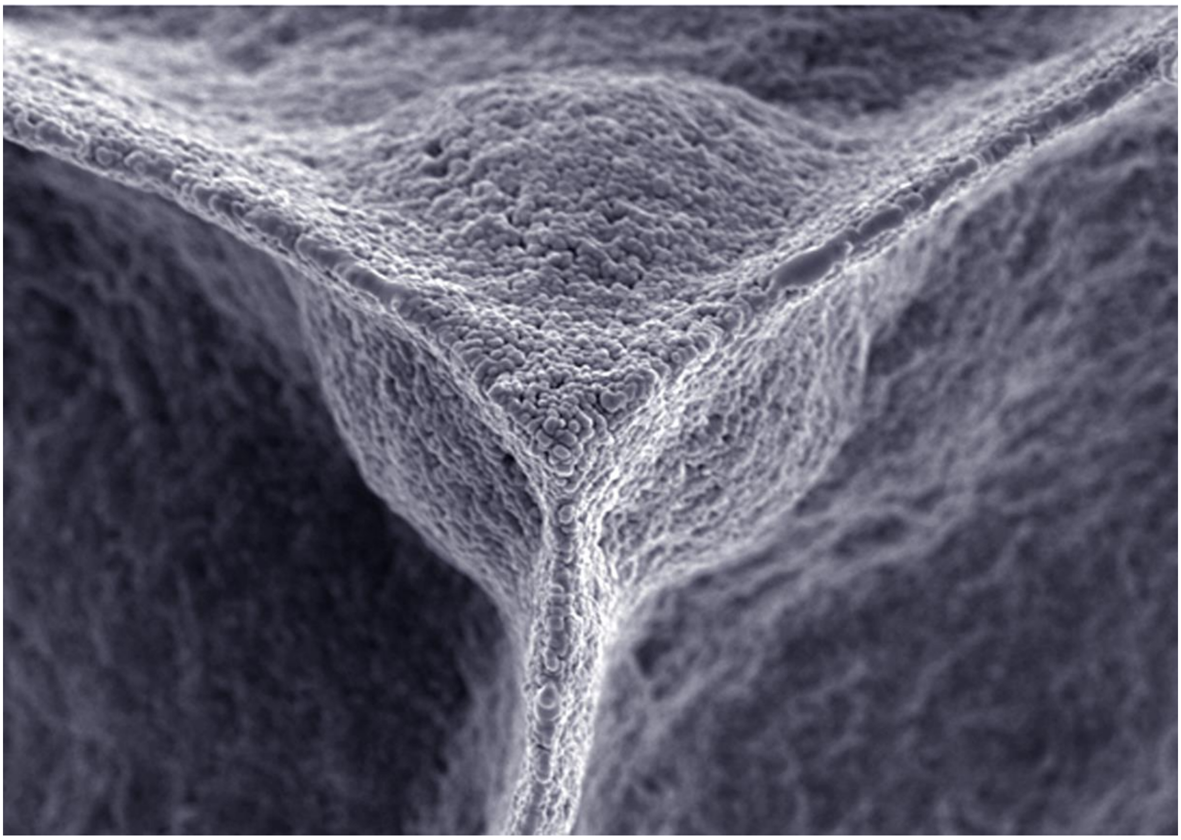
Centre for Advanced Structural Ceramics
Annual Report July 2012 – June 2013



SEM image of a complex ceramic structure obtained by self-assembling ceramic particles and soft templates with responsive polymers. The bubble behind the strut illustrates the efficient packing of droplets that builds a well-organized structure from nano to macro-levels. These strong cellular ceramics are promising materials for applications as diverse as lightweight thermal insulators with structural capability, catalytic supports or tissue engineering scaffolds.

Contents

1 Introduction

As part of its 4th Science and Innovation Call the EPSRC funded Imperial College to set up a UK Centre for Advanced Structural Ceramics (CASC). We have created a world-leading, multidisciplinary Structural Ceramics Centre between the Materials and Mechanical Engineering Departments with a strong critical mass at Imperial College but with buy-in from industrial and university partners in UK and abroad.

CASC has addressed the lack of critical mass of UK expertise in the fundamental understanding of structural ceramics that is highly relevant to key areas of the economy including, energy generation, aerospace and defence, transport and healthcare. Our structural ceramics vision extends to structural issues with functional ceramics. This is our fifth and final Annual Report during the EPSRC funding period, covering progress in the period 1 July 2012 to 30 June 2013. However, CASC will continue, building on the success enabled by the EPSRC funding so look out for CASC annual report 6 this time next year.

2 Overview of our plan and progress

CASC started in July 2008 with EPSRC funding (£5.5M) for a five-year programme and this report covers the fourth year, during which the main activities have been to:

- Develop current and new research programmes
- Continue to hold our successful summer on ceramics
- Maintain, use and make available to others' our large items of equipment
- Raise awareness of CASC nationally and internationally
- Continue to co-ordinate structural ceramics activities in the UK
- Strengthen contacts with structural ceramics groups in the UK and worldwide
- Initiate an Industrial Consortium to enable CASC to become self-sustaining after the EPSRC funding ends.

The most important needs in our five-year programme were acquiring, maintaining and developing top quality staff and additional research funds, developing space and building the community. As you will see in this report we have been successful in all these areas.

Our plan for CASC involved three phases which were tackled simultaneously:

1. **To create and manage a nucleus of key academic and support staff, postdoctoral researchers and PhD students**
2. **To build research capacity in the areas of property measurement and high temperature processing and modelling**
3. **To ensure sustainability, additionality and knowledge transfer**

In Phase 1 we have set up a Local Management Team (LMT) who meet monthly and a CASC Steering Group who meet annually and this will continue in the future.

We have built the team (section 4) and are publicising CASC via a range of activities including a web site (www.imperial.ac.uk/casc) which is updated regularly with information about the Centre and includes a list of conferences relevant to the ceramics community. Over the last twelve months we further expanded our equipment base for ceramic processing and characterisation. This includes the purchase of a high temperature modulus tester (section 5.11) (see section 5).

We are now well established in our refurbished study space and ceramics laboratory on the lower ground floor of the Materials Department, and have developed further space (room LG51 and LG55A) as part of the Department refurbishment programme in the MPAC (Materials Processing and Characterisation) area. LG51 now houses our high temperature vacuum furnace, modulus tester and hot press as well as providing additional general laboratory space in LG55A for the chemical processing of ceramics.

