurements allows qualitative and quantitative description of porous material.

In principal a non-wetting liquid such as mercury penetrates a porous medium under gradually increasing pressure. The method of measurement is based on the capillary phenomenon. If a capillary having the radius, r , is placed in a container with liquid, the level of the liquid in such capillary depends on surface tension of liquid, γ and the wetting angle of capillary material, θ , by the liquid in container. In a case of the wetting angle in excess of 90° the level of the liquid will eventually settle below the level of liquid in the container. In order to equalise the levels of liquid it is necessary to apply a pressure, P , such as:

$$P = -2\gamma \cos\theta / r \quad (1)$$

Since the different levels of pressure correspond with different radii of the penetrated pores, the volume of pores with radius between r_{n-1} and r_n can be easily determined. The number of measurements for increasing pressures allows the estimation of pore volumes as a function of their diameter, and the measurement of pore size distribution in the specimen tested. See example on Fig. 3 below.

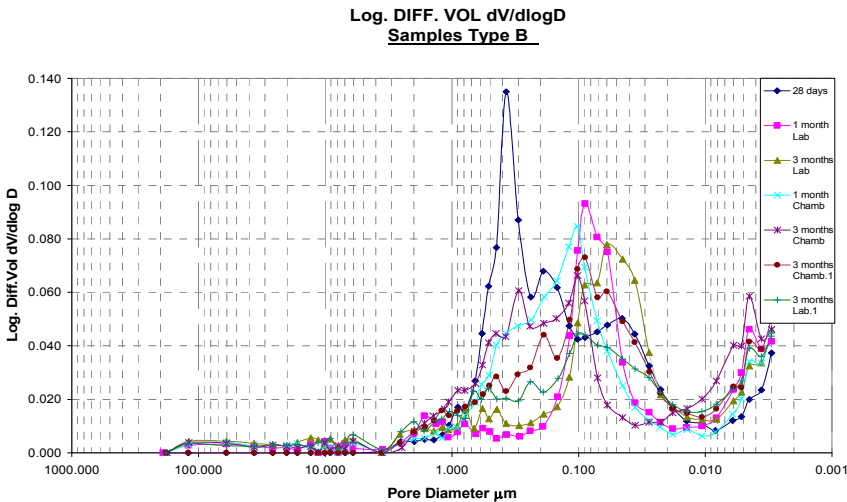


Figure 3: Example of a differential distribution curve.

Ability of the method to yield accurate information about the size of the pores and their shape depends on several factors and assumptions:

1. Compressibility of the solid, mercury, and residual air remaining in the sample space. All this factors may cause errors in the intrusion volume



measurements. For some porous materials the compressibility may be higher because of the presence of open or closed pores.

2. Breakdown of porous materials under pressure. When mercury is forced into pores, the larger pores may be subject to breakdown, especially if they have bottleneck type constricted openings. For an equal wall thickness, the smaller pores are much stronger than the larger pores. Sponge or foam type materials are especially subjected to this type of "squeeze" effect because their walls are thin and of low mechanical strength.

3. Kinetic hysteresis (time effect) and volume hysteresis (pore shape effect). Sometimes considerable time is required for the mercury to flow into the pores at a given pressure. This time factor may be reduced or eliminated by increasing the time allowed for equilibrium. Volume hysteresis is the retention of mercury by the pores of the sample after penetration and reduction of pressure to one atmosphere (Fig. 4). The pore diameter calculated by the Washburn equation (1) is the diameter of the opening of the pores and not necessarily the largest diameter of the pore; the latter depends on the pore's shape.

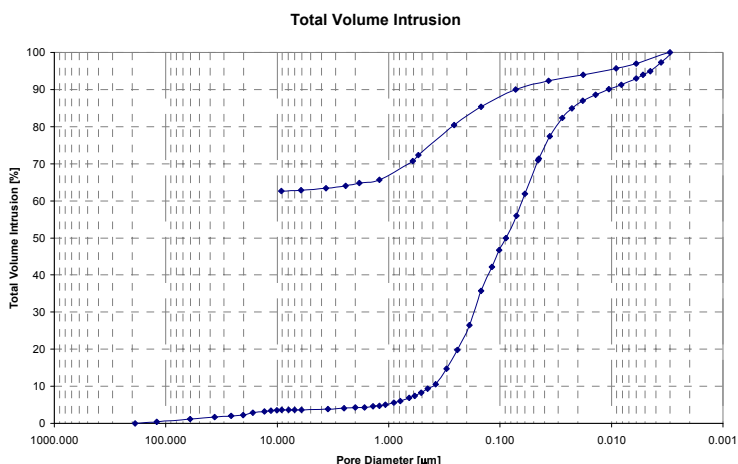


Figure 4: Example of a cumulative distribution curve.

4. Assumption of cylindrical pore model. The computations are based on a theoretical model in which the material is assumed to contain cylindrical and non-interacting pores. This is obviously not the case in practice.

5. Assumption of constant or given value for the surface tension of mercury. The degree of purity of mercury has a much greater effect on the surface tension of mercury, than the ambient temperature. Increase of contaminants will lower the surface tension of mercury and this may very well be the main factor in the wide spread of reported values for the surface tension of mercury in the literature.



6. Assumption of some constant value for the contact angle between mercury and the solid. Since this information is not always readily available, most workers usually assume, for the cementitious materials, either 130° or 140° , depending on their preference. For comparing porous materials of the same type, it does not really matter which value one chooses, unless an attempt is being made to obtain an exact measure of the pore openings.

4 Experiment

4.1 Material tested

The results presented in this report were obtained using polymer modified mortar with the cement/sand ratio 1:1 and 0.1% by weight MHEC - methyl hydroxyl ethyl cellulose. Samples were made in the form of prisms 50mm by 50mm by 200mm and they were cured in their moulds for 24 hours before being demoulded. The samples were then stored in the normal laboratory conditions for 28 days before testing [1].

4.2 Experiment

The Differential Scanning Calorimetry was used to monitor the process of water to ice transition in polymer modified mortar. The experiment was carried out using DSC system - UNIPAN 605 M. The basic technical tolerances of the equipment used were: calorimetric accuracy $\pm 2\%$, temperature accuracy $\pm 0.1\text{K}$, scanning speed 0.1K/min - 20K/min , the range of applied temperature $113 - 723\text{K}$, the cooling rate 2K/min . Measurements were carried out on minute samples of approximately 50 - 100mg weight which were extracted from the representative prisms. Specimens were saturated with water (48 hours) prior testing [2].

Mercury Intrusion Porosimetry method was used to determine total porosity, pore size distribution and total pore area. Small samples of about 2-3 g were tested in

Mercury Intrusion Porosimeter (Micromeritics AUTOPORE II 9220 V3.00).

5 Experimental results

5.1 Differential Scanning Calorimetry

Phase transition analyses were based on Everett [3] and the Everett and Hynes model [4]. The overall heat of phase transition, ΔQ was determined to be equal to 0.96545 J, leading to 18% increase in ice concentration. Heat emissions during three stages of phase transition i.e. nucleus creation, spontaneous growth of nuclei and growth of ice crystals, have been also separately estimated and presented in Tables 1- 3.

The temperature in the chamber has been gradually lowered at a constant rate of 2K/min . The value of the latent heat of solidification, ΔH_f , has been assumed



to be equal to 306.6 J/cm^3 . The total volume of created ice has been estimated by using the following formula: $\Delta Q = \Delta H_f \cdot V_{ice}$

Figure 5 below shows heat evolution during three stages of phase transition.

Heat emission during the first stage of the phase transition for studied sample reached a value of $Q_1 = 0.00845 \text{ J}$ (Table 1). During the first stage of transition, that value was equal to $V_1 = 2.75 \cdot 10^{-5} \text{ cm}^3$ and the critical temperature of transition corresponding with the beginning of spontaneous growth of nucleus was $T_{cr} = 268.4 \text{ K}$. The value of supercooling $\Delta T = T_{cr} - T_0$ ($T_0 = 273 \text{ K}$) of water in pores and capillaries in a tested specimen was taken as equal to $\Delta T = 4.6 \text{ K}$.

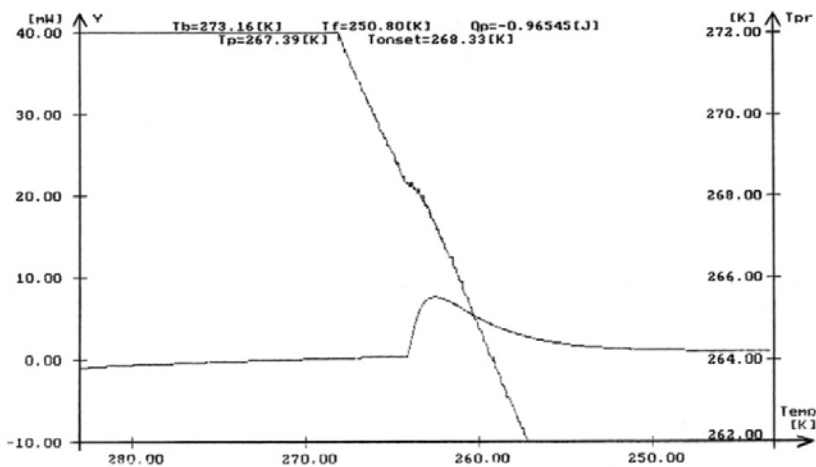


Figure 5: Differential Scanning Calorimetry curve.

Table 1: Stage I of transition - nucleus creation.

$\Delta Q \text{ [J]}$	$\Delta V_{ice} [\text{cm}^3]$	$\Delta \kappa \text{ [%]}$	$T_{cr} \text{ [K]}$	$\Delta T \text{ [K]}$	$r_{cr} \text{ [nm]}$
0.0084	$2.75 \cdot 10^{-5}$	0.2	268.4	4.6	541

Where: ΔQ - the heat of phase transition, ΔV_{ice} - the volume of ice, $\Delta \kappa$ - the increment of ice concentration, ΔT - the supercooling necessary to initiate the transition, T_{cr} - the critical temperature, r_{cr} - the critical radius of ice nucleus,

If the lower rate of the temperature decrease was assumed, which is a real condition, the value of supercooling would be much higher. At the critical temperature $T_{cr} = 268.4 \text{ K}$ nucleus or ice conglomerations, which are created in pores, reach their critical size. This quantity may be defined by using classical theory, which assumes the simplest way of nucleus creation i.e. when the nucleus



stays in contact with their initial phase. The process of each phase creation is associated with the change of Gibbs energy ΔG , which in turn consists of two components: volumetric energy ΔG_v and superficial energy ΔG_s . It is known, that if the temperature T is lower than the temperature of solidification T_o , the change of free energy associated with the freezing per unit volume of liquid is equal to:

$$\Delta G_v = (\Delta H_f/T_o) \Delta T \tag{2}$$

where: ΔH is the latent heat of melting and $\Delta T = T_o - T$ is the supercooling.

