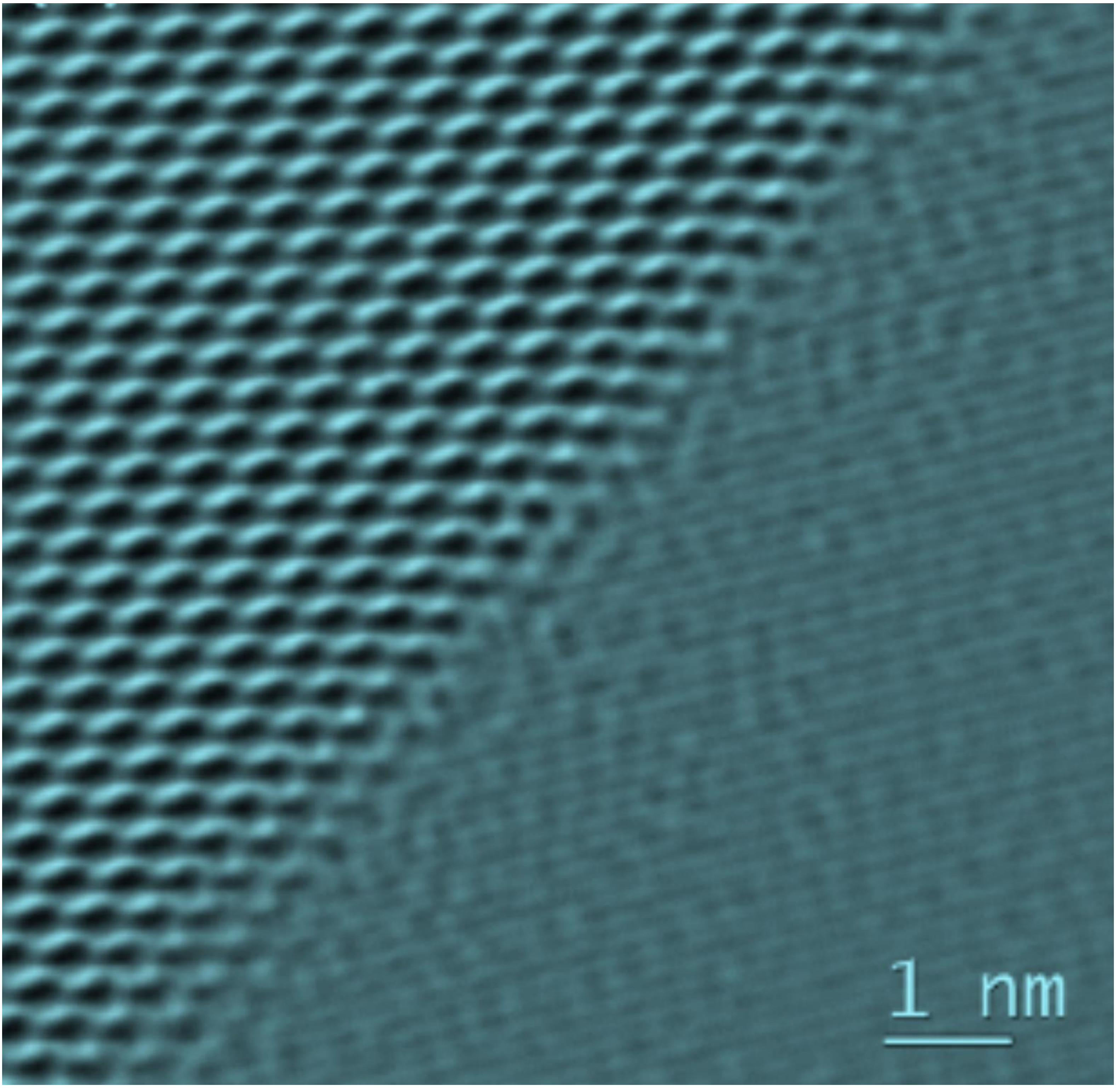
Imperial College London

Centre for Advanced Structural Ceramics
Annual Report – 2013



Grain boundary structure in Al_2O_3

Contents

Introduction

CASC started in July 2008 with EPSRC funding (£5.5M) for a five-year programme. The EPSRC funding has come to an end in June 2013, but CASC continues to prosper. The CASC has attained a large number of active industrial collaborations from abroad and in the UK.

An Industrial consortium has been set up to build on CASC's early success, enable its sustainability and to continue long-term and fruitful relationships between CASC-associated academics and the UK's industrial structural ceramics community.


MATERIALS

Management

The CASC was initially set up by Professor Bill Lee in 2008. Professor Eduardo Saiz took over as Director in (month) 2012.

Local management team (LMT)

The LMT is responsible for the direction of the science and engineering and meets monthly to oversee the pressing day-to-day issues of running the Centre. These issues include staff appointments, equipment purchases and building refurbishment, but are increasingly focussed on developing the Centres national and international profile, forging industrial links and financial sustainability. The LMT is chaired by Eduardo Saiz and other members are Dan Balint, Finn Giuliani, Julian Jones, Kamran Nikbin, Stephen Skinner, Garry Stakalls, Luc Vandeperre and Amutha Devaraj. LMT meetings are also attended by two representatives of the researchers and PhD students working on projects related to structural ceramics.

Industrial Consortium Group (ICG)

The industrial consortium group will start functioning from 2014 after the list of members is finalised in the upcoming steering group meeting held 17 January 2014. The ICG develops the CASC Business Plan which contains the Centre vision, objectives and an action plan to deliver the vision. It acts in an advisory role to the Director and to the Local Management Team, in particular providing advice on:

a. The strategic research focus of the Centre
b. The infrastructure, skills needs and links to industry and other research groups worldwide
c. The structure and content of any undergraduate and postgraduate courses provided by the Centre

A key part of CASC's sustainability is the development of a consortium of companies with interest in manufacture or use of structural ceramics. To build on CASC's early success, to enable its sustainability after the EPSRC funding ends in 2013, and to build long-term and fruitful relationships between CASC-associated academics and the UK's industrial structural ceramics community we have set up an industry consortium scheme. These plans were presented to our first Industry Day meeting on 17 May 2011, where they were well received by the industry representatives present, and were developed by our Steering Group on 4 July 2011. Our plan involves three levels of membership with a graduated annual fee and access to CASC facilities, people and projects as shown in the table below.

Diamond membership is aimed at large and multinational companies, who would like strategic advice and board-level interaction with senior academic staff at CASC. The relationship, which might include technical briefings and RAEng Industrial Fellowships, would be tailored to individual company requirements.

Sapphire and ruby memberships are aimed at smaller companies who want to collaborate with CASC on research and training; sapphire membership offers greater benefits that ruby membership.

All three levels of membership provide:

- Access to CASC equipment (including hot press, vacuum furnace, nanoindenter etc.) and Department of Materials central facilities (includes X-ray Diffraction, Electron Microscopy, Secondary Ion Mass

Spectroscopy and Thermal Analysis), with operator and interpretation included. Access is at preferential rates – much reduced compared to the norm for outside users of our facilities. The degree of access will depend on the level of membership.

- Access to CASC and CASC associated academics.
- Access to Materials, Mech. Eng. and CASC students as potential employees.
- Opportunity for secondment of industrial researchers to CASC.
- Opportunity to propose undergraduate final year research projects, at differing levels depending on membership. Projects run from October to May, descriptions needed by Easter previous year.
- Opportunity to propose research projects for students on Masters courses (Advanced Materials, Biomaterials & Nuclear), at differing levels depending on membership. Projects run from April to September, descriptions needed by October previous year.
- Opportunity to collaborate on out-of-term and industrial placements, Can interview from October onwards.
- Receiving annual report, CASC newsletter and information on CASC sponsored events
- Opportunity to propose a PhD consortium studentship subject. Members will have access to results and analysis resulting from the three year project.
- To date we have three members signed up at Sapphire level (Morgan Technical Ceramics, DSTL and Rolls Royce) and are in advanced discussions with several other companies. If you are interested in becoming a member of the CASC Industry Consortium, contact: Eduardo Saiz – e.saiz@imperial.ac.uk - 020 7594 6779

	Diamond	**Sapphire**	**Ruby**
Type of membership	Strategic	Research & Training	Research & Training
Steering Group member	Yes	Yes	Yes
Equipment use Free allowance up to Preferential rates for other use	 £10,000 Yes	 £3,000 Yes	 No Yes
Proposing MSc, BEng, and MEng projects	8	2	1
Access to CV's of graduating students	Yes	Yes	Yes
Free summer school positions	10	3	1
Membership fee	£50,000+VAT	£15,000+VAT	£5,000+VAT

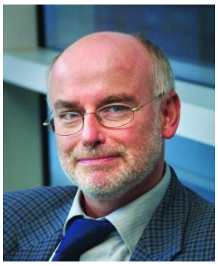
People

Staff

Professor Eduardo Saiz

The CASC Director since August 2012 is Eduardo Saiz, previously a Staff Scientist at the Materials Sciences Division of Lawrence Berkeley National Laboratory (LBNL), joined CASC in October 2009. Eduardo took over the role of Deputy CASC Director in July 2010. He is the current Vice-chair of the Basic Science Division of the American Ceramic Society.