In Phase 2 we continue to develop national and international links and have been visited by a number of leading researchers (section 4.3). In addition, we hosted and organising in London an International Workshop on Advanced Ceramics (IWAC05) in September 2012 (section 8.3) and a Workshop on Modelling of Structural Materials of interest to the defence community (December 2012 (section 8.3)). We have made several international visits to initiate collaborations (section 8.3). We submitted a number of proposals for funding in key areas and several of these were successful; these emerging research themes are described in section 7.

In Phase 3 it is important that we keep our profile in the ceramics community high and some of our efforts at gaining publicity are described in section 8. This year we initiated the Sir Richard Brook Prize for the best Ceramics PhD in the UK and obtained sponsorship from Morgan Technical Ceramics. We have ongoing joint PhDs with Cambridge, Sheffield and Queen Mary and have helped organise another UK 1-DRAC (1-Day Research meeting in Advanced Ceramics). As part of our plans to support CASC after the end of EPSRC funding we have initiated an Industrial Consortium with various levels of membership (described in section 7.9) and Morgan Technical Ceramics, Rolls Royce and DSTL have become our first members. We held Industry Days (July 2nd 2012 and May 24th 2013) to highlight progress and outline how industry can get more involved with CASC. Our original proposal for the Centre received enormous support from institutions and industry worldwide (listed below). Perhaps the biggest factor illustrating our success has been the funding for large proposals recently acquired by CASC academics including the Materials in Extreme Environments Programme Grant funded by EPSRC with Jon Binner at Loughborough as PI and Mike Reece at QMUL and Bill Lee and Mike Finnis from Imperial as Co-I's, and the BioBone European consortium led by Eduardo Saiz (see section 7.6.2). The S&I award aimed to give the UK the ability to acquire such large grants and our ability to do so confirms CASCs success.

Company	Institution
Adelan Ltd Advanced Defence Materials Ltd (ADML) Applied Functional Materials (AFM) Asahi Glass Company (AGC) Boeing, USA EdF Energy (was British Energy) Calcarb	AO Foundation (Switzerland) AtlanTICC Alliance Case Western Reserve University, USA Erlangen University, Germany European Virtual Institute on knowledge-based multifunctional materials IDEA League INSA Lyon, France

Ceram Research Ceramtec Corus/Tata DSTL Dynamic-Ceramic FCT IngenieurKeramik Hereaus Electro-Nite Kerneos, France Morgan Technical Ceramics National Nuclear Laboratory (was Nexia Solutions) Noraker Pilkington Powdermatrix Praxair Surface Technologies QinetiQ Repsol (Spain) Rolls Royce (Submarines) Rolls Royce Fuel cells RWE Npower Sintec-Keramik TWI Umicore, Belgium	Instituto de Ciencia de Materiales de Madrid, CSIC, Spain Lawrence Berkeley National Laboratory, USA Nagoya Institute of Technology, Japan Nanyang Technological University, Singapore (they are coming end of June) NASA, USA National Research Council Institute of Science and Technology for Ceramics, University of Tokyo, Japan Oak Ridge National Laboratory, USA Penn State University, USA Politechnico di Torino, Italy Queen Mary, University of London TU Delft, Netherlands Tsinghua University, China Universidad Politecnica de Catalunya, Spain University of Alabama, USA University of Bayreuth, Germany University of Cambridge University of Erlangen-Nuremberg, Germany University of Illinois at Urbana-Champaign, USA University of Leeds University of Limerick, Ireland University of Manchester University of Michigan, USA University of Missouri-Rolla, USA University of Mons-Hainaut, Belgium University of Oxford University of Santa Barbara, USA University of Surrey University of Warwick

3 Management

Good management is key to the success of CASC; we have an active Local Management Team (LMT) and a Steering Group that meets annually and will continue to do so to ensure this is achieved.

3.1 Local management team

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 Fraser Wigley and Amutha Devaraj. LMT meetings are also attended by two representatives of the researchers and PhD students working on projects related to structural ceramics.

3.2 Steering group

The Steering Group 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

The group is chaired by Dr Andrew Hosty (Morgan Technical Ceramics) and meets in London annually, in the middle of the year. Prior to the meeting the group are sent a draft of the Centre's Annual Report and the minutes of the previous meeting, for comment. The members are:

- Professor Jon Binner (University of Loughborough)
- Professor Peter Brown (DSTL)
- Professor Bill Clegg (University of Cambridge)
- Mrs Janet Edwards (EPSRC)
- Professor Graham Fairhall (National Nuclear Laboratory)
- Dr Neil Glover (Rolls-Royce)
- Professor Peter Greil (University of Erlangen-Nuernberg, Germany)
- Professor Martin Harmer (Lehigh University, USA)
- Professor Greg Hilmas (Missouri University of Science and Technology, USA)
- Dr Andrew Hosty (Morgan Technical Ceramics, Chair)
- Professor Tony Kinloch
- Professor Bill Lee (Founding Director)
- Mr Chris Parr (Kerneos, Paris, France)
- Professor Eduardo Saiz (Director)
- Dr Luc Vandeperre (Deputy Director)
- Dr Amutha Devaraj (Technical Manager)
- Professor Julie Yeomans (University of Surrey)

CASC academics, including those supervising external PhDs and those involved in related research at Imperial, also attend the Steering Group meetings. The Steering Group also choose the winner of the Sir Richard Brook Prize for best ceramics PhD awarded in the UK annually. In 2012 and 2013 this has been sponsored by Morgan Technical Ceramics.

4 People

The CASC team includes those funded through the EPSRC award (three academics, five PDRAs, one PhD, technical manager and technician) and those associated with the centre but not funded by the award (academics and researchers at Imperial and other institutions) helping to build the UK capability. We have spent much effort on appointing the directly-funded members and incorporating Imperial ceramics researchers into the team.

4.1 Staff

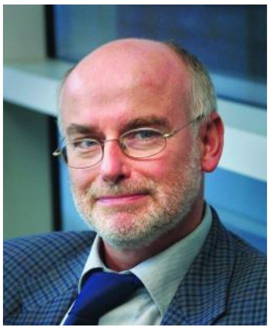
Selecting and appointing academic and support staff has been the most important of the Centre's continuing activities.

4.1.1 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. His chair is joint between the Departments of Materials and Mechanical Engineering. Eduardo took over the role of Deputy CASC Director in July 2010.

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.

4.1.2 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.