Hence the change of thermodynamic potential accompanying the transition of volume from unstable to stable phase can be expressed by: $4/3\pi r^3 \Delta G_v$ and the superficial energy of the nucleus is defined as: $4\pi r^2 \delta_{iw}$, where: δ_{iw} - the energy of the interphase is given as a function of the temperature.

During the phase transition the unstable phase with higher thermodynamic potential disappears and the new phase with lower potential is created. It is evident that the nuclei are stable when ΔG is decreasing e.g. after reaching their critical size:

$$r_{cr} = 2\delta_{iw}/\Delta G_v \tag{3}$$

The initiation of a spontaneous phase transition may occur when the nuclei of new phase reach their critical size. In a case of analyzed composite it can be presumed that critical radius of nucleus was equal to $r_{cr} = 541$ nm. That value has been obtained when $\Delta H = 306.6$ J/cm³ and $\delta_{iw} = 250 \cdot 10^{-6}$ J/cm² at $T = 268$ K are assumed.

During the second stage of transition the significant amount of heat, which caused the temperature increment has been emitted (Table 2). The temperature increase caused by the phase transition was equal to $\Delta T = 1$ K and the amount of liberated heat was $Q_{II} = 0.1954$ J. Again the increment of ice volume in the second stage was $\Delta V_{II} = 63.7 \cdot 10^{-5}$ cm³.

Table 2: Stage II of transition - spontaneous growth of nuclei.

ΔQ [J]	ΔV_{ice} [cm ³]	$\Delta \kappa$ [%]	ΔT [K]	Δp [J/cm ³]	R_{cr} [nm]
0.1954	$63.7 \cdot 10^{-5}$	3.6	5.6	6.29	795

Where: ΔQ - the heat of phase transition, ΔV_{ice} - the volume of ice, $\Delta \kappa$ - the increment of ice concentration, ΔT - the supercooling, Δp - the difference of pressures between ice and water ($p_w - p_i$), R_c - the smallest radius of capillary in which ice is formed.

The pressure difference between water and ice inside pores could be estimated by using the following relationship:

$$(p^* - p_i) = \Delta S_f (T - T_o) \tag{4}$$

When the entropy of phase transition was assumed to be equal to $\Delta S = 1.123$ J/cm³K and the supercooling $T - T_o = 5.6$ K, the pressure difference was $(p_i - p^*) = 6.29$ J/cm³. From the following relationship:



$$p_i \cdot p^* = 2\delta_{iw}/R_c \tag{5}$$

it was found that when $(p_i \cdot p^*) = 6.29 \text{ J/cm}^3$, ice penetration to capillaries having radius $R_c = 795\text{nm}$ can occur.

During the third stage of transition i.e. when the ice crystals started growing, the recorded amount of librated heat was $Q_{III} = 0.76997\text{J}$ and the corresponding increment of ice volume was $\Delta V_{III} = 251 \cdot 10^{-5} \text{ cm}^3$. This means, that after reaching a temperature $T = 250.8\text{K}$, 14.5 per cent of water was involved with the phase transition in studied composite (Table 3).

5.2 Mercury intrusion porosimetry

Figure 6 presents the results of pore size distribution in mortar sample, clearly indicating the dominant range of pores between 700nm and 2000nm.

It is evident that one of the most important factors in the application of mercury intrusion data is the value selected for the interfacial contact angle between the mercury and the solid. The better we can estimate the true contact

Table 3: Stage III of transition - ice crystal growth.

$\Delta Q \text{ [J]}$	$\Delta V_{ice}[\text{cm}^3]$	$\Delta \kappa \text{ [%]}$	$\Delta T \text{ [K]}$	$\Delta p[\text{J/cm}^3]$	$R_{cr} \text{ [nm]}$
0.7699	$251 \cdot 10^{-5}$	14.5	22.2	24.93	281

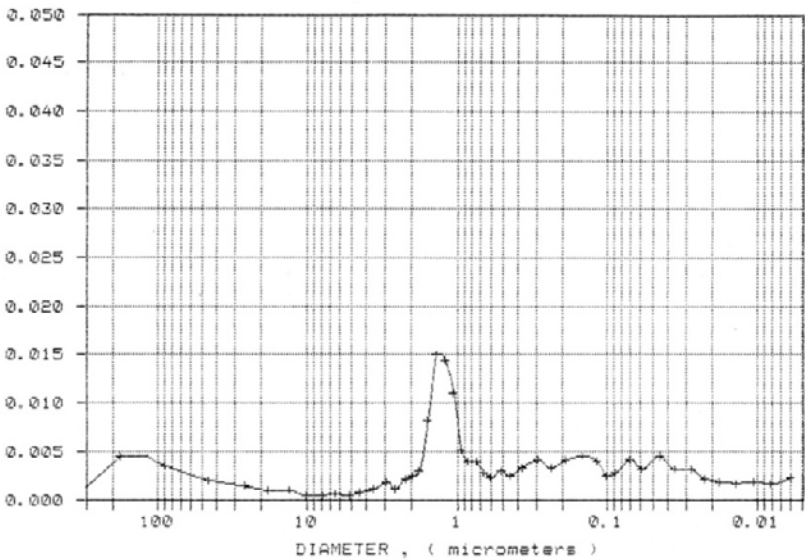


Figure 6: Differential distribution curve for the studied sample.



angle value, the more accurate will be our subsequent calculations. The value of contact angle was assumed to be $\theta = 130^\circ$ and surface tension of mercury $\gamma = 485 \text{ dynes/cm}$.

The cumulative distribution curve is shown on Fig 7. The following results were obtained: total porosity 0.148 mL/g , specific surface $2.843 \text{ m}^2/\text{g}$, median pore diameter (volume) $1.012 \mu\text{m}$, threshold diameter $2.594 \mu\text{m}$.

5.3 Discussion

Dominating range of pores in the MIP results lies between $700 - 2000 \text{ nm}$.

On the other hand, results from DSC indicate the importance of $600 - 1600 \text{ nm}$. Beginning of the spontaneous nuclei growth (2nd stage of transition) is associated with the increase of pressure between water and ice up to 6.29 J/cm^3 (912psi) and penetration of ice into pores of diameter 1590 nm . Further increase of pressure up to 24.93 J/cm^3 (3618psi) leads to penetration of 560 nm pores and marks the beginning of the 3rd stage of transition. Second stage of transition, which is mostly responsible for frost damage, mainly because of considerable increase of pressure over a relatively short period of time, is clearly placed in between these points. Higher volume of pores in this range (approximately 50%) facilitated spontaneous ice growth.

Saturation of samples with water prior to the DSC testing could lead to rehydration and possibly to shifting dominant range of pores towards smaller pores.

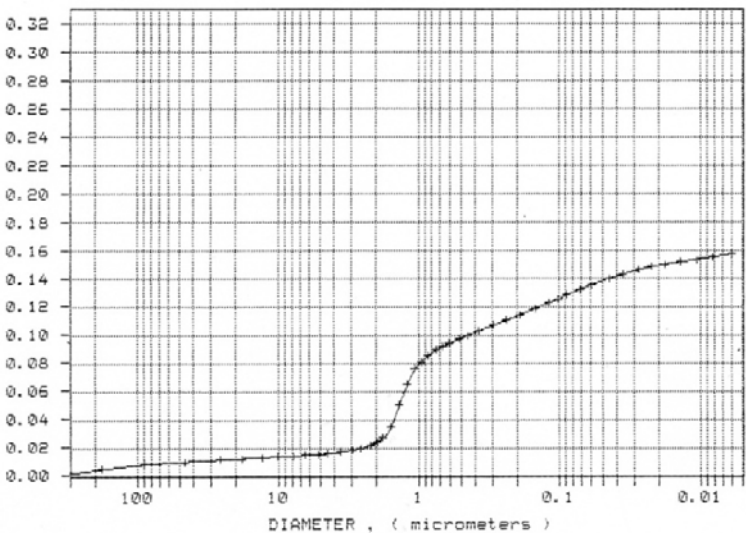


Figure 7: The cumulative distribution curve.



Penetration of mercury under similar pressures leads to much smaller pores being filled in, correspondingly 200 and 50nm. This should be associated with differences in contact angle between mercury-solid and ice-solid. Variation of contact angle due to differences in chemical composition of composites may further complicate analysis.

6 Summary

High percentage of 'ink bottle' shaped pores is always shown by the hysteresis on the mercury intrusion curves. The release of pressure is not accompanied by expulsion of the same volume of mercury as was intruded as the pressure rose. This means that for the mercury volume corresponding with the difference of these values, the porosity model used for the specific surface determination from the porosimetric measurements is inappropriate. This model assumes that the mercury can penetrate into cylindrical shaped pores and capillaries by order of their sizes, starting from the biggest pores and ending with the smallest ones. For a medium with a microstructure satisfying this condition, during the pressure reduction the mercury does not 'tear away'. But if the penetrating mercury was intruded through the 'inlet' into the larger pore it would be retained there. This means that the specific surface is calculated by the computer program with an error and indeed this value might be significantly lower than that from the test report. Unfortunately it is impossible even approximately to estimate this error. The method known from literature can only be applied to the specific samples which meet the condition mentioned above. At this stage an accurate estimation necessitate a change of the porosity model.