After graduating in Physics from Cantabria University in Spain he gained a PhD in Applied Physics from the Autonoma University of Madrid, working on the processing of ceramic superconductor thick films. In 1992 he became a Fulbright postdoctoral researcher at LBNL. He has worked extensively in the area of high-temperature capillarity and interfaces between dissimilar materials, developing new approaches to study spreading and adhesion in metal-ceramic systems – this continues to be a topic of research. Another area of interest is in the development of new hierarchical, hybrid materials and coatings (metal/ceramic, polymer/ceramic) as well as complex porous ceramics. One of the objectives is to develop high-temperature composites able to perform in extremely hostile conditions and increase efficiency in the transport and generation of energy. He is also working in the fields of biomineralization and the development of new ceramic-based biomaterials to enhance the osseointegration of orthopaedic implants and support the engineering of new bone and cartilage.



Professor Bill Lee

Professor Bill Lee was the founding Director of CASC from July 2008 until August 2012 and is the principal investigator of the EPSRC award. Bill is a Professor of Ceramic Engineering and was Head of the Department of Materials at Imperial College London from January 2006 to August 2010.

After graduating in Physical Metallurgy from Aston University he gained a DPhil from Oxford University on radiation damage in sapphire, was a post-doc at Oxford and Case Western Reserve Universities, Assistant Professor at Ohio State University, USA before becoming lecturer in ceramics at the University of Sheffield in 1989. While at Sheffield he was Manager of the Sorby Centre for Electron Microscopy and Director of the BNFL university research alliance the Immobilisation Science Laboratory. Bill was made a Fellow of the Royal Academy of Engineering in 2012 and his current research is focussed on ultra-high temperature ceramics for aerospace applications and ceramics for nuclear fuel and waste immobilisation applications.

Dr Amutha Devaraj

Amutha joined the Department of Materials as Technical Manager in April 2013. Prior to this she worked as a Team Leader (Quality and Materials) at Novacem, a carbon negative sustainable material development company. She is involved in technical and administrative activities of Centre for Advanced Structural ceramics (CASC). She has experience working on the development of wide range of materials including ceramics, glass and polymer for industrial applications. She also engages herself in the BioBone (European FP7 project) and Programme Grant (XMat, EPSRC) within the Department of Materials.

Garry Stakalls

Garry Stakalls started as technician for the Centre in July 2008. Prior to this he worked in

the Materials Processing Group within the Department of Materials, where he commissioned and ran large experimental rigs and was involved in the processing of wide range of materials. His main activities have been to use and train new users on the use of the thermal analysis equipment as well as operating the hot press for sintering and pressing. He also maintains the equipment while liaising with Netzsch for thermal analysis and FCT for the hot press.

Dr Finn Giuliani

Dr Finn Giuliani joined us in April 2009 as a lecturer joint between the Departments of Materials and Mechanical Engineering. Finn came to Imperial from Linköping University, Sweden where he was an Assistant Professor following.

Finn has a PhD from the University of Cambridge where he examined small scale plasticity in multilayered ceramics coatings. Particular emphasis was placed on measuring and observing small scale plasticity at elevated temperatures. His BEng in Materials Science and Engineering is from the University of Bath. While in Sweden he concentrated on deformation of a group of nanolaminated ceramics known as MAX phases. These are a group of ternary nitrides and carbides, for examples Ti_3SiC_2, which combine ceramic and metallic properties. However, of particular interest is their ability to dissipate energy through reverse plasticity. This continues to be a topic of research. He also has interest in ternary nitride systems which offer the possibility of an age hardenable ceramic. These systems are of particular importance to the cutting tool industry. He also has new projects starting in the area of boron carbide for amour applications. Finally, he has an interest in novel *in situ* mechanical testing regimes whether in TEM, SEM or synchrotron.

Dr Luc Vandeperre

Dr Luc Vandeperre, currently a senior lecturer in the Department of Materials, joined the CASC academic staff on 16 July 2010 to succeed Manish Chhowalla. Manish return to the US for personal reasons on 15 July 10 2010, but will remain associated with CASC and the Department of Materials as a visiting professor.

Luc joined Imperial College in 2006 from the University of Cambridge, where he was a post-doctoral research associate. During his PhD at the Catholic University of Leuven (Belgium), he investigated the electrophoretic deposition of layered ceramic shapes, and was awarded the 1997 Scientific Prize of the Belgian Ceramic Society for his work. Since then, he has worked in both commercial as well as academic environments researching the shaping of ceramics and understanding their thermo-mechanical properties. In addition to his PhD research he has carried out research on shaping ceramics and ceramic foams using natural binders such as starch and gelatine, thermal shock of ceramics, fracture of laminated ceramics, fracture of porous brittle materials, and the relation between hardness and deformation mechanisms. He also designed a device capable of thermal compensation of fibre Bragg gratings for optical data transmission.

Dr Vandeperre's current research spans two themes. The first is thermomechanical properties of structural ceramics, where he is investigating ceramics for use in high temperature environments and as ballistic protection. A second theme is environmental technologies. In this area, he is involved in research into cements for nuclear waste encapsulation, tailoring materials for anion removal from water and producing high value products from industrial by-products.

Researchers

Dr Suelen Barg	Marie Curie Fellow
Dr Doni Daniel	Research Fellow
Dr Miriam Miranda	Marie Curie Fellow
Dr Victoria Garcia Rocha	Marie Curie fellow
Dr Salvador Eslava	Post-Doctoral Research Associate
Dr Esther García-Tuñón	Post-Doctoral Research Associate
Dr Rui Hao	Post-Doctoral Research Associate
Dr Na Ni	Post-Doctoral Research Associate

PhD students

Omar Cedillos Barraza
Eleonora D'Elia
Edoardo Giorgi
Daniel Glymond
Robert Harrison
Zoltan Hiezl
William Montague
Nasrin Al Nasiri
Allen Madamombe
Amanda Quadling
Claudio Ferraro
Gil Machado
Cyril Besnard
Jennifer Alex

Academic Visitors

Akifumi Niwa	Asahi Glass Co.
Masaki Tsutani	JSPS International Training Program
Arash Mohavenian	Welland Medical

Research

PDRA Projects

Developing bio-inspired lightweight and tough ceramic-based composites.

Researcher: Suelen Barg
Supervisor: Eduardo Saiz
Sponsors: Marie Curie

It has long been recognized that ceramics combine low density with thermal and chemical stability in a way that is tremendously attractive for many structural applications. However, they are hampered by low toughness and flaw sensitivity and so far their technological use is limited. In this respect the lesson from natural materials such as bone or nacre is clear: it can be possible to generate unique combination of mechanical properties using *architectural designs that span nanoscale to macroscopic dimensions*, with *precisely and carefully engineered interfaces*. However, no engineering composite has reached such a degree of sophistication, and bioinspiration and hierarchical design have resulted in very limited practical advances.

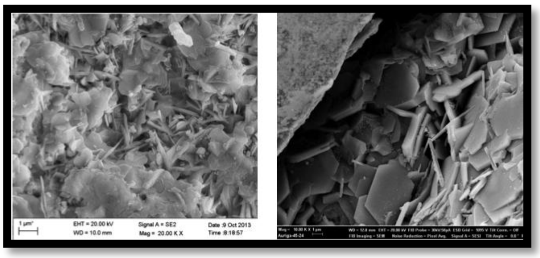
The goal of this project is to develop novel bio-inspired lightweight and tough ceramic-based composites. The vision is to achieve this goal by integrating two concepts: the use of *complex hierarchical architectures generated using processing techniques such as freeze casting and the engineering of the internal interfaces*. Processing is combined with multiscale characterization and systematic mechanical testing in order to define key design parameters that will guide the fabrication of new materials with improved properties.

Processing and characterization of ternary carbides

Researcher: Doni J. Daniel
Supervisor: Bill Lee
Sponsors: EPSRC XMat programme grant

A series of ternary carbides were fabricated by spark plasma sintering (SPS) technique as part of XMAT programme grant looking at materials for extreme environments. The ternary carbides are having increasing interest for use in severe environments owing to their high melting points, high mechanical properties at elevated temperatures, chemical stability, machinability, high fracture toughness and stiffness, etc. Although, 100s of ternary carbides have been prepared and documented, Hf -based ternary carbides are sparse.

Preliminary studies on the fabrication of Hf-Al-C ceramics for 3h at 1800°C by hot pressing technique show that grains have distinctive needle and platelet morphology as shown in Figure. Thermal conductivity of these ceramics measured up to 1300°C shows that they vary from 9 to 25 $w.m.K^{-1}$ for different stoichiometric compositions and they either remain unchanged from R.T to 1300°C or increase with an increase in temperature explaining the dominance of electron contributions at higher temperatures.



This study focuses on the nano analytical characterisation of ternary compounds using FIB, HRTEM and SIMS techniques. The atomic-scale microstructures of Hf-Al-C and Hf-Ta-C investigated through high-resolution imaging and Z-contrast imaging will be investigated. Furthermore, intergrowth examined between grains will be explained using HRTEM and SIMS analyses. Defects such as dislocations, stacking faults and twinning in these ternary compounds will be studied.

Hybrid organic-inorganic scaffolds

Researcher: Miriam Miranda
Supervisor : Eduardo Saiz
Sponsors: Intra-European Marie Curie Fellow

The project is aimed at developing a bottom up process for the creation of biomimetic organic-inorganic structures. The process goes from the molecular stage to prepare the phases involved, to the use of emerging techniques to fabricate bio-inspired structural materials with regenerative applications in the biomaterials field.