4.1.3 Fraser Wigley

Fraser Wigley, CASC Technical Manager UNTIL February 2013, graduated in Natural Sciences from the University of Cambridge and has worked on a range of ceramic-related projects in the Department of Materials at Imperial. He is involved in administrative, financial, equipment and building-related activities for CASC. Fraser worked half time for CASC, spending the rest of his time on similar activities within the Department of Materials.

4.1.4 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.

4.1.5 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.

Garry's 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.

4.1.6 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.

4.1.7 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

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.

Associate academic staff

A number of academic staff at Imperial currently work on projects involving substantial structural ceramics research. These include programmes on:

- Multilayer coatings and thin films: **Neil Alford**
- Ion-conducting ceramics in fuel cells: **John Kilner, Alan Atkinson and Stephen Skinner** in Materials and **Nigel Brandon** in Earth Science and Engineering
- Thermal barrier coatings: **Dan Balint** and **Kamran Nikbin** in Mechanical Engineering
- Bioceramics and glasses: **Julian Jones**
- Modelling of structural ceramics including oxides, spinels and pyrochlores: **Robin Grimes, Mike Finnis and Paul Tangney**

Project titles are given in Section 6, and more details about the projects and associate academics can be found in the Department's *Annual Report-Research in Progress 2011-12* document, which can be downloaded from www.imperial.ac.uk/materials.

Other associate academics include those with PhDs funded through the Centre (**Bill Clegg at Cambridge**, **Shaowei Zhang at Exeter** and **Mike Reece at QMUL**).

4.2 Researchers

The Centre's award included funding for 5 research associate and a PhD student to work with each of the three CASC academic staff, as well as external PhD students.

4.2.1 Research associates

Dr Vineet Bhakhri started work with Finn Giuliani in February 2010 after completing his PhD at the University of Western Ontario, Canada. He left CASC in June of 2013. He worked on N*ano-mechanical characterization of anisotropic ceramics by instrumented nano-indentation and micro-pillar compression testing techniques.* The aim is to extend their use to high temperatures to determine the fundamental plastic deformation properties of hard materials at elevated temperatures.

Dr Na Ni joined CASC in June 2011 after receiving her PhD from the University of Oxford, where she studied oxidation mechanisms of zirconium alloys by TEM and FIB/SEM. Before that she worked on metal/polymer nanocomposite thin films for sensor applications for her masters at the University of Kiel, Germany. She is interested in the study of materials structure and chemistry using combined FIB/TEM/STEM techniques. Having been awarded an EPSRC Doctoral Prize Fellowship, she is currently focussed on the study of *ceramic-metal interfaces to understand mechanisms of adhesion and atomic transport across the interfaces*. She is also working on TEM characterization of other materials, including graphene and ceramic/polymer composites.

Dr Rui Hao started working with Dr Finn Giuliani and Prof Saiz Gutierrez Eduardo in July 2012. She has been involved in an industrial project to investigating glass/ceramic interfaces.

Dr Jianye Wang joined CASC in June 2012 after receiving his PhD from the Imperial College London. He is now working with Dr. Luc Vandeperre on high temperature mechanical properties of UHTC materials.

Dr Osama Farid Mohammed joined CASC in June 2012. He is now working with Prof Bill Lee on Spectrophotometric determination of the oxygen to uranium ratio in uranium oxides during the preparation of simulated spent nuclear fuel

4.2.2 Internal PhD students

Nasrin Al Nasiri is a third year PhD student looking at *Fatigue mechanisms in SiC*, supervised by Finn Giuliani, Luc Vandeperre and Eduardo Saiz.

Jianye Wang has completed his PhD *Predicting in service thermo-mechanical performance of ultra-high temperature ceramics,* supervised by Luc Vandeperre and Finn Giuliani.

Constantin Ciurea has submitted his PhD on *High temperature deformation properties of TiAlN*, supervised by Finn Giuliani and Neil Alford.

Eleonora D'Elia is a second year student carrying her PhD project with Eduardo Saiz and Finn Giuliani on *Polymer/ceramic self-healing composites.*

Omar Cedillos Barraza is doing a PhD with Bill Lee on the *Development of non-stoichiometric ternary carbides in the TaC-HfC system for aerospace thermal protection systems*

4.2.3 External PhD students

Philip Howie has completed his PhD on *Small-scale plastic deformation of brittle ceramics* at the University of Cambridge, supervised by Bill Clegg (Cambridge) in collaboration with Luc Vandeperre and Finn Giuliani.

Ben Milsom is in the third year of his PhD research into T*he effect of carbon nanotubes on the sintering behaviour of hard and ultra-high temperature ceramics* at Queen Mary University of London, supervised by Mike Reece (QMUL) in collaboration with Eduardo Saiz.

Jianke Ye is in the third year of his PhD into *Preparation and characterisation of novel carbon materials for refractory applications* at the University of Sheffield, supervised by Shaowei Zhang (now at Exeter) and Bill Lee.

The research projects of these PhD students are described in more detail in Section 6.

4.2.4 Alumini

Some of the initial CASC students and postdocs have left the centre and joined other companies and organizations.

- Dr. Claudia Walter-IBM
- Mr. Constantin Ciurea-Rolls Royce
- Dr. Bai Cui-postdoctoral researcher at Urbana Champaign University-USA
- Dr Naeem Ur-rehman-postdoctoral researcher at KAUST

4.3 Visitors

We are developing links with institutions that have outstanding capability in structural ceramics research. We have hosted short and long visits from a number of individuals (listed below).

Date	Name	Organisation
02/07/2012	Dr Xiang Zhang	Ceram
02/07/2012	Ms Sarah Huelin	Brick Development Association
02/07/2012	Dr Milena Salvo	Politecnico di Torino, Italy
02/07/2012	Professor Monica Ferraris	Politecnico di Torino, Italy
02/07/2012	Dr Mashud Ahmed	Morgan Technical Ceramics
02/07/2012	Dr Laura Cohen	British Ceramic Confederation
02/07/2012	Dr John Fernie	AWE
02/07/2012	Mr Charles Marsden	Dynamic Ceramic
02/07/2012	Professor Peter Brown	DSTL
02/07/2012	Dr Paul Andrews	Rolls-Royce
02/07/2012	Professor Greg Hilmas	Missouri University of Science & Technology, USA
02/07/2012	Dr Andrew Hosty	Morgan Crucible
02/07/2012	Mr Chris Parr	KERNEOS Alumina Technologies, France
02/07/2012	Professor Mike Reece	QMUL
02/07/2012	Professor Julie Yeomans	University of Surrey
02/07/2012	Mrs Janet Edwards	EPSRC
02/07/2012	Dr Andrew Heaton	DSTL
02/07/2012	Professor Jon Binner	University of Loughborough
02/07/2012	Professor Martin Harmer	Lehigh university, USA
02/07/2012	Mashud Ahmed	Morgan Technical Ceramics
10/07/2012	Dr Janet Cotton	One Eighty (PYT), South Africa
06/09/2012	Mr Yasutaka Ishihara (PhD student)	Nagoya Institute of Technology
01/10/2012	Mr Akira Kawai (PhD student)	Nagoya Institute of Technology
01/10/2012	Professor Joel De Conninck	Mons University, USA