The complicated nature of pore structure causes difficulties since their sizes are categorised by only one geometric quantity i.e. the exit diameter of the pore. Nevertheless, it is assumed for analysis purposes, that the pores are open at both ends and have a cylindrical shape. Although according to Diamond [5], the failure of the MIP technique mostly originates from the accessibility effect rather than shape irregularities. It is due to the fact that the Washburn's relation Eq.1 assesses the dimension of a pore at a given pressure, on condition that mercury has accessed that pore. The interior of a sample is accessible only through a chain of pores varying in size and shape. Mature cement pastes contain a large number of randomly distributed segmented capillaries, which are interconnected solely through gel pores.

Another problem is associated with difficulties in determination of surface tension of mercury. One can attempt to correct for this by measuring the surface tension of mercury prior to using it, and after the run has been completed, determine if contamination of mercury in contact with the sample has occurred. This would result in a corresponding lowering of the surface tension.

It should be also stressed that if the samples differ in their chemistry changes in the contact angle should be expected. In such cases, the contact angle should be either measured directly or the pores examined under an optical or electron microscope, to establish the relationship for the actual pore size opening to that measured by mercury intrusion. Problem is even more complex if samples



contain air entraining admixtures with the hydrophobic properties of entrained bubbles. Differences in contact angle in original pores and air entrained bubbles always result in an increased overall volume of pores of very low diameters. Estimation of contact angle is impossible by using standard techniques. It is therefore proposed to adopt more complex approach by simultaneous application of methods such as MIP, DSC and possibly SEM. Qualitative systematic analysis should enable estimation of an error made in pore size distribution measurements.

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Surfology: concrete surface evaluation prior to repair

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Abstract

The study of adhesion of repair materials on concrete structures implies a good knowledge of the influence of concrete surface treatment. The effects of surface preparation technique are rarely clearly described and parameterised: it is consequently difficult to point out the real influence of roughness on adhesion results. A large research project has been realized with regards to the influence of concrete substrate strength and preparation technique efficiency. The surface roughness of concrete has been quantified by means of the projection “Moiré” technique, which is an interferometrical measurement method. Comparison between polished, scrubbed and hydro-jetted surfaces evaluation is presented.

Keywords: concrete, surface, micro-cracking, NDT, roughness.

1 Introduction

The study of adhesion of repair materials on concrete structures implies a good knowledge of the influence of concrete surface treatment (Courard et al. [1]). Many authors describe the influence of the surface preparation technique on the superficial cohesion of concrete (Bissonnette et al. [5]) or the adhesion (Garbacz et al. [6]). However, the effects of surface preparation technique is never clearly described or quantified: it is consequently difficult to point out the real influence of roughness on adhesion results, as this is disturbed by other effect like microcracking or bond coating (Bissonnette et al. [5]). A first step was made by using mechanical profilometry to differentiate polished and sandblasted concrete surfaces (Courard et al. [2], Courard and Nélis [3] and Courard [4]). This



technique is very accurate for investigations in laboratory, on a limited surface area. If Quality Control is requested or if it is impossible to core samples from the site, other procedures should be followed. That is the reason why optical analysis has been developed (Perez [7] and Perez et al. [8]) in order to analyse larger surfaces. Some considerations about the two techniques are given hereafter.

2 Description of materials and surface preparation

Different types of surface preparation techniques were investigated: scarifying (SC), high pressure water jetting (HPW) and polishing (PTW) (Courard et al. [2]). The visual observation of the concrete surfaces indicates that the high pressure water jetting technique induces a particular texture characterized by large waves mostly parallel to the water flow while scarifying will generally induce some oriented macro-roughness (grooved surface) (Fig. 1).

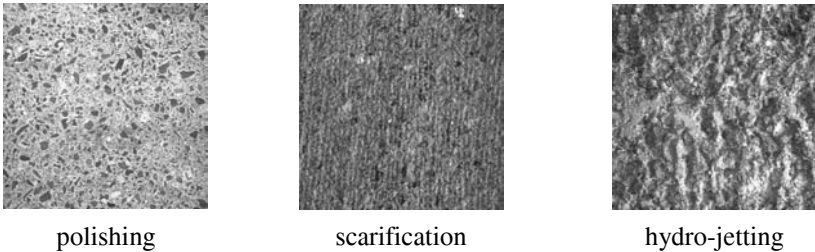


Figure 1: Different types of concrete surface preparation.

3 Scale effect and roughness parameters

After treatment, concrete surfaces present fractal topography. As for any fractal object, it is possible to break up this surface or this profile in a sum of under-profiles. Each under-profile can be differentiated in terms of wavelengths; there is however no limit or precise criterion to validate the choice of decomposition method (Fig. 2). As the two surfometry methods have different resolutions, they make it possible to reach complementary scales of topography.

The method with mechanical stylus and high resolution reaches two scales of roughness named: roughness (R) and waviness (W). The optical method, with a resolution of 0.200- μm , makes possible to reach two higher scales named meso-waviness (M) and form (F).

A series of parameters make it possible to break up a total wave into two waves. The determination of surface parameters (Table 1) is realised on the basis of the mean line as a reference line (Courard [4]). Interesting information from surface analysis is the bearing ratio (Courard and Nélis [3]) and the Abbott's curve (Fig. 3).

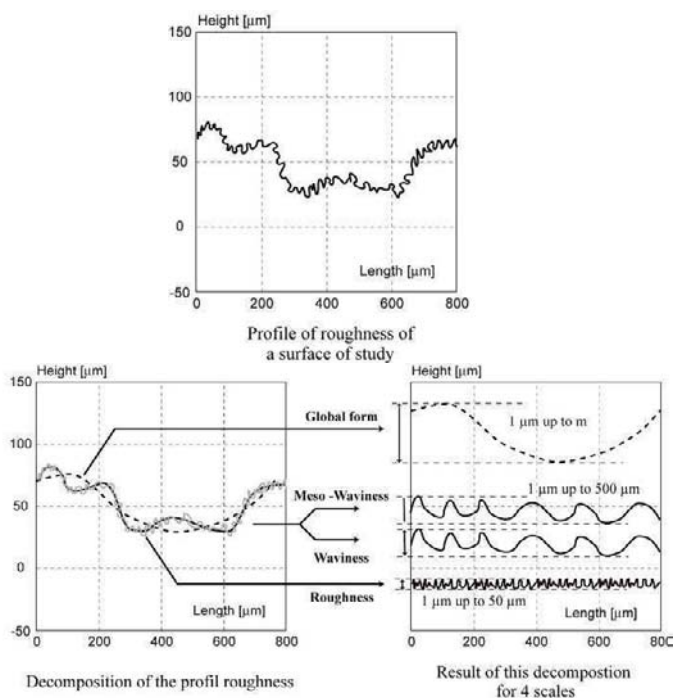


Figure 2: Scale effect on profile decomposition.

Table 1: Profile amplitude and statistic parameters.

Parameter	Definition
X_t	total height of the profile
X_v	maximum depth of the profile (holes)
X_p	maximum height of the profile (peaks)
X_a	arithmetic mean of the deviation of the profile from the mean line
X_q	quadratic mean of the deviation of the profile from the mean line
S_k	skewness of surface height distribution
S_m	mean spacing between profile peaks at the mean line, measured over the assessment length

The surface parameters defined on the basis of this curve let us to analyse not only the depth of the holes but also the shape of the profile: C_F represents the depth of the profile, excluding high peaks and holes; C_L is the relative height of the holes and C_R the relative height of the peaks.

The C_F parameter gives an idea of the flatness of the surface: the lower it is, the more flat the profile is. Parameter C_L gives an idea of the volume of voids, beneath the mean line of the profile, which could be fulfilled by the bond coat or the repair material.



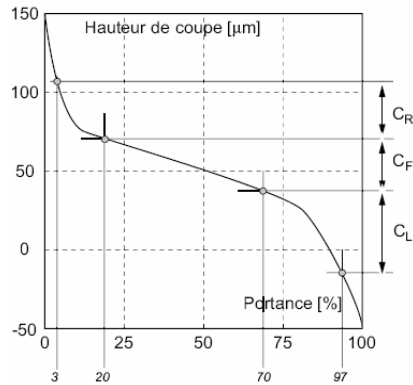


Figure 3: Abbott's curve (curve of bearing ratio) and curve parameters.



Figure 4: Stylus walking on the concrete surface.

4 Evaluation of the profile roughness by mechanical surphometry

The technique has been already described in details (Courard and Nélis [3]) and is only here rapidly remembered. A stylus is walked along the surface to be analysed and the profile is continuously registered (Fig. 4). The total registered profile is filtered in high and low frequencies in order to separate roughness and waviness, respectively (Courard and Nélis [3]). Filtering will reduce to 50% of the initial amplitude of a wave when its wavelength corresponds to the filter characteristic.

5 Evaluation of the profile roughness by opto-morphometry

The projection “moiré” technique is an interferometrical measurement method. The “moiré” phenomenon appears when two networks of light rays, made of equidistant lines – alternatively opaque and transparent –, are superimposed.

The technique of identification of relief is based on the deformation's measurement of a parallel fringes pattern projected on a surface (Fig. 5). The moiré's fringes are similar to level lines representing the variations height of the object. By projecting a network of parallel fringes on a plane surface, this network will not be deformed; however, when projected on an unspecified form, this same network will be deformed according to the level of rise in this form (Fig. 5).

Moreover, there is a relation between rise in the form and distance between each level line.

The measurement accuracy (Perez et al. [8] is directly related to the density of the fringes network and the capacity of differentiation of the network by the system of image analysis (Fig. 6).

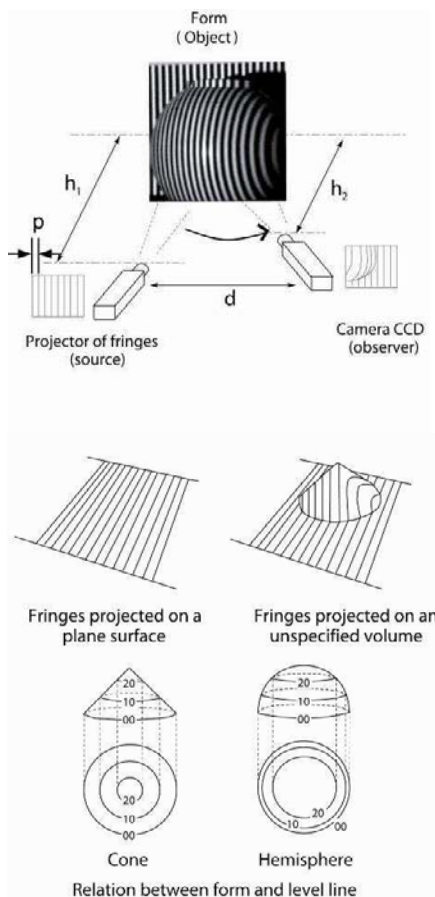


Figure 5: Principles of the Moiré projection technique.