A key point in the hybrid materials is the adhesion at the organic/inorganic interface. This interface is quite often the "weak link" that determines to great extent the mechanical response of many natural and synthetic composites. The project involves analysing the adhesion between different synthetic and natural biopolymers and calcium phosphates typically used in biomedical applications. The approach enables a systematic study of the effect of the environment (quantification of the detrimental effect of humidity) and diverse coupling agents on the interfacial strength in many practical systems. These studies provide fundamental data needed to understand the basic mechanisms that control interfacial adhesion and engineer the interfaces of hybrid materials.

The last part of the project will be creation of three dimensional hybrid scaffold materials inspired in hierarchical natural structures, like nacre or dentine. The freeze casting technique will be used including a study of the different forming conditions (additives, freezing rate) both in the final structure and in its properties. The project will be completed with a microstructural, chemical and mechanical characterization of the final materials.

Synthesis of Chemically Modified Graphene

Researcher : Salvador Eslava
Supervisor : Eduardo Saiz
Sposnors: EPSRC (graphene engineering)

The overall aim of the project is to integrate graphene in 3D structures, films and polymer-based materials. The key challenges are the dispersion and functionalisation of well-defined graphene material, and the development of processing routes to combine it with the selected polymer and ceramic systems.

Graphene Oxide (GO) [(~C_8 O_2 H)] is an atomically thin layer of graphene covalently functionalized with oxygen groups. These are epoxy and hydroxyl groups in the basal plane and carboxyl and carbonyl at the edges. It can be easily obtained by exfoliation of graphite oxide in aqueous solution *via* a mild stirring. The yield of exfoliation is nearly ~100% due to the increased interlayer spacing in graphene, induced by the presence of oxygen functional groups, and to the hydrophilic character imparted by the oxygen functional groups. Therefore, once exfoliated, GO can be dispersed in water-based solutions that can be used to process structures and composites. Unlike graphene, GO is an insulator because the sp^2 network is compromised[9] by the oxygen functionalities, which convert sp^2 carbon into sp^3 carbon. However conductivity is restored by oxygen removal, via chemical or thermal treatment, and the material exhibits electrical properties spanning over more than 6 orders of magnitude, rendering it very versatile for different applications. Chemical composition and oxygen content can be finely controlled between 33%- 3% via thermal or chemical reduction.

The wide varieties of chemical compositions that reduced graphene oxide and GO can present are often named "chemically modified graphene". CMG is mechanically as strong as graphene and therefore can be also applied in nanomechanical systems and its topological shape can be modified. The objective is to to pass from a table top experimental scale of production of milligrams of CMG to develop scalable synthesis protocols for the fabrication of hundred of grams of CMG and to tailor its surface chemistry *via* thermal treatments, covalent functionalization exploiting the already existing oxygen functional groups, sulfurization or decoration with metallic and oxide nanoparticles. To support this project we are installing a modular reactor system to enable the systematic manipulation of the materials size and chemistry to prepare "feedstock" suspensions and powders for different applications.

Colloidal processing of responsive particles

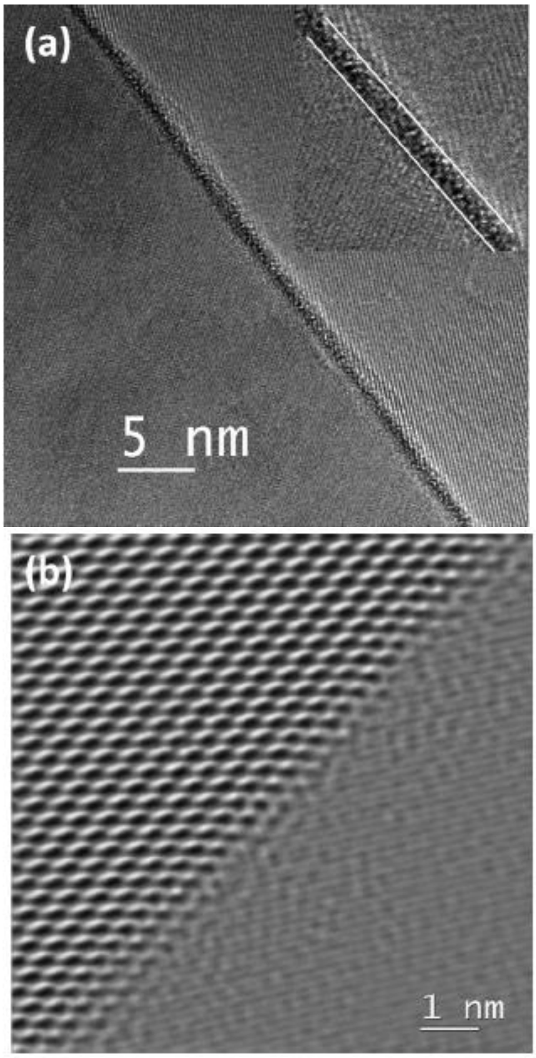
Researcher : Esther Garcia-Tunon Blanca,
Supervisor: Eduardo Saiz

The aim of this project is to develop new manufacturing routes based on the design of 'smart' and responsive particles that 'self-assemble' on-demand into complex architectures. We also aim to formulate novel and universal inks for 3D printing. By combining wet-processing techniques with surface engineering, we can produce responsive particles capable of building hierarchical structures following a *bottom- up* approach from the nano- to the macro scale. Our goal is to manufacture ceramics with complex architectures with improved functionalities for tissue engineering, catalysis or membranes, while delving into the basic science behind the mechanisms involved in the process. The process could then be extended to other organic and inorganic materials.

Interfacial Energies and Mass Transport in the Metal/Oxide System at Very Low Oxygen Activities

Researcher : Na Ni
Supervisor: Eduardo Saiz
Sponsors : EPSRC

A systematic investigation of the interfacial energies (including the grain boundary energy) and the atomic transport rates at the metal/ceramic interface was carried out for the Ni-Al/Al_2O_3 system. The goal was to understand the role of oxygen activity when the system is close to the low $p(O_2)$ limit of the compatibility region.



The metal/ceramic and metal/vapor interfaces exhibit increased faceting at low $p(O_2)$, suggesting an increasing anisotropy in the interfacial energies. A novel approach for the measurement of grain boundary groove angles was developed by imaging the grain boundary groove directly with SEM-FIB, which enables a reveal of more detailed groove profiles at the groove root and measure the angle with a higher accuracy. The results confirm that all the interfacial energies (metal/Al_2O_3, Al_2O_3 surface and grain boundary energy) are smaller at reduced $p(O_2)$ than those of stoichiometric interfaces. Detailed TEM investigations revealed a segregation of Ca and a disordered structure (Figure a) at the grain boundary for the sample exhibiting the lowest grain boundary energy. An excess of Al at the grain boundary was found for grain boundaries with less Ca segregation and an ordered structure (Figure b).

The atomic transport rate at the metal/Al_2O_3 interface was found to decrease initially with decreasing $p(O_2)$ but rises significantly after further decreasing the oxygen activity. This is due to an increase in the oxygen content in the alloy caused by the strong Al-O interaction.

These results provide insights on the capillary evolution of interfaces in metal/ceramic systems at very low $p(O_2)$. The work also opens some important questions regarding the influence of low oxygen activity on the structure of ceramic grain boundaries. These conditions are relevant for a wide range of technological applications where interfaces often control structural evolution and determine performance.

Metal/ceramic bonding at the nanoscale

Researcher: Rui Hao
Supervisors: Eduardo Saiz and Finn Giulliani

Ceramic-metal interfaces are a critical feature in many material structures for example thermal barrier coatings and microelectronics. The purpose of this project is to investigate the mechanical properties of extremely thin metallic interlayers (< 500 nm) within ceramic bi-crystals and the adhesion at the ceramic-metal interface. The samples are prepared using the following sputtering of metallic films on ceramic surfaces followed by diffusion bonding diffusion bonded at temperatures ranging between 1200. From this bonds samples for mechanical testing at the microscale (e.g. micropillars) are produced with the focused ion beam. The samples are tested in situ in the SEM, which provide real-time load-displacement data.

PhD Projects

Process development and characterisation of (Ta,Hf)C ultra-high temperature ceramics

Researcher: Omar Cedillos Barraza
Supervisors: Bill Lee and Luc Vandeperre
Sponsors: CONACYT

Thermal protection structures with superior properties are needed for next-generation

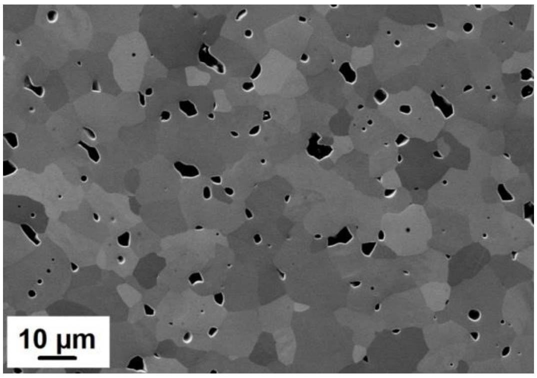


Figure Backscattered electron image (BSE) of a polished surface of 4TaC-1HfC sintered at 2450°C by SPS

(hypersonic) re-entry space vehicles which, when equipped with sharp aerosurfaces like leading edges or nosecaps, have projected requirements for materials operating temperatures above 2000°C in both neutral and oxidising environments. Compounds in the TaC-HfC system have extremely high melting points often exceeding 4000°C making them potential candidates for these applications. Synthesis of TaC-HfC ceramics will be carried out by self-propagating high temperature synthesis (SHS), densification of ceramic powders by spark plasma sintering (SPS) and hot pressing (HP) at temperatures up to 2450°C. Mechanisms of formation of (Ta,Hf)C solid solutions will be analysed and discussed. Thermal and mechanical properties of these compounds will be measured. Oxidation studies will be carried out at temperatures in excess of 2000°C.