01/02/2013	Mr Osamu Sakamoto	Asahi Glass Co Ltd, Japan
01/02/2013	Mr Atsushi Ichikawa	Asahi Glass Co Ltd, Japan
20/03/2013	Professor Helmuth Coelfen	University of Konstanz, Germany
11/04/2013	Professor Wayne D Kaplan	Technion - Israel Institute of Technology
24/04/2013	Dr Nicholas Dunne	Queens University, Belfast
08/05/2013	Professor Paolo Colombo	University of Padova, Italy
23/05/2013	Professor Andreas Mortensen	Eccole Polytechnice Federale de La Switzerland
11/06/2013	Professor Joachim Bill	University of Stuttgart, Germany

Some of the visitors to CASC have made informal presentations as part of the newly-established series of Friday afternoon seminars, which are usually presented by CASC researchers or academics.

Extended visits over several months are important for developing long-term collaborations. We have supported and sought additional funding for visits from leaders of the US ceramics community, such as Arthur Heuer (Case Western Reserve University) or Martin Harmer (Lehigh University, USA). We have also invited several eminent materials scientist for short visits and deliver seminars. We plan to continue this policy and invite other eminent ceramists, particularly from Europe for short and long stays. We have also hosted and supported extended visits by younger researchers, integrating them into the Centre's activities.

5 Equipment

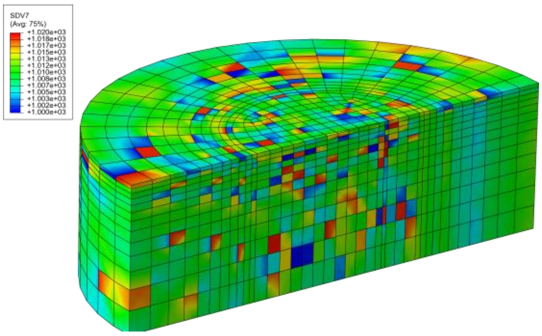
The purchasing and installation of large items of equipment by the Centre from the CASC funding, to improve UK capability in fabrication and modelling of structural ceramics, is now complete but we will continue to improve our experimental capability in this area using funds from other sources. All equipment 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.

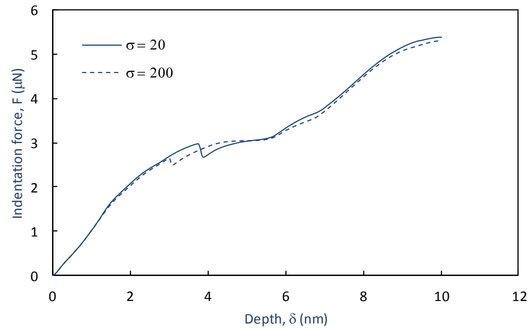
5.1 Nanoindenter

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).

5.2 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, σ, 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.





5.3 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.

5.4 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.

5.5 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.

Induction-heated thermo-mechanical

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

Crucibles of the high temperature combined TGA DTA

out up to 2000 °C. The pyrometer for temperature measurement up to 2400 °C has been commissioned but there were difficulties in 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.

5.6 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 .

5.7 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


Vacuum hot press

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.

5.8 Vacuum furnace

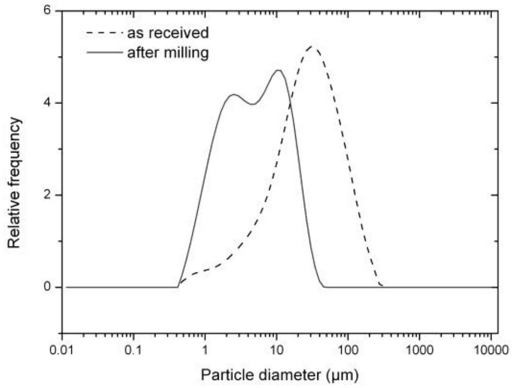
The vacuum furnace from Thermal Technology is now in place and after initial problems with the water cooling system the furnace is now in use. The furnace will heat a volume 5 cm diameter and 15 cm tall to temperatures up to 2500 °C under vacuum or a mixture of gasses. Opposed viewing ports will allow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

5.9 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.

5.10 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 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.



Examples of powder particles = distributions

5.11 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 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

Figure Set-up for room temperature measurements.

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.

5.12 Upcoming equipment

We have secure funding to buy several items of equipment that will be coming to the centre in the next few months. These include; a new optical microscope, a set-up for measuring contact angle and surface tension of liquids, a lab-scale tape caster and a robotic assisted deposition machine to print 3D ceramic parts following computer designs.

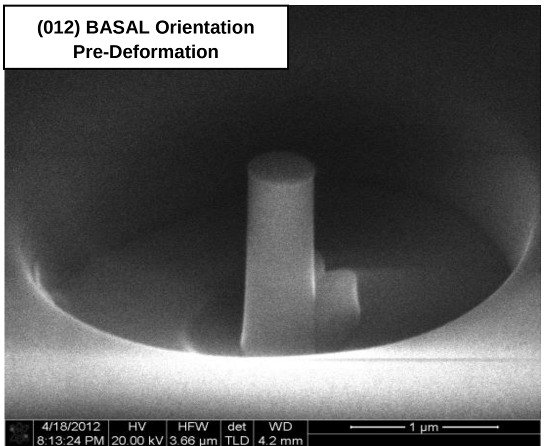
6 Research

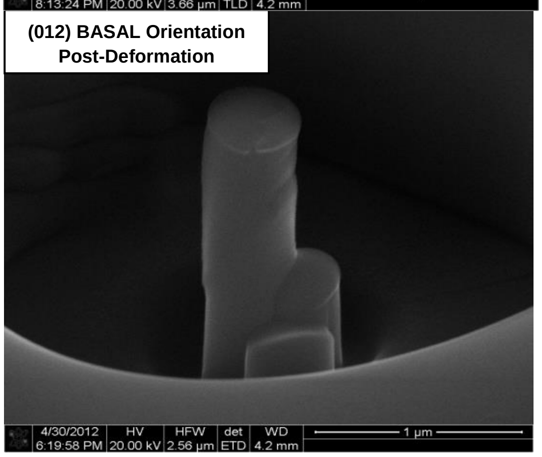
CASC is delivering world-leading research as demonstrated by publishing in top journals, getting invited to give lectures at other top institutions and at international conferences, and by acquiring funds for additional collaborative projects. Section 7 reports our progress in these areas. In this section we highlight some of our new research programmes.