Figure 6: Testing system with camera CCD and parallel fringes pattern on surface.

Because of the vertical resolution of the device, it is impossible, in this case, to separate roughness from waviness. A profile obtained through this approach will consequently give the description of meso-waviness and global form. A program – RugoDS – based on MatLab 7.0 (Courard et al. [9]) permits to process numeric data from representation of Moiré projection in order to get surfometric image of the profile (Fig. 6) as well as all the amplitude and statistic parameters before and after filtration (Table 2).

6 Results

6.1 Mechanical evaluation

A first evaluation by mechanical profilometry has been realized by means of a stylus with diamond sphere radius of $6\ \mu\text{m}$. The length of measurement was 8 mm and the filter used to separate roughness from the profile was fixed to 0.8 mm. Three profiles were registered on one sample of each kind of preparation; each profile on the sample was made in different directions. A second measurement was made with stylus of 79-mm long and a diamond of 1.5 mm radius, in order to point out waviness. The length of the measurement was enlarged to 30-mm or more. The filter was again chosen at 0.8-mm and the filter to separate shape from the profile was 16mm (two times the dimensions of the aggregates). Observation of the values of the roughness amplitude parameters (Table 2) clearly shows that R_a , R_q , R_t parameters are between 1.5 and 3 times smaller for the polished concrete profile than for water jetting and scarification,



and that the values of amplitude and statistical roughness parameters are equal for water jetting and scarification.

It is here confirmed that the surface treatment technique has no major influence on the micro-roughness (“high frequencies waves”) of the profile. However, the differences are more effective for waviness parameters (Fig. 7).

Table 2: Waviness (W) and roughness (R) parameters for mechanical evaluation (μm).

<i>Treatment</i>	Polishing	Water jetting	Scarification
Wa	6	420	127
Wp	13	1003	346
Wq	9	501	158
Wv	47	923	445
Wt	60	1926	791
Ra	5	14	15
Rq	7	17	19
Rt	70	96	102
C _R	4	152	412
C _F	10	228	827
C _L	14	231	537

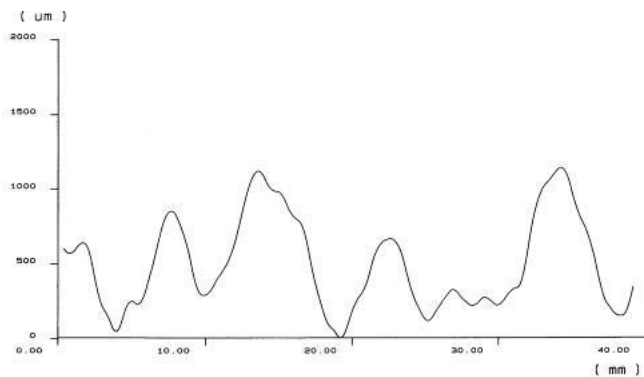


Figure 7: Waviness profile after hydro-jetting surface treatment.

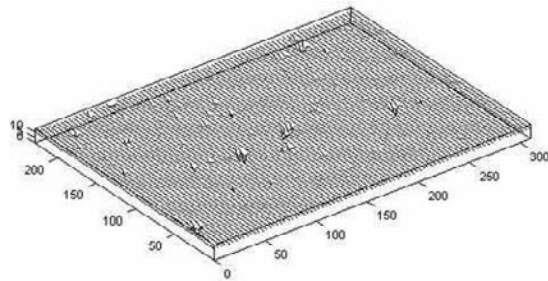
6.2 Opto-metrical evaluation

As the same way to mechanical evaluation, optometric topography evaluations have been realized. Fig. 8 presents the statements of the optical measurements. At this scale, water jetting seems to induce the largest “roughness”. Polishing and scarification are quite similar.

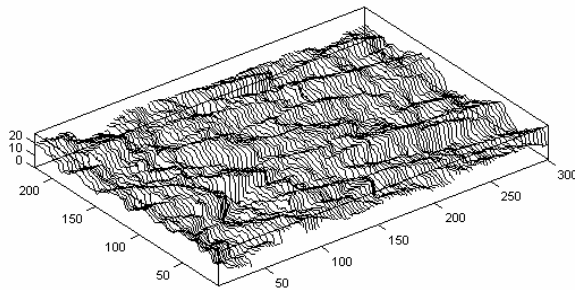
It is probably due to the bubble effect at the surface which gives roughness aspect.



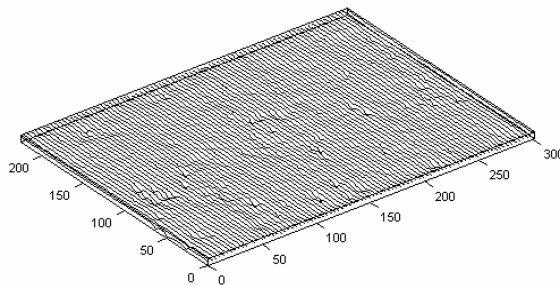
Observation of the values of the roughness amplitude parameters (Table 3) clearly shows that M_a parameter is 20 times more important for hydro jetting than for scarification and polishing. At this scale, the other treatments induce smooth surface. Polishing gives the less rough surface. The major part of apparent roughness of polishing surface comes from the bubble.



(a) *polishing*



(b) *hydro jetting*



(c) *scarification*

Figure 8: Meso-waviness profiles (mm).

7 Conclusions

The following conclusions may be reached from the present investigations. For mechanical analysis technique, one may consider that:

stylus: because of the shape of the stylus, it is impossible to make measurements on very rough surfaces prepared by hydro-jetting for example;

air bubbles: some of the air bubbles in concrete are so large that the stylus falls and the measurement is interrupted. That means that the selection of the zone to be investigated is very important;

dimensions: this measurement is very high time consuming and it is the reason why the surface of investigation is limited. Moreover, this system is not usable on site.

Table 3: Global form (F) and meso-waviness (M) parameters for opto-metric evaluation (mm).

Treatment	Polishing	Water jetting	Scarification
Fa	0.137	0.358	0.326
Ft	4.1	10.8	12.6
F Sm	129	85.3	102.3
Ma	0.169	2.85	0.315
Mt	19.7	27.8	10.2
M Sm	15.3	36.5	22.5
C _R	0.30	4.65	0.41
C _F	0.29	5.76	0.55
C _L	0.35	5.71	0.81

Considering the use of opto-morphometry technique for the concrete surface roughness characterization, it is important to point out that:

- all the amplitude and statistic parameters are higher for hydro-jetting than for scabbling and polishing at the end which is the equivalent of aggressiveness of treatment. Decreasing values are obtained for scabbling and polishing, respectively;
- for each profile, there are more high peaks than deep valleys. The highest asymmetry is present for scabbling profile;
- opto-morphometric technique allows one to analyze large surface areas (1000cm², with horizontal resolution of 500μm and vertical resolution of 300μm);

But it remains that the filtration process has a major influence on results and profiles; it should be clearly discussed, as well as the accuracy that is needed for roughness profile representation, with regards to adhesion.



Acknowledgements

This research project was financially supported by the Government of Québec (MRI), Canada, the Government of Poland and the Regional Government of Wallonia (DRI), Belgium.

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Development of new approaches to moisture content measurement for building materials

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Abstract

The measurement of moisture in building materials has been of importance to building professionals for many years to aid the diagnosis of the nature and cause of building defects. Measurements of moisture content of the building fabric are often carried out on elements where there is uncertainty about the material composition, uncertainty about the dimensions of individual components, and where there is an existing problem there can be some degradation of the materials themselves. Accurate measurements of the moisture within such walls present many challenges.

Research has been undertaken to evaluate the practical application of three relatively new techniques in building science: dual probe heat pulse method; time domain reflectometry; and more sophisticated electrical approaches. Although these techniques have been used in different sciences, the application to actual buildings can present a challenge. This paper details the development of these techniques from theoretical concept through to a practical technique successfully applied for real measurements. The techniques have been calibrated against X-ray absorption measurements using materials of well-defined properties such as sandstone and autoclaved aerated concrete. This calibration allows absolute measurements of moisture content to be made. Finally the paper explores the practicalities of using these approaches for in-situ measurements and identifies particular opportunities and limitations for future application.

Keywords: moisture content, practical application, time domain reflectometry, heat pulse measurements, electrical measurements.



1 Introduction

The diagnosis and remediation of many building defects requires measurement of moisture in building materials. Moisture content measurements of building fabric are often carried out on elements where there is uncertainty about the material composition, uncertainty about the dimensions of individual components, and where there is an existing problem there can be some degradation of the materials themselves. Accurate measurements of the moisture within such walls can present many challenges.

Research has been undertaken to evaluate the practical application of three relatively new techniques: dual probe heat pulse method; time domain reflectometry; and more sophisticated electrical approaches. Although these techniques have been used in different sciences, the application to actual buildings can present a challenge. This paper reports the relative merits of the different techniques and comments on their scope for practical application.

2 Practical limitations of site measurements

Site measurements techniques should give consistent results and be relatively simple to use. Although the main commercial techniques used for site measurements have changed relatively little in the last few decades, some research tools have been examined for potential site applications. For example, the development of portable NMR systems [1] has been investigated. As with commercial techniques, there are associated limitations with research techniques applied to site measurements. These limitations are associated with the building itself and with the measurement method. These are described in more detail below.

2.1 Building limitations

It is rare for the exact design and material composition of a building to be known and its properties catalogued. Although an experienced surveyor may make judgements about the construction of a building, there will often be variation. This is particularly true for old stone buildings.

Within the laboratory environment, equipment can be calibrated for measurements of specific materials, achieving high measurement accuracy. Preconditioning of samples within the laboratory can achieve defined initial moisture contents and identifiable moisture histories. Samples can be produced of known homogeneity and dimensions, whereas on site the nature of the building fabric is typically less accurately described. Uncertainty in the materials used for the construction gives increased errors associated with the measurement. There is also the potential for materials to be present (for example salts), which may not be visible, and which interfere with some types of measurement. The accuracy that can be realised with site measurements will be significantly less than that which can be achieved using the same technique in the laboratory.