Bio-Inspired Self-healing Composites

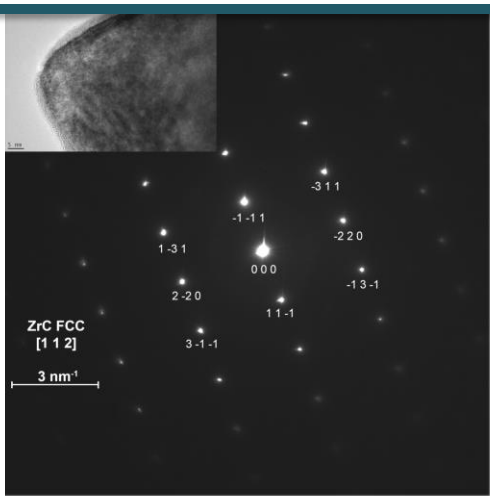
Researcher : Eleonora
Supervisors: Eduardo Saiz, Finn Giuliani
Sponsors: EPSRC

Biological tissues such as bone and nacre show remarkable properties such as high strength and toughness and the ability of self-repair. To a large degree the unique performance of natural materials is due to the presence of thin, interfacial organic layers. Therefore, mimicking natural hierarchical organic/inorganic structures requires careful engineering of the interfacial adhesion between the components based on a deep understanding of the role of the organic "soft" phase. In this work we use Double Cantilever Beam (DCB) tests of silica glass/polyborosiloxanes interfaces that exhibit self-healing properties based on the use of interfacial sacrificial hydrogen bonds. The healing process is divided in two steps, one is the reforming of bonds and the other is the spreading of the soft phase to refill the interface. These materials are used to build brick-and-mortar and laminate structures that exhibit toughness higher than the single components. Furthermore, three point bending studies show that these structures are able to heal completely and recover their properties few days after fracture. These results show that the use of a self-healing shear-thickening soft interface is a promising approach to build biomimetic hierarchical structures.

Processing and Diffusion Properties of Substoichiometric Zirconium Carbide for Nuclear Applications

Researcher: Edoardo Giorgi
Supervisor: Bill Lee, Robin Grimes
Sponsors: EPSRC

The refractory and high temperature properties of zirconium carbide are of great interest for nuclear fuel applications such as with the TRISO particles. As a group IV transition metal carbide ZrC exists in a wide sub-stoichiometric ratios over which its properties vary (such as conductivity). Within



the life cycle of a TRISO particle the deposited sub-stoichiometric ZrC as a fission product barrier acquires carbon from the surrounding graphitic environment. It is hence important to evaluate whether this affects the effectiveness of ZrC at retaining the metallic fission products.

The research project includes a processing investigation looking into the Reactive Spark Plasma Sintering (RSPS) carbothermic route to rapidly manufacture non-stoichiometric ZrC monolithic samples. The main focus of the project is a combined computational and experimental study of the effect of non-stoichiometry on the properties of ZrC as a viable fission product barrier looking at defect clustering and diffusion mechanisms.

Fracture toughness and creep of mullite and mullite composites

Researcher : Daniel Glymond
Supervisors; Luc Vandeperre and Finn Giuliani
Sponsors: US Naval research laboratory (NRL)

Mullite is considered a promising candidate for ceramic recuperators in turbo propelled engines, due to due to its low thermal conductivity, adequate thermal shock resistance, low cost, low density, thermodynamic stability, and reasonable strength at high temperatures. Unfortunately, the limited fracture toughness of mullite (~1.8-2.8 MPa $m^{1/2}$) is considered too low. This work has concentrated on improvement of the fracture toughness, and the effect of toughness enhancement methods on the creep resistance.

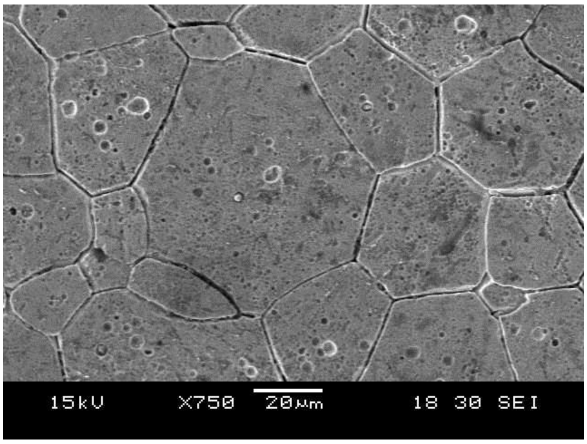
A reliable way of improving fracture toughness in a range of materials has been to tailor the microstructure to contain elongated grains capable of bridging cracks. A range of processing methods are used in this work: reactive sintering of mixtures of alumina and silica, sol-gel synthesis of mullite and the use of sol-gel derived additives to enhance the sintering of commercial mullite powders.

The addition of ceria stabilised zirconia has been shown to improve the room temperature toughness of mullite to 4.7 MPa $m^{1/2}$. In this work the toughening mechanisms of this and two other mullite zirconia composites (monoclinic zirconia and yttria stabilised zirconia) are investigated, as well as the effect of temperature on the toughness of the composites. It is unknown exactly what effect the addition of the zirconia materials to mullite will have on the other properties of the material. In this work the effect on the creep resistance is investigated.

Processing and Characterisation of Simulant Non-oxide Fuels for Generation IV Reactors

Resarcher: Robert Harrison
Supervisors: Bill Lee, Robin Grimes

Currently there is a renewed interest in nuclear power as it offers an economical, low carbon solution to the planet's growing energy demand. Six systems have been proposed for new nuclear power plants, these reactors will



operate under harsher radiation and chemical

Figure 2 SEI image of ZrN sample

environments compared to previous reactor fleets and so oxide fuel materials may not be able to operate adequately, however non-oxide ceramics such as carbides and nitrides show many of the properties required

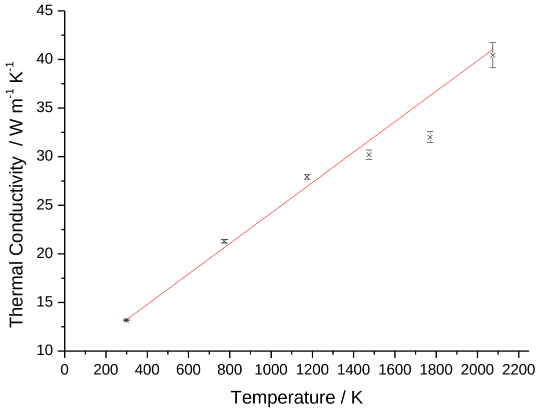


Figure 1 Thermal conductivity data for ZrN sample

Research interests include the processing and characterisation of non-oxides for use in Generation IV nuclear reactors with main interest focused on the gas cooled fast reactor (GFR). Several reference fuel concepts exist for the GFR such as dispersion of fissile phases (such as uranium carbide or uranium nitride) in a non-fissile material in the form of a pellet and advanced fuel particles consisting of a coated fissile kernel. This project aims to investigate processing routes to these composite fuels using actinide surrogates, such as CeN, DyN and NdN. Suitability of these materials as actinide surrogates will be assed with the aim to produce simulant composite pellets by several densification techniques, assessing the effect of processing route and microstructure on thermal and physical properties.

Current work is focused on optimising the processes of carbothermic reduction/nitridation of CeO_2, Dy_2O_3, Nd_2O_3 and ZrO_2 to their respective nitrides. The reaction takes part in two steps, first the reduction of the oxide to the carbide, followed by the nitridation of the carbide to the nitride. The candidate materials for the non-fissile phase are well known for their accommodation of non-stoichometry. Another area of interest is the effect of this non-stoichiometry on thermophysical properties such as thermal conductivity.

Effect of microstructure and grain boundary chemistry on the mechanical behaviour of silicon carbide

Researcher: Nasrin Al Nasiri
Supervisors: Finn Giuliani, Luc Vandeperre and Eduardo Saiz

Silicon carbide (SiC) is being used increasingly as a room temperature structural material in environments where moisture can't always be excluded. Due to the covalent nature of bonding in SiC, it is expected to have excellent resistance to environmental assisted failure. Unfortunately there have been almost no studies of slow crack growth in SiC at room temperature. To address this gap, slow crack growth in silicon carbide materials was studied using constant stress rate testing with loading rates varying between 20 MPa s^{-1} and 0.02 MPa s^{-1} in water and double torsion testing with crack speeds ranging between 10^{-7} to 10^{-4} m s^{-1} in air and water. Considering that, silicon carbide based materials are produced with a wide range of grain boundary chemistries as well as a range of microstructures, two typical chemistries solid state (SS) sintering using carbon and boron and liquid phase (LP) sintering using a mixture of alumina and yttria additives and two types of microstructures (equiaxed fine grained materials and materials with elongated larger grains) were investigated to clarify the role of microstructure and chemistry. Although many studies have been performed on the effect of these additives on strength and toughness, less is known about the way they influence the resistance to environmentally assisted failure. To ensure that the behaviour could be linked to the normal fracture response, the R-curve behaviour and closing bridging stress were measured using double cantilever beam testing. It is found that fracture in the LP sintered materials is intergranular while it is transgranular in the SS sintered SiC's and that as a result only the LP sintered materials show a rising R-curve in the long cracks regime. However, for short cracks, the closing tractions on the crack are larger in materials containing elongated grains, irrespective of the chemistry. The slow crack growth exponent, *n*, for the materials produced using oxide additives is lower than the ones produced using non oxide additives. Again an influence of grain size was found with larger grains less sensitive to slow crack growth than materials with fine grains. It is proposed that the larger, short range, closure tractions in materials with elongated grains lead to a reduction in the stress intensity and hence the ability of the stress to activate the corrosion.