6.1 Direct CASC Funded Research

6.1.1 Research Associate projects

6.1.1.1 Developing high temperature nano-mechanical testing- *Dr Vineet Bhakhri working with Dr Finn Giuliani.*

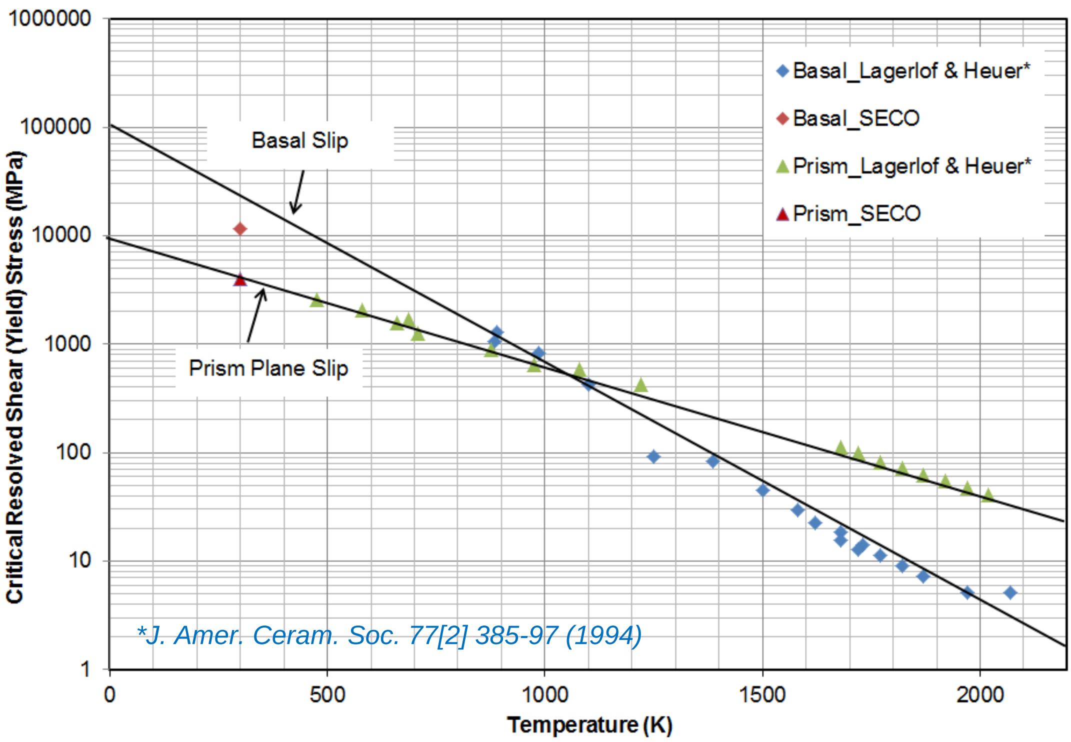




Vineet is currently involved in development and calibration of small scale testing techniques such as nanoindentation and micro-pillar compression. The aim is to extend their use to high temperatures to determine the fundamental plastic deformation properties of hard materials at elevated temperatures. Initial work has been centred on high temperature nanoindentation of bulk single crystal (001) TiN and 3 μm thick $Ti_{0.44}Al_{0.56}N$ coating deposited on (001) MgO. Indentation hardness drastically dropped for bulk single crystal (001)TiN from 21.2(±0.5) GPa at 298K to 10.7(±0.45) GPa at 623K. On the other hand, hardness of cubic $Ti_{0.44}Al_{0.56}N$ coating was quite stable in the measured temperature range, 29.5(±1.3) GPa at 298K and decreased slightly to 25.9(±2.3) GPa at 573K. These findings are in line with the literature where it is shown that the addition of Al to TiN significantly improves its mechanical stability with temperature. Indentation hardness data from these ceramic materials is further analysed to extract the fundamental deformation parameters at 293K to 623K. The measured activation volume was estimated to be of the order of $0.75\times b^3$ for both TiN and $Ti_{0.44}Al_{0.56}N$ (b is the Burgers' vector). The calculated activation energies were in the range of 0.76 eV for single-crystal TiN and 1.28 eV for $Ti_{0.44}Al_{0.56}N$ and are typical of lattice-controlled dislocation glide mechanism.

The use of a sharp tip Berkovich indenter during indentation tests results in the activation of multiple slip systems due to the non-uniform deformation and it invokes high strain-gradient in deformed material in the plastic zone beneath it. Micro-pillar uni-axial compression testing provides a way to study the mechanical behaviour of materials in a much simpler stress state and plastic flow in individual slip system can be studied. This technique is employed to investigate room-temperature plasticity of otherwise brittle Al_2O_3 coatings deposited on TiCN substrates (provided by SECO Tools, Sweden). Nano-pillars with approximate dimensions of 0.5 μm in diameter and 1.5 μm in height were fabricated on the coating surfaces oriented preferably for (012) Basal and (001) Prismatic slips. These nano-sized structures were then subjected to compression using a flat-punch indenter tip at a constant loading rate of 0.15mN/s. The estimated critical resolved shear-stress (CRSS) was found to be of the order of 11.5GPa for Basal slip and 4.0GPa for prismatic slip. These results are consistent with the data obtained by Lagerlof & Heuer for these two slip orientations at elevated temperatures. Higher CRSS for Basal slip in Al_2O_3 is attributed to the splitting of a dislocation into two non-colinear partials separated by high-energy stacking faults. However, the dislocation structures in Prism slip were shown to dissociate into three collinear partials separated by low-energy stacking faults resulting in lower CRSS.

Further experimentation is underway at moderately elevated temperatures (below 673K) for these orientations to acquire the data set at temperatures where limited or no plasticity has been observed in Al_2O_3 by conventional compression tests on bulk material.