2.2 Technique limitations

Each individual technique has particular strengths and weaknesses. The following is an indication of the nature of some of the weaknesses with respect to site application:

- Duration: The length of time taken to make a measurement may make the technique unsuitable for rapid assessment of a large area, or for long term monitoring of a building.
- Destructive Nature: Holes are required for some techniques to either remove material, or insert a probe. This can be unsuitable for important historic materials.
- Susceptibility to Interference: The presence of metal components or salts close to the measurement location can strongly affect some techniques.
- Contact Issues: The quality of contact between a probe and the material being measured can be very important for some techniques. Poor surfaces, treated surfaces, or difficulties installing probes may lead to inaccurate measurements.

3 Techniques investigated

Techniques used in other fields of science are being developed for moisture measurement in buildings. Two approaches have been identified, which may have significant development potential for building applications: The Dual Probe Heat Pulse Method [2], and Time Domain Reflectometry [3] (TDR). A third approach being investigated is the development of a more sophisticated instrument based on the measurement of electrical resistance [4]. The theory and performance of the techniques is described in detail elsewhere [2, 3]. These techniques have been successfully applied in laboratory conditions by the authors.

3.1 Time domain reflectometry

TDR measures the transmission time of a signal along parallel stainless steel waveguides and its subsequent re-reflection to give a measurement of the relative permittivity (ϵ_r) of the surrounding media, which is directly correlated with moisture content. Equation (1) relates the signal transmission time (t), with the relative permittivity, the length (L) of the waveguides and the velocity of light (c) in a vacuum.

$$t = \frac{2L\sqrt{\epsilon_r}}{c} \quad (1)$$

Each measurement takes little time and has no significant impact on the substrate so TDR can monitor changes of moisture content over a long period.



However, the transmission time for a signal and its reflection is extremely short so high precision quality electronics are required to minimise systematic error.

Probes can be calibrated with liquids of defined dielectric properties to ensure that accurate measurements of the relative permittivity can be achieved with the probes. This is strongly related to the moisture content of the material, and some of the most promising models for calibrating the relative permittivity stem from the work of Lichtenecker [5], who showed that the relative permittivity of a medium with N phases could be expressed by Equation (2).

$$\varepsilon_r = \left(\sum_{i=1}^N \theta_i \varepsilon_i^\alpha \right)^{1/\alpha} \quad (2)$$

where θ_i is the volume fraction of phase i , ε_i is the permittivity of phase i , and α is a constant between -1 and 1.

Equation (2) can be rearranged to describe a porous material which has a solid matrix, and pores that may be filled with air or water. This has been utilised by Plagge [6] to give Equation (3).

$$\varepsilon_r = \left[\theta \varepsilon_w^\alpha + (1 - \phi) \varepsilon_s^\alpha + (\phi - \theta) \varepsilon_g^\alpha \right]^{1/\alpha} \quad (3)$$

where ε_w is the relative permittivity of water, ε_g is the relative permittivity of air (≈ 1), ε_s is the relative permittivity of the solid matrix material, θ is the moisture content of the material and ϕ is the porosity of the material (open porosity for this application). To use this function for material measurement a value for α and ε_s must be determined from regression analysis of measurements of relative permittivity over a range of known moisture contents. Clearly some precalibration is required for accurate absolute moisture content measurements to be made.

For application to building materials TDR probes with two parallel waveguides have been developed. In soil sciences triple waveguide probes have become common, but for practical considerations associated with limitations of precise drilling of holes to accommodate waveguides a dual waveguide configuration has been adopted. Probes with waveguides of various diameters have been investigated and found to work in laboratory experiments. However, it has been observed that significant wear of drills and associated practical difficulties can occur when installation is attempted into some granular masonry materials such as sandstone. To help achieve realistic installation at a repeatable quality of contact, probes with waveguides of diameter of 4mm were adopted. This increased diameter is easier to install using stiffer masonry drills, which are able to drill the sandstone in the dry state without overheating of the drill bit. The contact quality between waveguide and the building material is important, and affects the calibration between absolute moisture content and measured relative permittivity.



3.2 Dual Probe Heat Pulse Method

The Dual Probe Heat Pulse Method uses a dual element probe which has a heating needle and a temperature sensing needle at a precise spacing. A short duration pulse of electrical energy (typically 10 seconds in duration) is applied to a wire within the heating needle. The temperature sensing needle, incorporates a thermocouple and measures the maximum temperature rise in the material at the set distance from the heating needle. This temperature rise, combined with the volumetric heat capacity of the dry material allows the moisture content to be determined. The technique is effectively insensitive to the presence of salts in the material being measured. If the physical properties of the substrate are not known, the relative changes in moisture content can still be accurately determined. The need for the substrate to cool back down to background levels after a reading means that at least one hour is needed between readings.

3.3 Electrical techniques

Electrical resistance or conductivity techniques are based on the principle that the conductivity of a material is dependent on its moisture content. In building investigations these techniques rely on the current being carried through the material by the ions in the pore solution and consequently are unsuitable for materials that exhibit electronic conduction. It follows that porosity is a major influence in the electrolytic conductivity of the material and hence calibration procedures are required for each material in order to relate the resistivity to the moisture content. Some materials have been widely investigated, most notably wood for which calibration tables are available for a wide range of species [7].

Basic electrical resistance or conductivity methods offer a simple low cost strategy for measuring moisture in building materials. The most basic systems operate by applying a d.c. voltage between two probes and measuring the resultant current. Although commercially available these devices offer very poor performance due to polarisation and electrode contact issues. Better performance is achievable using an a.c. excitation potential or current to overcome electrolytic polarisation of the probes. However, electrode contact problems may still be present.

The technique investigated in this study uses a constant a.c. current applied to the material under investigation by two probes. The resultant potential difference is measured with a lock-in amplifier and a data logger. Simple stainless steel anchor bolts are used as probes, which give good contact with the material.

4 Calibration of test measurements

All of the experimental techniques investigated are capable of producing a relative measurement of moisture content, by which the variation of moisture content with time can be assessed. However, to achieve accurate measurements of the absolute moisture content requires detailed calibration of probes in each



material. In order to achieve this, a laboratory X-ray absorption method was used as the reference method.

The equipment (Figure 1) measures the absorption of X-rays which may be scanned in two dimensions over a sample [8]. Collimators placed in front of a Cadmium-Zinc-Telluride high-resolution detector can be used to define the spatial resolution of the X-ray system to less than one millimeter, with the positioning of the mechanical scanning system being repeatable to within $\pm 0.01\text{mm}$. As a measurement at each point requires only a few seconds, transient changes can be evaluated in real time. A dedicated PC allows fully-automated measurement, data collection and results analysis, with measurements being carried out in pre-determined patterns. Sequential measurement of a number of different samples mounted within the equipment is possible.

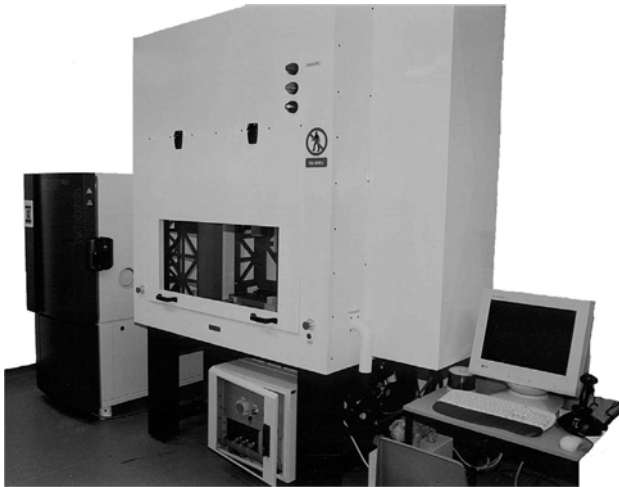


Figure 1: The X-ray facility at Glasgow Caledonian University.

The four vertical faces of a sample are covered with a water impermeable material, e.g. cling film or aluminium foil - it may then be assumed that the moisture distribution across the sample is reasonably uniform, since evaporation of moisture at the vertical faces is prevented. The sample is then mounted with its base on spacers in a container within the X-ray chamber.

A reference ('dry') scan is first made of the sample. The scans correspond with the location of the probes inserted for calibration. Water is then introduced to the base of the sample. Subsequent scans of the moist material are made in precisely the same positions as the reference scan. The Beer-Lambert law is applied to determine the moisture content as a function of the ratio of the X-ray absorption of the wet and dry material. For example, the volumetric moisture content may be expressed as follows:

$$\theta = \frac{\ln\left(\frac{I_{dry}}{I_{wet}}\right)}{d\mu_w\rho_w} \quad (4)$$

where I_{dry} is the transmitted X-ray intensity of dry sample, I_{wet} is the transmitted X-ray intensity of wet sample, d is the thickness of the sample (m), μ_w is the mass attenuation coefficient of water and ρ_w is the density of water.

Introduction of a water source to the underside of the block of material in the X-ray apparatus allows the wetting, and upon removal, drying, behaviour of the material to be observed. By undertaking simultaneous measurements of the X-ray apparatus and the moisture sensor the calibration of sensor output against moisture content can be established through a long period of measurements. Full details of the calibration of the sensors has been described elsewhere [2, 3]. Unless explicit information is available to describe the material in detail, a calibration function is needed for each material to be measured. An example of a calibration function is shown in Figure 2, which relates the output from one of the improved electrical techniques to the moisture content within sandstone.

Polynomials, or other calibration functions, for example Equation (3) in the case of TDR, can be fitted to the calibration data to allow signal output to be interpreted in terms of absolute moisture content.