Processing of hard ceramic composites for use in armour

Researcher: Allen Madamombe
Supervisor: Luc Vandeperre
Sponsor: Morgan Ceramics and DSTL

High performance ceramics are an integral part of modern weapons and defence systems and are used extensively. Incorporating a ceramic in an armour system can deliver two vitally important functions: (i) provided damage can be suppressed or delayed, the ceramic layer can delay the penetration of the projectile and erode it on the surface and (ii) after failure the ceramic layer can still break up and erode the projectile while it penetrates the ceramic. Both processes aid in distributing the load to a wider area on the metallic, polymer or composite layers behind it and enhance the ability to withstand high velocity projectiles. Over the past several years' significant research has been directed at improving such ceramics to enhance the reliability and to reduce the weight of the armour.

The study will investigate the processing of silicon carbide (SiC)/ boron carbide (B_4C) composite ceramic materials with potential to deliver even higher quality armour components. Pressureless sintering of these composites is investigated with the aim of reducing the financial cost associated with hot-pressing processing traditionally employed for ceramic armour components. The research involves a strong production and characterisation (of produced composite materials) element. The entire ceramic production process will be undertaken, from powder processing and sintering (pressureless), through to the ballistic testing (by outside contractor) of the produced component.

The role of aggregates in Mg-PSZ crucible thermal shock resistance

Researcher: Amanda Quadling
Supervisors: Luc Vandeperre and Bill Lee
(self-funded with contribution from Morgan Advanced Materials)

Three commercial MgO-partially stabilised zirconia refractories were image analysed, using scanning electron microscope (SEM) images, to obtain grain size distribution curves

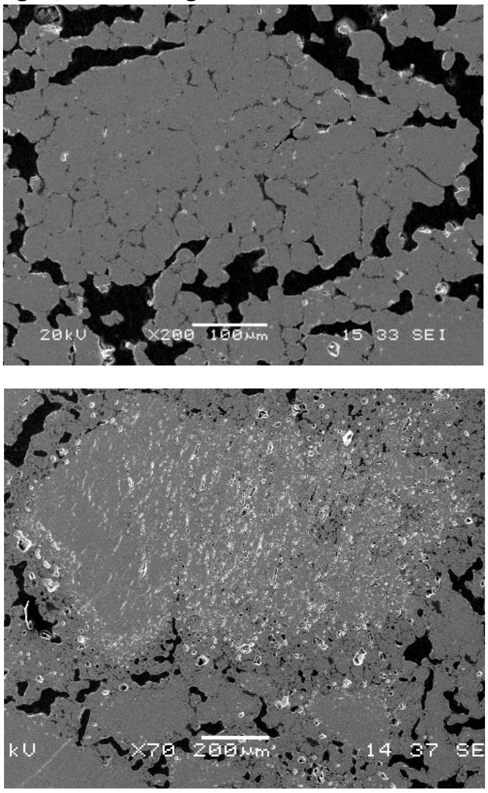


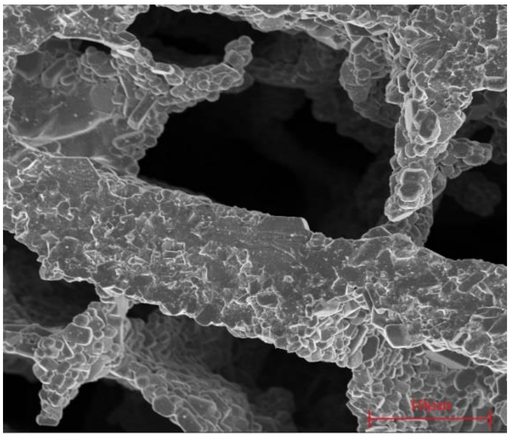
Figure : Coarse aggregates from a commercial Mg-PSZ refractory, after 8 thermal cycles to working temperatures

for their coarse, medium- and fine-grained aggregate phases respectively. The three sample types were each subjected to 80 hours of resonance frequency measurement (using impulse excitation) during thermal cycling to working temperatures, to determine Youngs modulus. Stiffness is shown to remain stable over eight thermal cycles for the larger aggregate grain samples but systematically and significantly (44%) degrades for the finest aggregate sample over the same time period. SEM comparison of the sample microstructures pre- and post-thermal cycling reveals that many of the coarser aggregates decompose physically, or become extensively microcracked (see Figures below) while the finer aggregates remain intact. Electron probe microanalysis indicates elevated MgO levels in the physically decomposing aggregates of the two larger aggregate sample types. Samples are currently being prepared for R-curve measurement. Raman studies on phase transformation are underway. The project aims to determine to what extent - and why - larger aggregate size ensures thermal stability during working cycles for these refractories, and is due for completion late 2014.

Bio-inspired ceramic-based composites

Researcher : Claudio Ferraro
Supervisors: Eduardo Saiz, Julian Jones
Sponsors: Marie Curie ITN – FP7 project

Ceramics exhibit high hardness and compression resistances however they are susceptible to brittle fracture. Traditional structural ceramics show low values of fracture toughness and, for this reason, new production methods have been developed to improve it.



Taking inspiration from nature, and more specifically from the peculiar structure of nacre (mother of pearl), composite materials based on freeze cast ceramics have been studied. The process of freeze casting, which uses ice crystals as template, has been used to obtain fine lamellar porous ceramic scaffolds. In order to mimic the nacre composite structure, where the ceramic part is alternated in a layered structure with a polymeric soft phase, the porosity of the freeze casted scaffolds has been infiltrated with a metallic phase and with the same purpose a polymeric phase will be used in following studies. Two different types of ceramics have been considered, alumina (Al_2O_3) and silicon carbide (SiC).

Alumina freeze casted scaffolds have been successfully infiltrated with an aluminium alloy (Al-4wt% Mg) using two different techniques: pressureless infiltration and squeeze casting using a modified spark plasma sintering equipment (SPS). Microstructural analysis and X-ray analysis have been used to compare the two methods. Infiltration with nickel has been attempted unsuccessfully. In this case also other methods of infiltration have been taken in consideration.

Strong SiC scaffolds obtained via freeze casting have been developed. For this reason the sinterability of SiC freeze casted scaffolds has been studied. Both liquid and solid phase sintering have been compared using the hot press (HP) and the spark plasma sintering (SPS). Density and porosity measurements have been measured using the Archemide's method and a microstructural analysis has been done using scanning electron microscopy and x-Ray diffraction.

An investigation of the suitability of magnesium phosphate cements for encapsulation of metallic uranium

Researcher : William Montague
Supervisors : Luc Vandeperre & Martin Hayes
Sponsor : National Nuclear Laboratory (NNL) and EPSRC

Cementation using Portland cement based products is the dominant encapsulation technology for UK intermediate level nuclear waste (ILW). Given the wide variety of nuclear wastes to be encapsulated, there is a case for developing a wider toolbox of encapsulation matrices so that waste and encapsulant can be matched. In this project magnesium potassium phosphate cement (MKPC) is investigated as an alternative encapsulation system for uranium metal. Testing of processing properties performed on a broad range of MKPC formulations has established a formulation envelope within which the requirements for bleed production, fluidity and workability are met. Additionally, compressive strength, SEM and XRD techniques have been used to study property evolution with curing age for multiple formulations and curing temperatures. Ash (PFA) inclusion was found to be the crucial component for slurry workability whilst providing strength enhancement; high PFA formulations reached compressive strength values of 34±2 MPa at 28 days. The rate of cement strength development was observed to reach a maximum between curing temperatures of 47 °C and 72 °C. In the current stage of the research the evolution of the cement with longer ageing times is being compared to that of cements which have encapsulated uranium together with measurements of the rates of corrosion, if any, when uranium is encapsulated in magnesium phosphate cements.

Calcium phosphate scaffolds with controlled composition and structural properties

Researcher : Gil Costa Machado
Supervisor: Prof. Eduardo Saiz
Sponsor: Marie Curie ITN – FP7 project

Calcium phosphate materials are usually considered ideal materials for hard tissue engineering due to their high chemical similarity with the inorganic phase of natural bone. However, despite numerous studies and approaches to the use of calcium phosphates, a truly successful application with such materials is still to be achieved. Despite the development of many different processing routes, there is still a clear need of adequate techniques to create calcium phosphate ceramics with controlled chemistry and structure.