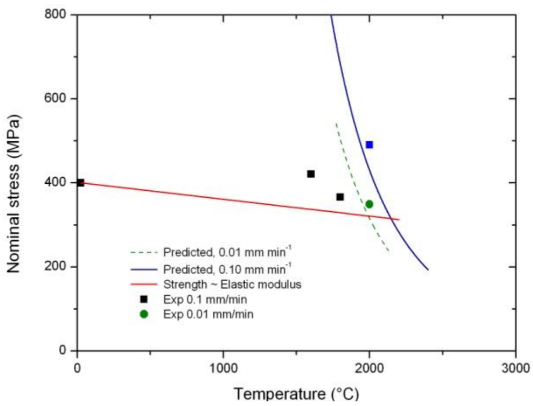


Besides work on indentation, Dr Bhakhri is also involved in the synthesis and characterisation of Si-doped boron carbide. This is a potentially interesting material as it has been theoretically predicted that the addition of Si would suppress a potentially weak poly-type of boron carbide resulting in significant increase in performance particularly for armour applications.

For this work, a variety of synthesis routes were researched and tested in an attempt to synthesise silicon-doped boron carbide nanostructures. The material was synthesized by the solid-liquid-solid method in an argon atmosphere at 1500°C from submicron boron powder, silicon powder and activated carbon, with sodium chloride and cobalt catalysts in a tube furnace. To increase the yield, the vapour pressure was increased by increasing the volume of reactants relative to the volume of the furnace. The resulting material was made up of platelets with composition including stable poly-types $B_{11}C_3$/$B_{13}C_2$. The material was subjected to plasma treatment to burn excess carbon at University of Birmingham and subsequent *in-situ* high pressure testing (up to 50GPa) was carried out at I15 (diamond light source) in collaboration with the Edinburgh University. Results were consistent with the suppression of the weak poly-type. Following HRTEM work on the compressed pellets recovered after pressurization at I15 (Diamond Light Source) also supports the suppression of pressure-induced amorophisation in Si-doped boron carbide compared to pure boron carbide material where micro-cracking was observed.

6.1.1.2 High temperature mechanical properties of UHTCs- *Dr Jianye Wang, PDRA, previously internal PhD student, now working with Dr Luc Vandeperre*

This work follows on from the internal CASC PhD on the processing and deformation of ZrB_2 based ceramics in which pressureless sintering of zirconium diboride was investigated as well as the deformation behaviour using indentation testing. As reported in the previous annual report, this work culminated in proposing a deformation mechanism map for zirconium diboride. In the current project, the predictions of the mechanical behaviour made from hardness tests are being compared to experimental measurements in 3 point bending at high temperature. Results to date show that zirconium diboride can retain its room temperature strength up to 2000 °C, at which point the measured strength becomes strongly dependent on the effective strain rate as permanent, plastic, deformation starts to occur. Moreover, the apparent strength levels for 2 deformation rates agree with what is predicted by finite element calculation of the response using the constitutive equations for the mechanical behaviour derived in the PhD project. (see the figure). In contrast, HfB_2 still fails by brittle failure at 2000 °C. Given its higher melting point, this was to be expected. To confirm this further, it is planned to measure the hardness evolution of HfB_2 with temperature as well.



Measured 3 point bending strength of ZrB_2 compared with predictions for 2 deformation rates as derived from hardness measurements.

Another project being carried out by the PDRA in collaboration with King Abdullah University of Science and Technology (KAUST) in Saudi Arabia is the use of spinodal decomposition of SiC-AlN alloys to influence the high temperature properties. To date, it has been confirmed that alloys consisting of 50 wt% SiC and 50 wt% AlN can be produced as a single phase material with a hexagonal microstructure and that upon heat treating this material gradients in SiC and AlN concentration do form. The next step is to determine whether this indeed leads to better mechanical properties.

6.1.1.3 Transport and adhesion at metal ceramic interfaces- *Dr Na Ni with Prof Eduardo Saiz*

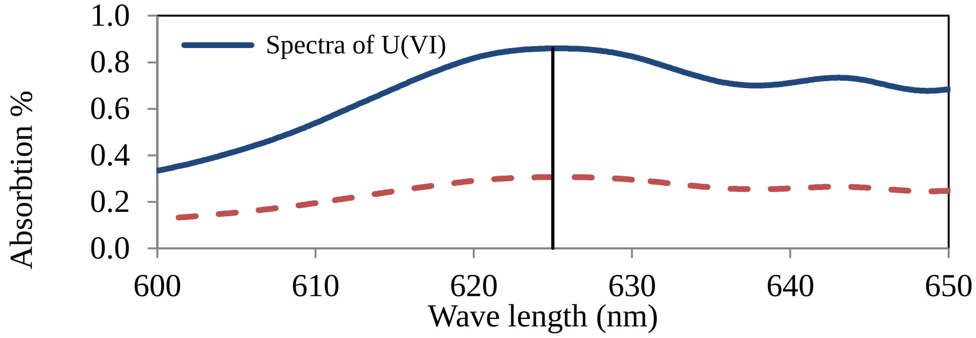
Na is working on the analysis of metal/ceramic interfaces. Adhesion and atomic kinetics at metal/ceramic interfaces at high temperature plays a determining role in many modern technologies, from brazing and soldering to composites and thin films. It is becoming universally accepted that in many of these complex, multiphase technologies the interface between different constituents is the “weak link” that determines properties, controls structural evolution and compromises the overall stability. The current work is focused on the fundamental effect of oxygen partial pressure on boundary segregation and mass transport at the oxide/metal interface using aluminium oxide and Ni as model materials. Particular attention is placed in the low oxygen activity regime that is closely related to important technological applications such as oxide scales or thermal barrier coatings. The interfaces are being fabricated under controlled temperature and atmosphere in liquid state using high purity polycrystalline ceramic substrates and analysed using advanced transmission electron microscopy as well as atomic force microscopy. The results have revealed that the both the metal/ceramic interfacial energy and the ceramic grain boundary energy reduce at reduced oxygen partial pressures, and the interface transport rate increases dramatically when the oxygen activity is very low. Atomic scale characterization by TEM has revealed that the ceramic grain boundaries with lower grain boundary energy exhibit a structural disorder as well as excess of Al and segregation of Ca at the grain boundary.

Na has been also carrying out TEM work on several other projects in collaboration with other members in the department, which spans from the study of the atomic structure of graphene and other low dimensional materials such as WS_2, the graphene/ceramic composite, the nano-porosity in polymer foams, to the study of grain boundary properties in ceria and their influence on the electrical conductivity.