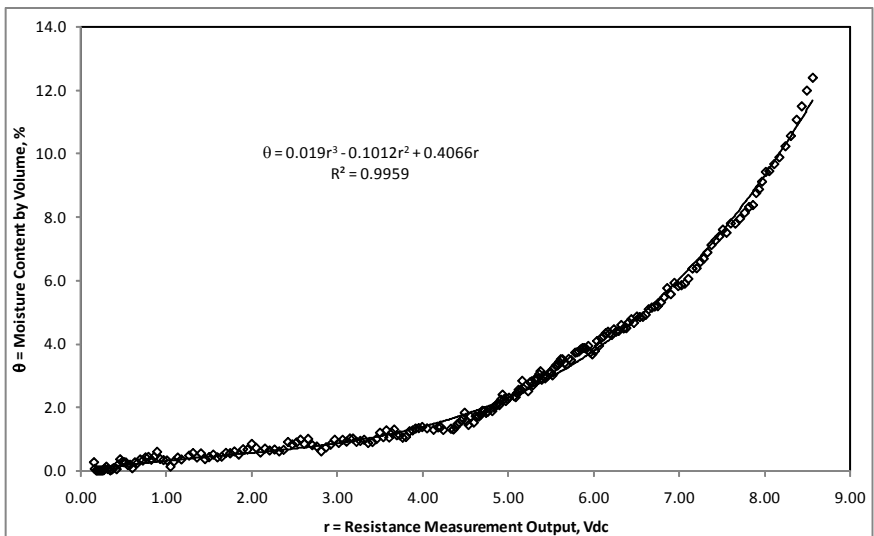


Figure 2: Calibration of electrical resistance measurement in comparison with moisture content measured by the X-ray absorption method.



5 Practical application

The experience of using these techniques and application to a sandstone test wall is given below.

5.1 Installation

The original intention of the research had been to apply the techniques to a real wall on site. However, the logistics of keeping 3 separate systems installed for a period of time without the mass of cabling and logging equipment posing a nuisance to occupants was thought to be difficult and eventually a laboratory based practical application was adopted. A stone wall was available for testing in an environmental chamber which was a closely controlled environment to which the public had no access. In addition the authors were able to intervene by introducing effective flood conditions to the base of the wall to induce changes in the moisture content of the wall, and therefore allow the dynamic responses of the different sensors to be compared.

The intention of the installation was to mimic the conditions we would expect to see in a typical building under investigation, and as a consequence hardware for installing probes was limited to devices that could be easily carried and could be powered from mains electricity. Sophisticated workshop cutting techniques are unlikely to be ever available for drilling on site.

5.1.1 Time domain reflectometry

Installation of the probes into the test walls required the wall surface to be made flat using an angle grinder. An uneven stone wall surface will be the worst case for monitoring, however, no significant problems were encountered smoothing the surface. Drilling the twin holes for the waveguide used a template to ensure correct spacing was achieved for probe insertion. Holes were produced to the required tolerance to enable satisfactory fitting of the probe into the wall.

The decision to use larger 4mm diameter waveguides for the TDR measurements made the installation of the probe far easier in sandstone. Time and attention to detail was needed to install the probe correctly, however the installed probe has been found to be responsive to the changing conditions of the test wall. Relative moisture contents can be inferred directly from the measured relative permittivity, and because the material has been tested in the laboratory against dedicated x-ray measurement equipment, a calibration curve can be used to assess absolute moisture content.

5.1.2 Dual probe heat pulse method

As with the TDR, the installation of the probes required that a flat surface be achieved with the sandstone test wall. The diameter of the probes used with this approach is just 1mm, necessary for the technique to work effectively. These small holes require a specialist drill and drill bit. A template was used to locate exactly the position of the holes. Problems were encountered trying to drill the dry sandstone with the drill head melting. Wetting of the material before and during drilling allowed holes to be successfully drilled, however, a number of



drills were snapped in the process. The probes were installed into the material with a thermal paste used to eliminate any contact issues between the probe and the sandstone.

The installation of such fine probes into an abrasive material like sandstone is difficult. The need to add water as a coolant during drilling was unavoidable, but changes the moisture content and history. Although the authors successfully installed the probes into the sandstone wall, the technique would be better suited for use in materials that are easier to drill, e.g. autoclaved aerated concrete.

5.1.3 Electrical techniques

Installation of sensor points into the sandstone wall were achieved with the least difficulty of all three techniques. Pilot holes of 6mm diameter were drilled into the sandstone and stainless steel expanding bolts were fixed into the material to achieve a good electrical contact with minimal risk of corrosion. Once in the electrodes are extremely difficult to remove so it is important to ensure that they are positioned correctly.

5.2 Results from test walls

The measurements of absolute moisture content determined using calibration functions and the output from the three sensor types on the sandstone wall are shown in Figure 3.

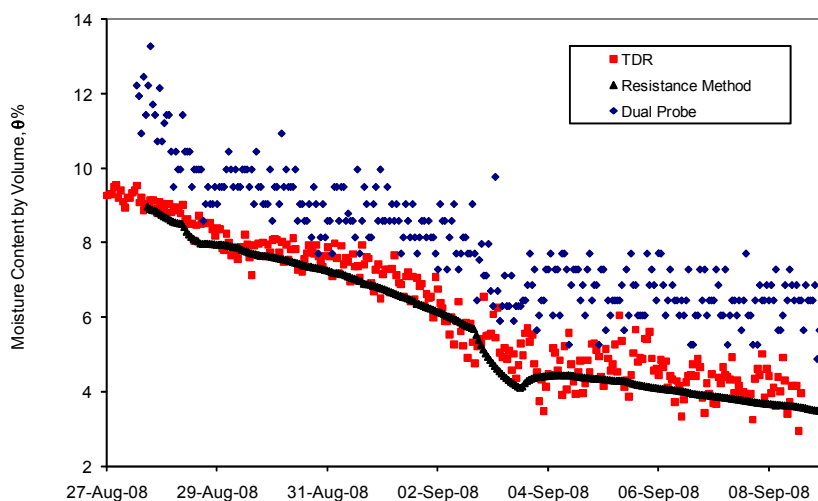


Figure 3: Absolute measurements of moisture content made for a stone test wall in an environmental chamber.

All three sensors show the same overall trend in the measurements of the absolute moisture content within the material. Some differences would be anticipated between the sensors as the volume of material measured differs significantly. For example, the TDR measures a volume of material up to 65mm



deep into the wall, whereas the dual probe technique measures the response much closer to the external surface of the wall. As the test wall is able to dry from all surfaces, there may be a difference between the moisture content within the core of the wall and that within the surface layers.

Each techniques has produced plausible measurements of the absolute moisture content, and so have the potential to be useful for the long term monitoring of the moisture behaviour of buildings or components.

6 Conclusions

Attention is needed when developing new moisture content measuring techniques for building materials to ensure that easy and consistent installation is possible. The quality of contact between measurement probes and the building fabric is important to achieve consistent measurements. Installation of probes on site with relatively limited mechanical tools requires both skill and a planned approach; it is therefore helpful if this practicality is considered at the design stage of the technique. Delicate and intricate probes require significant preparation to be installed into a material, and as found with the dual probe, some materials are extremely difficult to work with.

As the majority of existing laboratory based techniques with high accuracy are not portable, the development of research tools for site use is an important challenge for building physics. If research techniques are ever to become a mainstream measurement option for building professionals, they need to be able to be installed to a high standard with minimum effort.

All three techniques have shown promise in monitoring the test wall, although as noted above, the dual probe took an excessive amount of time to install in sandstone, its application may be better suited to other substrates.

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Cement-based composites for structural use

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Abstract

Reactive Powder Concrete (RPC), with compressive strength higher than 200 and up to 800 MPa as well as flexural strength higher than 60 and up to 150 MPa, at the moment potentially represents a new material for structural use in building and engineering in general, even though its application fields have not yet been well defined. RPC can be also considered as the ultimate step in the development of high performance concrete, even though its classification as a concrete material may be not quite proper, based on its microstructure and mechanical behaviour. Also, its production technology for higher performance, by pressure moulding as well as extrusion, takes it even further from a common concrete. The wide range of achievable strengths for RPC requires careful design of the material, strictly related to the structural design and appropriate to the specific project, with maximum cooperation between materials engineering and structural engineering. For this, RPC can be used at best by developing new shapes and structural types specially designed for it. In this paper potential application of RPC for structural elements is exploited and discussed in comparison with other materials typically used for structural application, with an eye to sustainability.

Keywords: cement-based composite, reactive powder concrete, structural use.

1 Introduction

Historically, new materials are related to the shape and development of new structural concepts. One need only think of the megalithic structures, in which stone prevented a span higher than 5 m, until the introduction of pozzolanic cement, used to join bricks and stones, which allowed the building of high spanning arch structures, covering up to about 50 m, like the Pantheon's dome in Rome.



Further evidence is provided by steel as a structural material, which became available between the eighteenth and the nineteenth century and whose high tensile strength permitted sweeping changes in building technology by allowing higher span beams, frame structures, truss girders, suspended structures, tall buildings, and so on.

In actual construction technology, structures are mainly built by concrete, timber or steel; however, new composite materials, reinforced by polymer, metal, glass, or carbon fibres, are in prospect of appearing, giving rise to new interesting practical applications owing to their improved mechanical performance [1].

A new general category of so-called CBC (Chemically Bonded Ceramics) materials resulted from recent research aimed at the attempt to reduce microporosity of cementitious materials. The term CBC attributed by Roy [2] to this new class of cementitious materials points out, beyond the chemical nature of the involved bond, the inorganic, non-metallic character of the material, which turns ceramic because of the particular processes involved in its manufacturing.

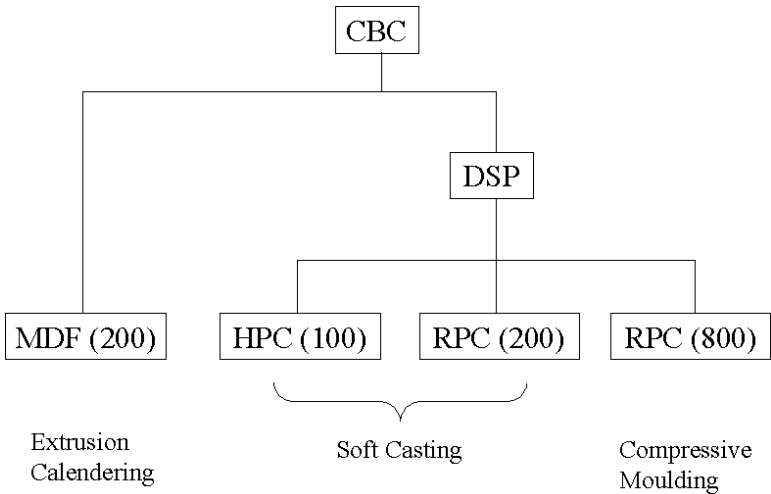


Figure 1: Outline of innovative cementitious materials and their related manufacturing process. Numbers enclosed in brackets, expressed as MPa, stand for compressive strength of HPC or RPC and flexural strength of MDF.