The main goal of the work developed so far has been to characterise biphasic calcium phosphate materials (composed of both hydroxyapatite and β-tricalcium phosphate) and to integrate different processing techniques to produce ceramic scaffolds with controlled properties: phase composition, density, surface roughness and topography, as

well as 3-dimensional structure and micro- to macroporosity.
The first stage of this project has addressed the characterisation of the sintering behaviour of such materials. Preliminary results have shown the initial particle size distribution (HA D50 = 0.471 µm, β-TCP D50 = 0.780 µm), confirmed material composition and elucidated the sintering behaviour of ceramic compacts up to 1400°C. Activation energies (calculated using the constant heating rate method) for HA and β-TCP were found to be 505 ± 31 kJ/mol and 435 ± 15 kJ/mol, respectively.
A first approach to making substrates with these materials was to use particle-stabilised emulsions as a type of soft template, to obtain materials with controlled microporosity and composition (see figure below). The production of such substrates is being optimised and their properties studied.
The results obtained so far provide essential information for the next stages of this work.

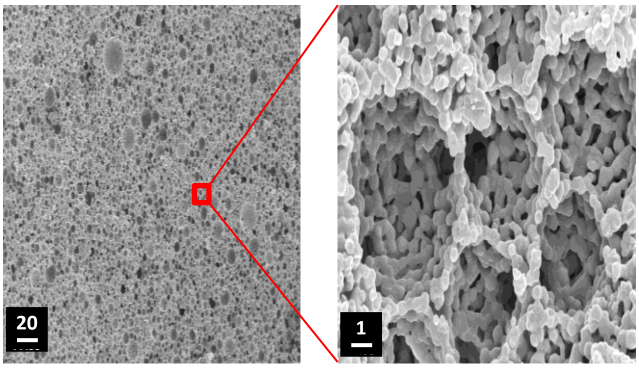


Figure: 70 wt% Hydroxyapatite in Branched Copolymer Surfactant; sintered at 1121°C for 15 min

Silicon doped boron carbide as a lightweight impact resistant material

Researcher: Cyril Besnard
Supervisors: Luc Vandeperre and Finn Giuliani
Center for Advanced Structural Ceramics
Sponsor: DSTL

The project is supported by the Defence Science and Technology Laboratory of the UK. The aim is to develop novel ceramics for use in armour. Lightweight impact resistance ceramics are still under development. B_4C is attractive and has already used for this application for many decades. However a catastrophic failure occurs in B_4C at the high pressures achieved during high velocity impacts, which is due to collapse of a weak polytype within the structure. Previous research has suggested that doping with silicon can eliminate this polytype and therefore improve the high velocity impact performance of B_4C. Therefore the aim of this project is to produce meaningful quantities of Si doped B_4C which can be used for high speed impact testing. This project will be in collaboration with the shock physics group at Imperial College.

Effect of Minor Elements on Calcium Aluminate Cement Refractories

Researcher : Jennifer Alex
Supervisors: Luc Vandeperre and Bill Lee
Sponsor: Keneos

The role of various oxides on the solid-liquid interactions in calcium aluminate cements (CACs) at high temperatures is being examined using phase and microstructural characterisation (SEM, TEM, XRD and TGA) and Gibbs energy minimisation computational modelling. In light of recent trends in the refractory industry to replace bricks by higher purity CAC-based monolithics for enhanced durability, performance and novel applicability, improved mineralogical control is of growing significance. The effect of minor elements on the development of a microstructure within these systems during processing and application is being examined with emphasis on potential mineralisation effects of liquid formation linked to these elements as well as the grain growth which occurs through dissolution/precipitation reactions. Furthermore, threshold values are being determined above which the presence of minor elements leads to a deterioration of desirable refractory castable properties.

Study about the interface of glass and ceramics

Academic visitor : Akifumi Niwa
Supervisor: Eduardo Saiz

In glass production, since the refractories and the molten glass are in contact in high temperature, it is very important to clarify the phenomena occurring in the interface thereof. For example, in the forming process, wettability and adhesion between the molten glass and the refractories greatly affects the forming characteristics of the glass. Further, because it depends on the glass type, it is necessary to understand the characteristics of each glass.

The main objective of this work is to study the interaction of glasses and refractory ceramics. The approach is to combine wetting/spreading experiments with high-resolution structural and chemical characterization and mechanical measurements to reveal the parameters that control wettability, dissolution and grain boundary infiltration in order to provide guidelines for the selection and fabrication of materials for glass processing.

The sessile drop method is used for the experiment to measure wettability under each temperature, each atmosphere for various kinds of oxides, carbides and nitrides. And interfacial analysis by SEM/TEM and Nano-indentation for these samples will be carried out.

Synthesis and evaluation of Na-geopolymer using seawater

Academic visitor: Masaki Tsutani
Supervisor :. Luc Vandeperre
Sponsor : JSPS International Training Program

Geopolymers have some potential for use as new construction materials, high temperature ceramics as well as toxic and radioactive waste encapsulation. Geopolymers are expected to become an alternative material to cement In the future. Merits of geopolymers include the use of industrial waste products as raw materials for synthesis, including aluminosilicate phases from Fly ash and slag from steelmaking, their lower embedded carbon dioxide content and better durability against acid attack. Geopolymers are synthesised by mixing an amorphous aluminosilicate with alkali activators, including sodium hydroxide, potassium hydroxide, sodium silicate and potassium silicate.

This research is focused on the synthesis of geopolymers using seawater. Alkali solutions with high concentration are used. As the cost of making geopolymers is high for mass production, In this research artificial seawater is applied as a source of sodium cation, instead of sodium hydroxide and water. Sodium hydroxide is replaced in some percentage for the synthesis of Na-geopolymer samples to decrease the cost. Characterization is performed to confirm the effect of the salt on compressive strength and other properties of the geopolymer samples.


NETZSCH
NETZSCH

Capabilities and facilities

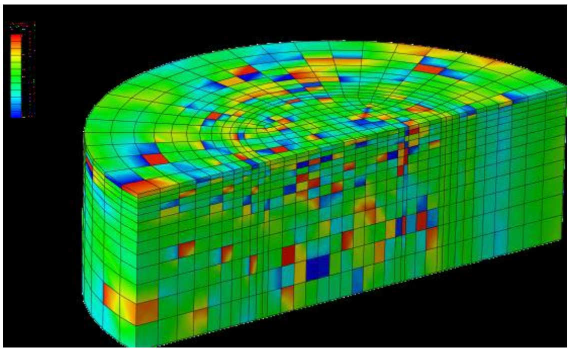
The purchasing and installation of large items of equipment by the Centre from the CASC funding, to improve UK capability in fabrication and modelling of structural ceramics, is now complete but we will continue to improve our experimental capability in this area using funds from other sources. All equipment is available to the UK ceramics community – please contact Amutha Devaraj (adevaraj@imperial.ac.uk, 020 7594 1170) or Garry Stakalls (g.stakalls@imperial.ac.uk, 020 7594 6770) if you wish to use any of these facilities.

Nanoindenter

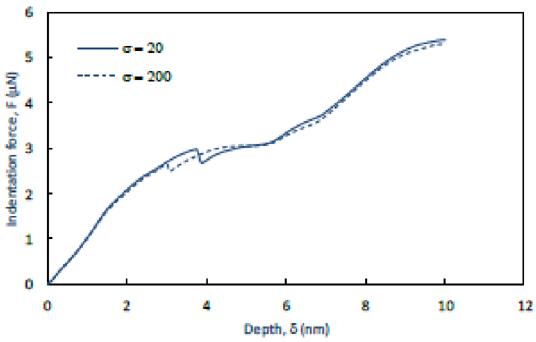
The high temperature nanoindenter manufactured by Micro Materials is located in the Structural Ceramics laboratory on the lower ground floor of RSM, to make use of the better control of air temperature and reduced vibration level. As well as being fully instrumented, the nanoindenter operates at temperatures up to 750 °C. Usage of the nanoindenter is high, and results obtained (Section 7) have been reported at international meetings these include, Third International Workshop on Mechanical Behaviour of Systems at Small Length Scales, Kerela, India , Fall MRS conference, Boston, American ceramics society meeting, Daytona beach, ICMCTF San Diego. There is also an ongoing projects with SECO Tools AB and Element 6 (total value ~£65K).

Server

CASC's multiprocessor server is being used for continued studies on the nanoindentation response of MgO. Three dimensional crystal plasticity simulations of nano-indentation of MgO are being carried out using parallel processing on the CASC cluster. The relation between primary and secondary slip system activation and the hysteresis, and the softening observed in the indentation force displacement response, have been simulated. As shown in the plot, using a normal random



distribution of the critical resolved shear stress throughout the model, greater standard deviation, , results in a decreased drop in the indentation force. This is being used to study the relation between the change in the slope of the loading curve (corresponding to the activation of the secondary slip systems) and



the spacing of hysteresis loops observed in the experimental data.

Freeze dryer

Freeze-drying is a drying process, where the solvent, normally water, is eliminated from the sample via direct sublimation from solid to gas phase. This is a useful way to eliminate the solvents by keeping the material structures intact for further processing like sintering. We currently use this process for drying freeze-cast materials like alumina, zirconia, zeolites and graphene oxide.

Thermodynamic software

FactSage version 6.1, together with three substance databases, has been purchased from GTT Technologies. A multi-user license for phase equilibria software has also been purchased from the American Ceramic Society. This thermodynamic calculation software is available over the network to anyone in the CASC offices and has been applied to range of projects including Si-stabilised B_4C and high temperature annealing of TiAlN, thermal treatments of high alumina castable refractories, producing composites of B4C and SiC.