6.1.1.4 Glass/ceramic interfaces- *Dr Rui Hao working with Prof Saiz Gutierrez Eduardo*

6.1.1.5 Spectrophotometric determination of the oxygen to uranium ratio in uranium oxides during the preparation of simulated spent nuclear fuel – *Dr Osama Farid with Prof Bill Lee*

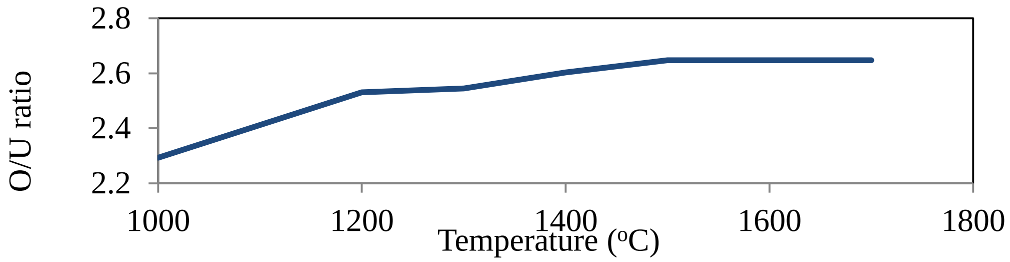
To prepare simulated nuclear fuel that replicates the chemical and microstructure of irradiated fuel, the determination of O/U ratio based on the dissolution of SIMFUEL in concentrated phosphoric acid under an inert atmosphere plays an important role to preserve uranium oxidation states. There are many instrumental and chemical methods available for the determination of the O/U ratio. Spectrophotometric methods for the determination of the O/U ratio do not require weighing and complete dissolution of the sample because both U(VI) and U(IV) are determined in the same aliquot. The determination of the O/U ratio is shown in Figure 1.



Absorption spectra of U(IV) and U(VI)

From the absorption spectra of U(IV) and U(V1) at 626 nm, it is seen that U(IV) and U(VI) have maximum values of 0.8601 and 0.307, respectively. The stoichiometry is 2.6431, which indicates that mixed of UO_2 and U_3O_8 exist within the sample. UV spectrometry may assist in understanding the electronic structure of the optical band gap of the material.

Uranium dioxide has a great affinity for oxygen and O/U values obtained changed based on sintered temperature of UO_2. In order to investigate the effect of sintering temperature, different pellets were sintered at different temperature and O/U values are shown in figure 2.



O/U ratio at different temperature

The reported absorptivity of U(IV) A_4 at 626 nm increased with increasing in temperature.

The increase in temperature changes UO_2 composition, as the theoretical ratio of oxygen to uranium (2) changes, the exact stoichiometry is seldom attained, because more than the stoichiometric amount of oxygen is almost invariably present. This is referred to hereafter as excess oxygen. It can concluded that in the oxidation of UO_{2+x} when x exceeds 2.25 and at temperatures greater than 1500K, a mixed phase of UO_2 and U_3O_8 results. In this phase, UO_2 is oxidised, and its structural properties change significantly.

6.1.2 Students Projects - PhDs

The CASC-funded internal PhD studentships are described below.

6.1.2.1 Effects of microstructure on environmental degradation and fatigue of silicon carbide - *Nasrin Al-Nasiri supervised by Finn Giuliani, Luc Vandeperre and Eduardo Saiz.*

Silicon carbide has attracted much attention as a candidate material for high temperature structural applications. In those environments, silicon carbide oxidises and this causes slow crack growth to become a problem. However, silicon carbide's properties such as a high specific stiffness, low thermal expansion and high thermal conductivity, make it an interesting structural material for space applications. Indeed silicon carbide is playing an increasingly more prominent role in the scientific missions of for example the European Space Agency. Since minimizing the mass of space components requires ideally that the materials can carry as much load as possible, using a high toughness silicon carbide appears appealing. However, such instruments tend to be developed over relatively long periods of time, and components sometimes need to be stressed for prolonged times on earth in environments where moisture can't always be excluded. Moreover, silicon carbide is becoming a potential candidate for biomedical applications and here also components will be stressed for prolonged times in wet environments.

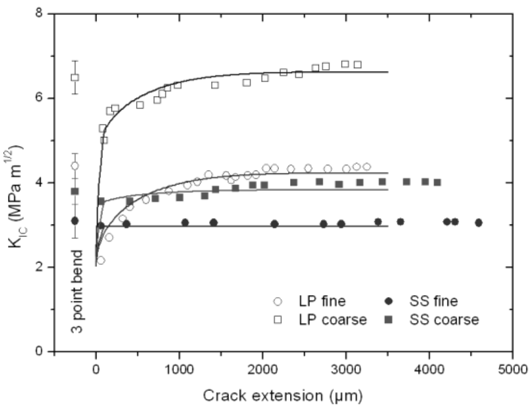


Figure: R-curves for the different types of SiC materials produced by either liquid phase (LP) sintering or solid state (SS) sintering. Only the LP sintered materials show a rising R-curve.

Unfortunately, there have been almost no studies of the sub-critical crack growth in silicon carbide at room temperature. In itself this is not surprising as the covalent bonds of silicon carbide should make it immune to corrosive attack by water. However, introduction of often oxide phases on the grain boundaries in the development of tougher microstructures could induce a sensitivity to stress corrosion cracking. The first aim of this paper was therefore to clarify the sensitivity to sub-critical crack growth for 2 typical silicon carbide materials with different grain boundary chemistry: solid state sintered silicon carbide with addition of boron and carbon and liquid phase sintered silicon carbide with alumina and yttria. To establish whether the microstructure and possibly the rising R-curve play a role, it was decided to study a fine grained microstructure and one with larger grains of each type of material.

Key results to date include the production of the 4 microstructures, the measurement of the short crack toughness and R-curve for all materials (see the Figure). The characterisation of the slow crack growth behaviour was performed using strength measurements at different loading rates. Some data of the crack velocity versus applied stress intensity has been measured directly also. The results confirm that oxides on the grain boundaries do induce sensitivity to aqueous corrosion but have also shown that grain size is important: microstructures with large grains much less sensitive to slow crack growth than fine grained materials.