The CBC materials (Fig.1) can be grouped in two large categories [3]: MDF (Macro Defect Free) and DSP (Densified with Small Particles) materials, the main difference being the role played by the polymeric component in the manufacturing process. In MDF materials [4] fully hydrosoluble polymers play a very important role in order to significantly change the rheology of the cement paste and so to obtain a dough material, able to be extruded or rolled. In DSP materials, instead, sulphonated or acrylic polymers make possible either the compressive moulding of wet powders or the soft casting of flowable mixtures.

Among the DSP materials, RPC (Reactive Powder Concrete), with compressive strength higher than 200 and up to 800 MPa as well as flexural strength higher than 60 and up to 150 MPa, at the moment represents potentially a new material for structural use in building and engineering in general, even though its application field has not yet been well defined. RPC can be also considered as the ultimate step in the development of HPC (High Performance Concrete), even though its classification as a concrete material may be not quite proper based on its microstructure and mechanical behaviour.

Also, its production technology, by pressure moulding as well as extrusion, takes it even further from a common concrete. The wide range of achievable strengths for RPC requires careful design of the material, strictly related to the structural design and appropriate to the specific project, with maximum cooperation between materials engineering and structural engineering. For this, RPC can be used at best by developing new shapes and structural types specially designed for it.

As for any new building material, one of the main issues in RPC initial use is represented by its high production cost, even if economy can be achieved in the long term by lower maintenance cost and longer service life, as a consequence of the extraordinary durability of RPC.

Another obstacle to remove is to consider RPC as an ordinary concrete by measuring its performance on traditional structures in which RPC strength levels are not required. This means that new shapes and structural typologies must be developed for this material in order to maximize its performance.

Within this framework, the paper presents the experimental results obtained by the mechanical characterisation of RPC prepared in the laboratory, and, based on these data, exploits its use for structural applications in comparison to other typical structural materials.

2 RPC mixture proportions and experimental approach

The achievement of DSP materials is based on combined use of water-soluble polymers and ultra-fine ($\leq 0.1 \mu\text{m}$) solid particles, which mainly consist of amorphous silica. The role of water-soluble polymers is to improve the rheological behaviour of cement mixtures with a very low amount of water. The role of ultra-fine silica particles is to reduce interstitial porosity among cement grains and to ensure the formation of calcium hydrosilicates by reaction with hydrolysis lime from cement hydration.

The ultimate goal is to produce easily formable materials through the soft casting technique in addition to the compressive moulding technique. By this method, even large sizes and complicated shapes may be produced, also by using extremely flexible reinforcing fibres (polymeric or amorphous cast-iron-based), instead of ordinary steel fibres.

In Table 1, typical mixture proportions of differently prepared RPC [5] are reported together with the achievable mechanical performance. However, being satisfied with not an ultimate performance, in this work a different aim was pursued: to obtain typical performance of RPC 200 by using in the mixture easily



Table 1: RPC mixture proportions, processing treatment and related mechanical performance.

<i>Ingredients [kg/m³]</i>	RPC	RPC 200	RPC 600	RPC 800
Portland Cement	955	1000	1000	1000
Silica Fume (18 m ² /g)	229	230	230	230
Fine Aggregate (150-400 µm)	1051	1100	500	-
Very Fine Quartz Sand (diameter 10 µm)	-	-	390	390
Amorphous Silica (35 m ² /g)	10	-	-	-
Superplasticizer	13	19	19	19
Steel Fibres (L = 13 mm, d = 0.18 mm, L/d = 72)	191	175	-	-
Micro-Fibres (L = 3 mm)	-	-	630	630
Metal Aggregates (diameter < 100 µm)	-	-	-	490
Water	153	190	190	190
<i>Treatment</i>	RPC	RPC 200	RPC 600	RPC 800
Compressive Stress (on the fresh mixture, MPa)	-	-	50	50
Curing Temperature, °C	20	90	250-400	250-400
<i>Mechanical Performance</i>	RPC	RPC 200	RPC 600	RPC 800
Compressive Strength [MPa]	200	230	680	810
Flexural Strength [MPa]	50	60	45	140
Elastic Modulus [GPa]	50	60	65	75
Fracture Energy [J/m ²]	20000	40000	12000	20000

available raw materials as in common practice for precast concrete. In this way, a cement type CEM II/A-L 42.5 R was used instead of CEM I 52.5 R as usual in RPC mixtures. Moreover, a limestone instead of quartz aggregate was used, which was also coarser (0.15-1 mm) than usual (150-600 µm). Finally, a lower quality black type silica fume was added. In this way, mechanical performance will remain a bit lower while promoting higher sustainability, in any case much higher than ordinary concrete.

According to this approach, the influence of an easily attainable thermal treatment, such as 24 hours air curing at 160°C, on the mechanical performance of this mixture was also evaluated. The thermal treatment was applied on demoulded H-shaped specimens after 1 day's casting. The two RPC materials in this way obtained are later on labelled RPC 200-a (without thermal curing) and RPC 200-b (thermally cured) respectively, notwithstanding that a compressive strength of 170 MPa was achieved instead of 200 MPa because of the change in the specification of the raw materials.



The mixture proportions of the RPC materials prepared for this work are reported in Table 2 together with the experimental results of the tests performed on them.

Table 2: Mixture proportions, processing treatment and related mechanical performance of laboratory prepared RPC 200 materials.

<i>Ingredients [kg/m³]</i>	RPC 200-a	RPC 200-b
CEM II/A-L 42.5 R Cement	960	960
Silica Fume (18 m ² /g)	250	250
Limestone Aggregate (0.15-1 mm)	960	960
Acrylic-based type Superplasticizer	96	96
Brassed Steel Fibres (L/d = 72)	192	192
Water	240	240
<i>Treatment</i>	RPC 200-a	RPC 200-b
Curing Temperature, °C	20	160
<i>Mechanical Performance</i>	RPC 200-a	RPC 200-b
Compressive Strength [MPa]	150	170
Flexural Strength [MPa]	33	34
Tensile Strength [MPa]	14	15
Fracture Energy [J/m ²]	44000	45000
Secant Elastic Modulus [GPa]	36	40
Tangent Elastic Modulus [GPa]	63	77
Poisson Modulus	0.19	0.17
Bond Strength with Steel [MPa]	32	34

Table 3: Characteristics and performance data of different construction materials.

	R.C.	Glulam	Steel	RPC 200	RPC 800
Elastic Modulus [GPa]	25	12	210	60	75
Compressive strength [MPa]	30	32	360	200	800
Tensile Strength [MPa]	3	15	360	45	100
Flexural Strength [MPa]	5	32	360	60	130
Unit weight [kN/m ³]	25	5	78.5	23	28
Specific Elasticity [10 ⁶ m]	1.0	2.4	2.7	2.6	2.7
Specific Strength [10 ³ m]	1.2	6.4	4.6	8.7	28.6
Elastic Strain [%]	0.15	0.25	0.18	0.33	0.80
Ultimate Strain [%]	0.30	0.25	14	2	2
Ductility [%]	2.0	1.0	77	6.1	2.5
Fracture Energy [J/m ²]	300-400	-	-	20000-40000	20000



3 Comparison of structural characteristics of different construction materials

In Table 3 a comparison is made, in terms of characteristics and performance, between five different structural materials usable for structural elements.

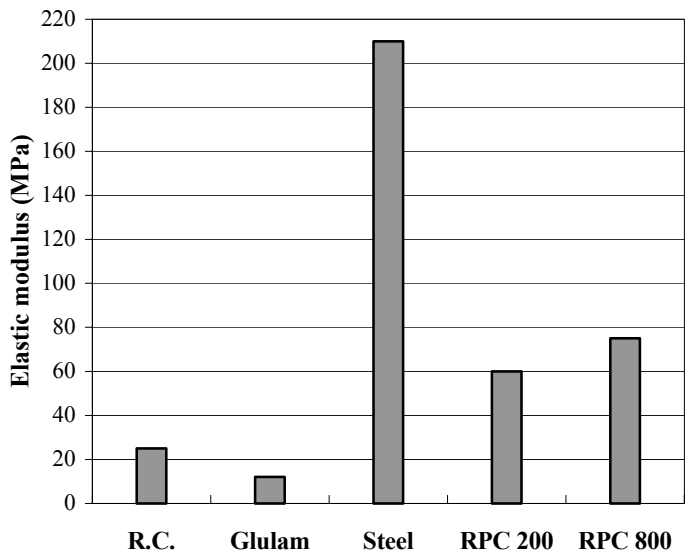


Figure 2: Comparison of elastic modulus of different construction materials.

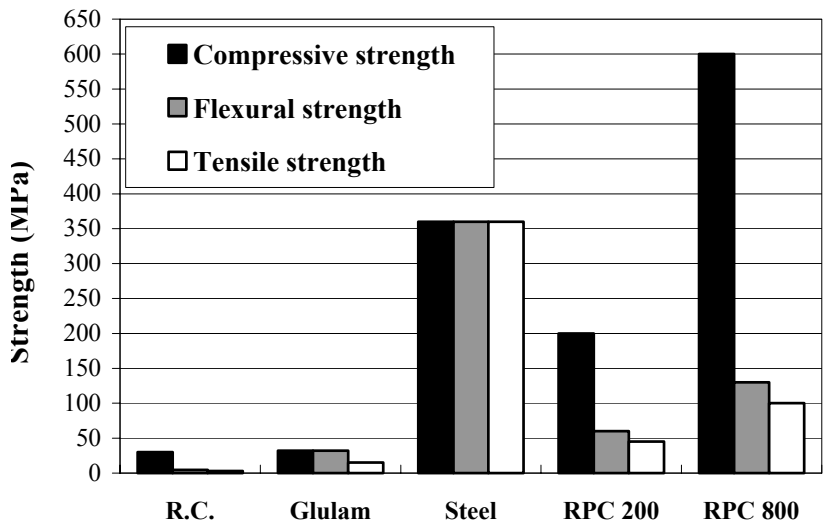


Figure 3: Comparison of mechanical strength of different construction materials under compression, bending and tension.