Thermal analysis

A suite of high-temperature thermal analysis equipment from Netzsch has been installed in the Department of Materials, in a basement room that was converted specifically for this use. The equipment comprises:

- Simultaneous TG-DTA to 2000 °C
- Laserflash (thermal diffusivity) to 2000 °C
- Dilatometer (thermal expansivity) to 2400 °C

Netzsch have provided multiple training sessions, and all three items of equipment now run at temperatures up to 2000 °C. The facility is heavily used and starting to attract external users.

The **dilatometer** has two set-ups: an alumina tube and pushrod for measurements up to 1600 °C and a graphite set-up for measurements up to 2400 °C. In a first phase measurements were limited to 1600 °C; this year measurements have been carried out up to 2000 °C. The pyrometer for temperature measurement up to 2400 °C has been commissioned but there were difficulties in

Induction-heated thermo-mechanical test rig


Crucibles of the high temperature combined TGA DTA

reaching 2400 °C with the current furnace. In-house developments in the past year have made it possible to use the dilatometer to measure hardness too and initial tests have been run to use it for creep measurements. Examples of CASC projects using the dilatometer have been measuring the thermal expansion of refractory materials for estimation of the risk of thermal shock damage, characterising a wide range of ultra-high temperature ceramics, studying the sintering of mullite and the residual stress in mullite zirconia composites, hardness measurements of ZrB_2 and Al_2O_3, cracking due to shrinkage in geopolymers and sintering of silicon carbide-boron carbide composites. Measurements for Rolls Royce have also been carried out.

The **combined TGA-DTA** has been used to characterise the mass loss during drying of geopolymers, the decomposition of magnesium phosphate and magnesium silicate cements for nuclear waste treatment, reactions during sintering of silicon carbide, decompositions during heating of reactive sintering mixtures for mullite, determining the carbon yield from various ceramic additives and characterisation of raw materials in general, investigating the oxidation of a range of UHTC's. Usage for third parties included a large set of runs for Professor Jon Binner, Loughborough University, a set of measurements for Dr Bai Cui, University of Illinois, characterisation of derivative products from commercial paper mills, and to carry out urgent measurements for Morgan Technical Ceramics.

The equipment for measuring **thermal diffusivity via laser flash** has been used extensively to characterise a wide range of ultra-high temperature ceramics and carbon-ceramic composites for CASC, but it has also been used to measure a range of new materials under development at Rolls- Royce and Morgan Technical Ceramics and to characterise thermo-electric materials for Professor Reece at Queen Mary, University of London.

Vacuum hot press

Thermo-mechanical testing

The high-temperature mechanical testing equipment from Instron is located in the Mechanical Engineering Department. One frame incorporates a vacuum system and a furnace from Materials Research Furnaces with a maximum temperature of 2000 °C. Training has been given and is now in full use and is starting to get interest from outside users such as Seco Tools AB, Sweden. The second frame has induction heating up to 1200 °C. Control hardware and software has been updated, and training has recently commenced. In the past year it has been used for a range of projects including measuring the properties near the service temperature of commercial cutting tools, creep of different types of mullite, and measuring high temperature strength of UHTC’s and commercial refractories .

Vacuum hot press

The vacuum hot press from FCT Systeme has been commissioned and full training given. After initial problems with the water cooling system the equipment is now in full use and is heavily used. The press will operate at temperatures up to 2400 °C for sintering and 2100 °C for hot pressing with a maximum force of 250 KN and at atmospheric pressure or under vacuum. The pressed volume is 8 cm diameter and 10 cm tall. The larger diameter of 8cm allows more samples to be produced from one pressing run. Most runs have been for CASC members working on e.g. silicon carbide, boron carbide and composites of silicon carbide and boron carbide, silicon carbide – aluminium nitride alloys, zirconium carbide, tantalum and hafnium carbide, joining of UHTC’s, glass ceramic-SiC composites, nacre-like SiC structures and mullite. The unique capability of going to high temperature has enabled producing a solid solution phase of HfC and TaC, which lead to a best poster prize at the ECI conference on ultra-high temperature ceramics at Hernstein, Austria. However, runs for other university groups including tests on forging of functional ceramics for Prof Alford, Imperial College London, and treatment of UHTC precursors for Prof Binner, Loughborough University, have also been carried out.

Vacuum furnace

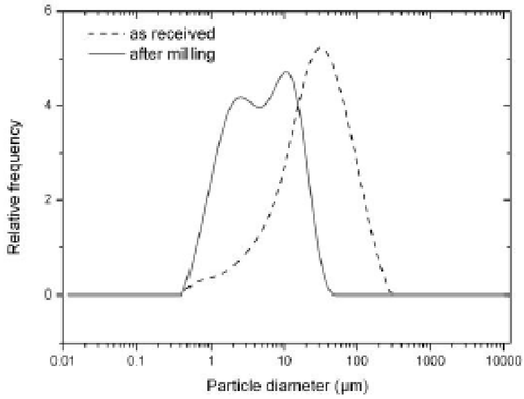
The vacuum furnace from Thermal Technology is now in place and after initial problems with the water cooling system the furnace is now in use. The furnace will heat a volume 5 cm diameter and 15 cm tall to temperatures up to 2500 °C under vacuum or a mixture of gasses. Opposed viewing ports will allow observation of the sample during heating, and a sample elevator and cooling chamber will allow exchange of samples whilst the furnace is at temperature.

Wet grinding mills

We have purchased and installed a wet grinding mill capable of low-amplitude grinding of up to 5kg of ceramics in five different chambers and a ball rolling mill for homogenisation of suspensions and breaking up of agglomerates before processing.

Particle Size Analyser

The Department has provided funds to acquire a laser particle size analyser. The equipment uses scattering of light by particles in dilute



Examples of powder particles = distributions

solutions to determine the size distribution and has the ability to measure from 0.01 to 10,000 μm without needing to change the optics as in older instruments making it much more convenient.

High Temperature elastic properties by impulse excitation

Early May 2013 saw the installation of a new piece of equipment for determining the Young and shear modulus and Poisson ratio of materials. The measurement principle is based

Figure Set-up for room temperature measurements.

on the relationship between shape, density and stiffness and the natural vibration frequencies of a sample. For example, for determination of the Young modulus, typically a bending vibration mode is excited by hitting a sample supported on the nodes of the vibration with a small projectile in the centre. The resulting vibration is picked up with a microphone and analysis of this signal using the Fourier transformation yields the frequency of the vibration. The software also analyses the decay in amplitude of the vibration with time to determine a value for the damping of the vibration. The model installed at CASC comes with a furnace capable of operating to 1750 °C in air or inert atmosphere and hardware and software enabling fully automated excitation and measurement, making it possible to investigate the variation of the elastic properties with temperature but also to characterise transitions in the materials behaviour from the changes in internal damping of the vibration signal. Some examples from the literature of phenomena giving rise to damping are the glass transition temperature, the hopping of oxygen vacancies bound to dopants in response to stress at low temperature in doped zirconia, and the softening of grain boundary glassy phases in sintered silicon nitride.

3D printer

A robotic assisted deposition system from 3D Inks (USA) system based on continuous extrusion to build three-dimensional structures "on demand" following a computer design. The system can reach submicron-printing precision. The printer has 3 nozzles that allow the combination of three different inks to fabricate multiphase structures.

Optical Microscope Axio Scope A1

Optical microscope with reflected and transmitted light, bright and dark field, DIC, camera and software for image acquisition and analysis is installed recently. The microscope has a modular design that will facilitate the installation of different set-ups to do in-situ experiments, for example, mechanical testing or freezing of colloids.

CASC

CASC Research Portfolio

Funded proposals

- Bill Lee and Doni Daniel, , Processing of C Fibre UHTC Composites,2013-2015, US Navy ONR Global, $250K.
- Bill Lee with J Binner (PI, LBoro), M Finnis and M Reece (QMUL), , Understanding and Designing Materials Systems for Extreme Environments, 2013-17, EPSRC, £5.8M (£2.8M to Imperial).
- Bill Lee, AWE and Imperial College, William Penney Fellowship, 2013-15, £164K.
- Bill Lee, AWE and Imperial College, Centre for Engineering and Manufacturing Studies kick-start projects, 2013-2014, £160K.
- Bill Lee with Chris Gourlay, AWE, PDRA on Ag wetting, 2013-15, £140K
- Bill Lee, EPSRC, Sellafield, NNL, NDA., DISTINCTIVE (Decommissioning, Immobilisation and Storage SoluTIons for NuClear wasTe InVEntories) consortium, 2014-19, £450K to Imperial.
- Luc Vandeperre, UHTC-3, third phase of work on ultra-high temperature ceramics and composites, DSTL, £120k.
- Luc Vandeperre, Ceramic materials and shaping technologies for short life propulsion systems, Microturbo & MoD ITP-CM , £162k.
- Luc Vandeperre Ballistic ceramic composites, PhD studentship, Morgan Ceramics & DSTL, £75k.
- Luc Vandeperre Advanced Ceramic Luc Vandeperre Processing, PhD studentship, DSTL, £105k.
- Eduardo Saiz, Co-Investigator, Novel nanocomposites for bone regeneration, BRP-NIH, $2.5M.
- Eduardo Saiz, Bioinspired Structural Materials, Marie Curie International Reintegration Grant, EU, €100K.
- Eduardo Saiz, Bioinspired Ceramic/CNT composites-phase 2, The US Army Engineer Research and Development Center, $ 200K.
- Eduardo Saiz Co-I, Amelogenin Degradation by MMP20 and KLK4 in Enamel Biomineralization, NIH (USA), $ 1.4 M.
- Eduardo Saiz, Bioceramics for bone repair, Marie Curie Initial Training Networks (ITN), €3.6 M.
- Eduardo Saiz, Glass-ceramic Interfaces, Asahi Glass Company, £150K.
- Eduardo Saiz, Biomimetic organic-inorganic hybrid structural materials, Marie Curie Intra-European Fellowships, 1 April 2012-30 March 2014. €300K.
- Eduardo Saiz, Advanced composites inspired by nature, Marie Curie Intra-European Fellowships, 1 March 2012-28 February 2014. €300K.
- Eduardo Saiz, Graphene 3D networks, 1 Feb 2013-30 January 2017, EPSRC, £2K.
- Eduardo Saiz Co-I, Engineering with Graphene for Multi-functional Coatings and Fibre-Composites, 1 Feb 2013-30 January 2017, EPSRC, £1.3K.
- Eduardo Saiz, Graphene Enhancement of the Photocatalytic Activity of Semiconductors, Marie Curie Intra-European Fellowships, 1 November 2013 30 October 2015, €300K.
- Eduardo Saiz, Novel Wound Management Dressing, Welland Medical, £50K.
- Finn Giuliani, Silicon stabilised boron carbide, DSTL, 2013, £190k
- Finn Giuliani, £120K SECO tools AB Deformation of Alumina Coatings
- Finn Giuliani, Deformation of Polycrystalline Diamond. Element six, 2013, £60K