These materials are: reinforced concrete (RC), glued laminated timber (Glulam), steel, RPC 200 (made by soft casting) and RPC 800 (made by pressure moulding and high temperature curing). In Fig.2 and 3 also a comparison is made, in terms of elastic modulus and strength respectively, between these materials.

4 RPC structure design trial

In the absence of a precise frame of reference standards, calculations of RPC elements have been carried out by way of reference to Eurocode 2 (Parts 1-1, 1-3, 1-5), Document UNI/CIS/SC4-SFRC n°29 (Design of structural elements made of fibre reinforced concrete), AFGC (Association Française du Génie Civil) Recommendations on “Ultra High Performance Fibre-Reinforced Concretes”.

Preliminary dimensioning of structural elements

Firstly, dimensioning of structural members made of the different construction materials reported in Table 3 was carried out. Seven beams were designed according to EC2, EC3, EC5 in order to bear the same bending stress with the same deflection. The seven beams were made of:

- C 30/35 concrete reinforced with FeB44k steel;
- C 40/45 concrete reinforced with pre-stressed tendons (2 ducts containing 6 strands each);
- a truss-girder with members made of steel Fe 360;
- glued laminated timber (glulam) BS16 according to EC5;
- steel Fe 360 (full cross section beam);
- RPC 200 reinforced with FeB44k steel only at the lower flange in tension;
- RPC 800 reinforced with FeB44k steel only at the lower flange in tension.

The dimensions for each beam resulting from calculations are compared in Fig. 4.

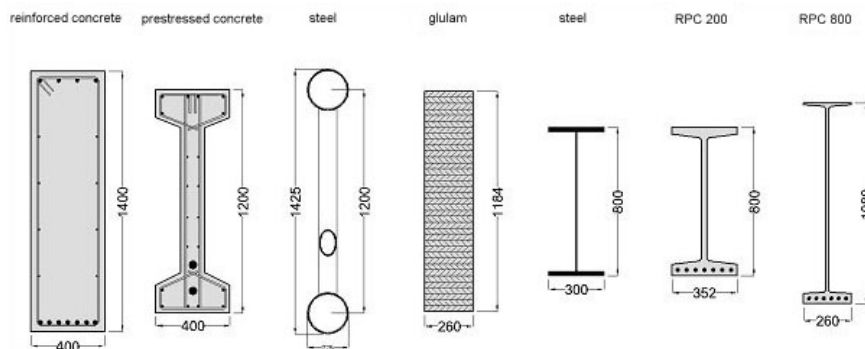


Figure 4: Comparison of equivalent strength beam cross sections obtained from calculations with seven different structural materials (all dimensions are in mm).



An unusual problem for concrete beams

Due to RPC high strength and consequently to high slenderness attainable for RPC elements, a new problem can arise, unusual for concrete: local instability of thin parts making up the RPC beam, analogously to steel beams. This issue compels to verify the equilibrium stability of compressed parts in the element section, as for instance the web of a H-shaped beam subjected to normal and/or shear stress, or its compressed flange (Fig. 5).

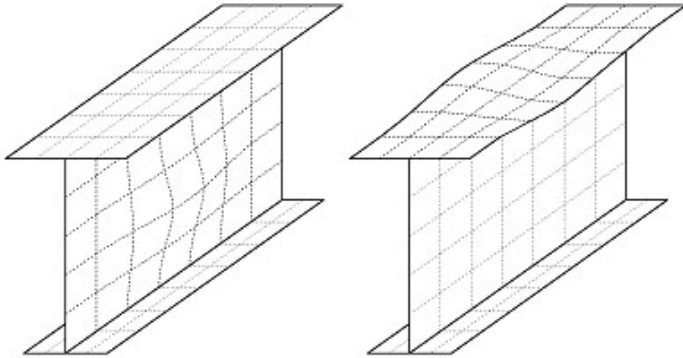


Figure 5: Schematic representation of local instability phenomena of slender parts in structural elements, like the web (left) and the flanges (right) of a beam.

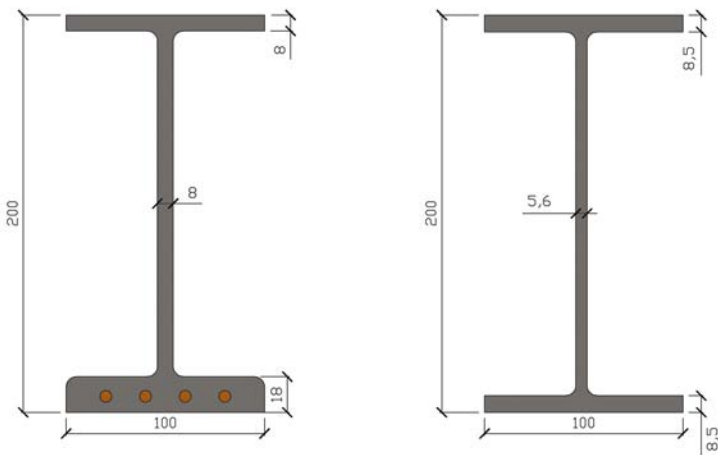


Figure 6: Comparison between RPC 200 (left) and steel (right) equivalent strength I-shaped beam cross section (sizes in mm). The lower flange is reinforced with 4×ø6 mm steel bars.

Preliminary testing of a real scale RPC 200 beam under flexure

Firstly, an I-shaped RPC 200 beam 2 meters in length with steel reinforcement embedded in the lower flange, has been manufactured according to the



dimensions reported in Fig. 6 in comparison with the equivalent strength steel beam cross section.

Then, the 2 meter long RPC 200 beam underwent the bending test (Fig. 7) according to the European Norm UNI EN 12390-5:2002, and, in spite of the cementitious nature, it quite surprisingly twisted like steel (Fig. 8).



Figure 7: Four-points bending test on the RPC 200 beam.



Figure 8: The RPC 200 beam after the bending test. No crack can be observed in the shear-stressed area (left) of the twisted section (right).

This behaviour opens new scenarios for revolutionary structures, since RPC proves to be an innovative material able to outrun traditional limits of cementitious materials, as well as to compete with structural steel in challenging structures.

5 Conclusions

RPC material shows very high compressive and tensile strength as well as high toughness according to its high fracture energy.

This excellent behaviour, which takes RPC further from a common concrete, is due to accurate mixture proportioning and processing with selected raw materials. However, even using more easily available ingredients in order to make RPC more affordable, this work shows that very high mechanical performance can be usefully achieved, allowing one to avoid steel reinforcement for compression and shear and use it only for tension. This approach makes the girder cross section much more slender, which gives rise to unusual structural issues for cementitious elements, as high strain and equilibrium stability of the beam web. These problems can be in any case overcome by externally pre-stressing the RPC beams. In this way, external pre-stressing, which permits one to completely avoid traditional steel reinforcement, suits extremely well calendered or extruded RPC beams. Further, external pre-stressing can disallow any cracking under the service conditions, and significantly increases the durability of the structural member.

In conclusion, RPC proves to be a usefully innovative material able to outrun the traditional limits of cementitious materials, as well as to compete with structural steel in challenging structures.

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Surface Effects and Contact Mechanics IX

Computer Methods and Experimental Measurements

*Edited by: J.T.M De HOSSON, University of Groningen, The Netherlands and
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The importance of contact and surface effects in modern engineering and their combined effects led the organisers to reconvene this 9th International Conference, which covers two related topics: Computational Methods and Experiments in Contact Mechanics and Surface Effects.

Nowadays the importance of contact and surface problems in many technological fields is well understood. They are complex and inherently non-linear due to the moving boundary and the different properties of materials, particularly along the contact surfaces. Structural components fail by wear, corrosion, high cycle fatigue etc, that is to say they are affected by surface conditions. The use of surface treatments can reduce the cost of components and extend the life of the elements for surfaces undergoing contact, a problem that is specifically addressed by the Conference.

This book contains papers from the Ninth International Conference on Surface Effects and Contact Mechanics Computational Methods and Experiments will discuss the following topics: Multiscale Experiments; Size Effect on Confined Systems; Corrosion Problems; Fracture Fatigue; Nano Characterisation; Test Methodology; Computer Simulation; Surface Modification; Surface Treatments; Surface Problems in Contact Mechanics; Fracture Mechanics; Coupled Analysis and Experiments; Thin Coatings; Thick Coatings; Contact Mechanics; Material Surfaces in Contact; Applications and Case Studies; Indentation and Hardness; Adhesion Bonding.

WIT Transactions on Engineering Sciences, Vol 62

ISBN: 978-1-84564-186-3 2009 288pp

£125.00/US\$225.00/€158.00

eISBN: 978-1-84564-363-8

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WIT Transactions on Engineering Sciences, Vol 65

ISBN: 978-1-84564-192-4 2009 apx 400pp

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Simulation of Electrochemical Processes

Edited by: C.A. BREBBIA, Wessex Institute of Technology, UK, V.G. De GIORGI, Naval Research Laboratory, USA and R.A. ADEY, Wessex Institute of Technology, UK

This book contains papers from the conference that brought together researchers who have made significant developments in the area of Electrochemical modelling over recent years. Electrochemical processes are used by engineers to protect structures against corrosion, to apply coatings and paints, and as a manufacturing process. However, until recently, engineers had to use experimental testing or frequent surveys to ensure the adequacy of a design as sophisticated prediction models were not available. The papers presented at this conference demonstrate the major advances that have been made in computational modelling to enable the most complex processes to be simulated.

The papers in this book are divided into the following main topics: Modelling of Cathodic Protection Systems, Electrodeposition and Electroforming, Modelling Methodologies, Modelling Coatings. With chapters including Cathodic Protection Systems; Modelling Methodologies and Modelling Stress Corrosion Cracking and Corrosion Fatigue.

WIT Transactions on Engineering Sciences, Vol 48

ISBN: 1-84564-012-8 2005 264pp

£99.00/US\$159.00/€149.00

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