Publications

Books and Book Chapters

- WE Lee, MI Ojovan and CM Jantzen (Editors), Radioactive Waste Management and Contaminated Site Clean-up: Processes, Technologies and International Experience, (Woodhead, 2013).
- WE Lee and MI Ojovan, Fundamentals of Radioactive Waste (RAW): Science, Sources, Classification and Management Strategies, chapter 1 pp. 1-47 in Radioactive Waste Management and Contaminated Site Clean-up: Processes, Technologies and

International Experience, (Woodhead, 2013).

- CM Jantzen, MI Ojovan and WE Lee, Radioactive Waste (RAW) Conditioning, Immobilisation, and Encapsulation Processes and Technologies: Overview and Advances, chapter 6 pp. 171-246 in Radioactive Waste Management and Contaminated Site Clean-up: Processes, Technologies and International Experience, (Woodhead, 2013).
- Z Fan, Y Liu, J Wang, Z Pan, G Ren and WE Lee, China: Experience of Radioactive Waste (RAW) Management, chapter 22 pp. 697-721 in Radioactive Waste Management and Contaminated Site Clean-up: Processes, Technologies and International Experience, (Woodhead, 2013).
- Farid, K Shih, WE Lee and H Yamana, Fukushima: The Current Situation and Future Plans, chapter 24 pp. 744-769 in Radioactive Waste Management and Contaminated Site Clean-up: Processes, Technologies and International Experience, (Woodhead, 2013).

Journal Papers

- B Cui and W E Lee, High-temperature Oxidation Behaviour of MAX-phase Ceramics, Refractories World forum 5 [1] 105-112 (2013). WINNER of 3rd place in Gustav Eirich Award 2012.
- B Cui, E Zapata-Solvas, MJ Reece, C Wang and WE Lee, Microstructure and High-temperature Oxidation Behaviour of Ti_3AlC_2/W Composites" J. Am. Ceram. Soc. 96 [2] 584-591, 2013.
- E Zapata-Solvas, DD Jayaseelan, HT Lin, P Brown and WE Lee, Mechanical properties of ZrB_2- and HfB_2-based ultra-high temperature ceramics fabricated by spark plasma sintering, J. Euro Ceram. Soc. 33 [7] 373-86, 2013.
- D Manara, HF Jackson, C Perinetti-Casoni, K Boboridis, MJ Welland, L Luzzi and WE Lee, The ZrC-C Eutectic Structure and Melting Behaviour: A High-temperature Radiance Spectroscopy Study, J. Euro. Ceram. Soc. 33 1349-61, 2013.
- WE Lee, M Gilbert, S Murphy and RW Grimes, Opportunities for Advanced Ceramics and Composites in the Nuclear Sector, J. Am. Ceram. Soc. 96 [7] 2005-30, 2013.
- J Ye, S Zhang and WE Lee, Molten Salt Synthesis and Characterization of SiC Coated Carbon Black Particles for Refractory Castables Applications, J. Euro. Ceram. Soc. 33 2023-29, 2013.
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- J Ye, RP Thackray, S Zhang and WE Lee, Microstructure and Rheological Properties of Titanium Carbide Coated Carbon Black Particles Synthesised from Molten Salt, J. Mater. Sci. 48 [18] 6269-75, 2013.
- A Quadling, L. Vandeperre, P. Myers and W.E. Lee, High Temperature Characteristics of Refractory Zirconia Crucibles Used for Vacuum Induction Melting, pp 102-107 in Proc. Unified International Technical Conference on Refractories, UNITECR '13, Victoria, British Columbia, Canada, 2013.
- SK Kubal, C Pleydell-Pearce, JR Powson and WE Lee, Post Mortem Analysis of BOF Tuyeres, pp.442-447 in Proc. Unified International Technical Conference on Refractories, UNITECR '13, Victoria, British Columbia, Canada, 2013.
- J Alex, L Vandeperre, B Touzo, C Parr and WE Lee, Effect of Sodium Impurities on Phase and Microstructure Evolution in Calcium Aluminate cement Bonded Castables at High Temperatures, pp. 832-837 in Proc. Unified International Technical Conference on Refractories, UNITECR '13, Victoria, British Columbia, Canada, 2013
- M. Boix, S.Eslava, G. Costa Machado, E. Gosselin, N. Ni, E. Saiz, J. De Coninck, Adsorption of albumin and fibrinogen on thin calcium phosphate films measured by in-situ ATR-FTIR spectroscopy, submitted to Acta Biomaterialia in December 2013
- D.D. Jayaseelan, P. Brown and W.E. Lee, Development of ultra-high temperature ceramics (UHTCs) for hypersonic applications, AMPC 2013, Chennai, India, Feb. 6 -8, 2013 (Invited Lecture).
- D.D. Jayaseelan, Materials for extreme environments, The Indian Ceramic Society –

Chennai Chapter, India, Feb. 5, 2013 (Guest Lecture).

- O. Cedillos, D.D. Jayaseelan and W.E. Lee, Process development and microstructural characterization of (Ta,Hf)C ultra-high temperature ceramics, ECERS XIII, Limoges, France, June 23-27, 2013.
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Outreach

Newsletters

An occasional CASC newsletter, together with the annual report, provides news and contact information for visitors to the Centre and for dissemination at meetings and international visits. A newsletter was circulated in September 2013, covering additional CASC research and equipment, visitors to the Centre and the second summer school on ceramics. (https://workspace.imperial.ac.uk/structuralceramics/Public/Newsletter%205%20for%20CASC%202013.pdf)

Website

The website (www.imperial.ac.uk/casc) contains details of CASC staff, visitors, equipment and activities. Meetings organised by CASC, as well as future UK and international ceramic-related meetings are advertised on this website. The previous annual reports and other publicity material can be downloaded from this website. More information about CASC staff, and their research activities and presentations, is being added to the website.

Richard Brook Prize

In 2010, CASC set up the Professor Sir Richard Brook Prize for the best ceramics PhD thesis in the UK with sponsorship from Morgan Ceramics. This prize aims to increase the sense of community amongst PhD students researching ceramics in the UK and to mirror the IOMMM's AT Green Award that is available to undergraduates. Two nominations were received for the 2013 prize, which was won by Dr Huixing Zhang. Huixing's research on *Microstructural Evolution and Oxidation Behaviour of Spark Plasma Sintered MAX Ceramics* was supervised by Professor Ping Xiao at University of Manchester. The award in general covers a certificate, plaque and £1000 cheque.

CASC Industry Day

A third CASC Industry Day has been organised for 24 May 2013. About 11 industrial attendees from, Morgan Technical Ceramics, Dynamic Ceramics, Elements six and Ceram and Precision ceramics attended. One aim of this Industry Day is to present current research at CASC and associated universities to industrial partners. Research Associates gave short overviews of their research, and research staffs and research students presented posters for discussions. A second aim is to continue CASC activities and strengthen our relationship to industry. This includes the formation of an Industrial Consortium that, between other things, will allow industry access to state of the art facilities, expertise and educational activities. A questioner has been included to hear the feedback from industries that could help us very much to shape this Consortium and our relationship with Industry.

CASC Summer School on Ceramics

The fourth CASC Summer School on Ceramics held from 18 to 20 September 2013 at Imperial College London. The summer school provided tutorials focussing on current developments in ceramic synthesis, processing and mechanical characterisation with particular emphasis on the practical aspects and hands-on experience. These tutorials were aimed at early career engineers and researchers – working in universities or industry – who wish to enhance their ceramics background. Topics covered were ceramic powder synthesis, wet processing and mechanical testing at micro and macro scales. Tutorial sessions covered the state-of-the-art ceramic processing techniques and advanced mechanical characterisation.

Presenters were:

- Dr Tim Van Gestel (Forschungszentrum Jülich, Germany)
- Prof Jozef Vleugels (K.U.Leuven, Belgium)
- Dr Jon Molina (IMDEA, Spain)
- Prof Eduardo Saiz (CASC, Imperial College, UK)
- Dr Severin Hofmann (DLR, Germany)
- Prof John Fernie (AWE, UK)