6.1.2.2 Development of non-stoichiometric ternary carbides in the TaC-HfC system for aerospace thermal protection systems - *Omar Cedillos Barraza supervised by Bill Lee*

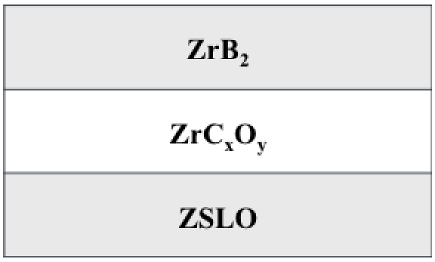
Thermal protection structures with superior properties are needed for next-generation (hypersonic) re-entry space vehicles which, when equipped with sharp aerosurfaces like leading edges or nosecaps, have projected requirements for materials operating temperatures above 2000°C in both neutral and oxidising environments. Ternary compounds in the tantalum-hafnium system have extremely high melting points often exceeding 4000°C making them potential candidates for these applications. This project is synthesizing using self-propagating high-temperature synthesis and sinter using spark plasma sintering, hot pressing and pressureless sintering, different ternary compounds and measure their thermo-mechanical properties. Oxidation studies are being carried out at temperatures in excess of 2000°C.

6.2 Other Associated Projects

6.2.1 Research Associate Projects:

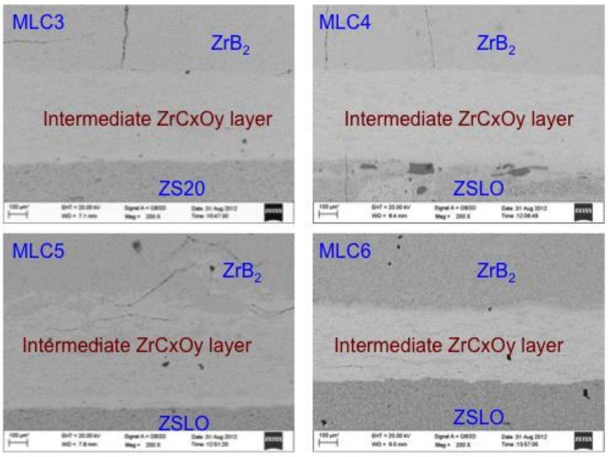
6.2.1.1 Ultra high temperature ceramics for extreme environments *(Dr Doni Daniel, Dr Luc Vandeperre and Prof Bill Lee)*

Dr Doni Jayaseelan Daniel, a Research Fellow in CASC has made progress in the quest to develop materials capable of withstanding severe conditions for hypersonic space travel. There is a strong interest in the development of reusable systems to access and return from space. These reusable systems demand a huge effort, not only in the development of materials but also in the integration of them into the subsystems. Current state-of-the-art thermal protection system (TPS) materials is mainly based on bulk ceramics or on CMCs coated by HfC, ZrC, SiC by CVD technique. Currently, new approach based on bulk ceramic multilayer design, which should allow a higher flexibility for integration with ceramic composite substrate has been carried out.

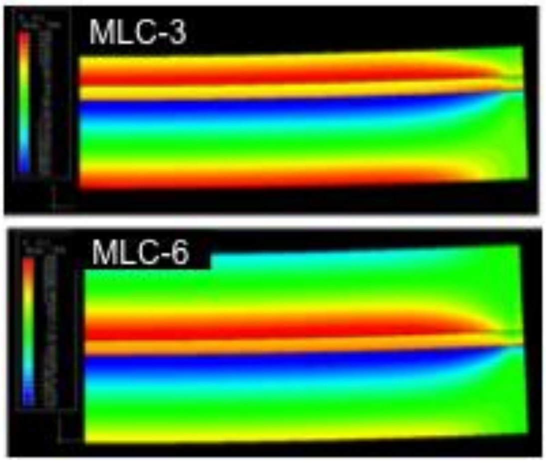


Schematic design of multi-layered composites

Multi-layers consisting of a ZrB_2 top layer, a Zr-oxycarbide intermediate layer and a bottom layer of ZrB_2 with silicon carbide (ZS20) or ZrB_2 with silicon carbide and lanthanum oxide (ZSLO) were carried out. For a 3 mm bottom layer, a 0.5 mm interlayer and a 1 mm top layer of ZrB_2 – MLC3, MLC4 and MLC5, cracks from at the interface and grow to the surface of the ZrB_2 layer and cracks can be seen in the bottom ZS20 layer too. In contrast when the ZrB_2 thickness is also increased to 3 mm no cracks appear to be present on the surface. Further inspection shows that there are some cracks but they do not penetrate through the ZrB_2 layer thickness. Indicative calculations of the residual stresses confirm that a compressive stress due to bending of the disks can stop cracks growing through the ZrB_2 layer when its thickness is increased to 3 mm, and that the tensile stress in the bottom layer is reduced also.



Cross section microstructures of multi layered composites



Finite element calculations of the stresses in MLC-3 and MLC-6

6.2.1.2 *Biomimetic organic-inorganic hybrid structural materials-Dr Miriam Miranda, Prof Eduardo Saiz*

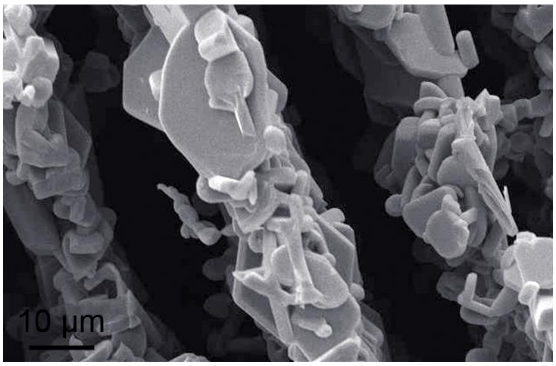
Dr Miriam Miranda (Intra-European Marie Curie Fellow) is working on the mineralization of organic scaffolds. The project is aimed at developing a bottom up process for the creation of biomimetic organic-inorganic structures. The process goes from the molecular stage to prepare the phases involved, to the use of emerging techniques to fabricate bio-inspired structural materials with regenerative applications in the biomaterials field.

The first part of the project will be the synthesis of different hydrogels for the organic phase. These hydrogels will be formulated in base of modified polymers. The selected polymers are chitosan (as a natural polymer) and poly(2-hydroxyethyl methacrylate) (PHEMA, as a synthetic polymer), that will be chemically and physically modified to improve a subsequent mineralization with the inorganic phase. The hydrogels will be used as templates for the crystallization of apatite nanoparticles. Before carrying out a bulk mineralization, a complete study of this stage will be performed in thin films (2D study) with the aim of studying and characterizing the mineralization mechanisms and the organic-inorganic interface.

The last part of the project will be the mineralization of the hydrogels and the creation of three dimensional 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.

6.2.1.3 *Advanced composites inspired by nature*

Working with Eduardo Saiz and in collaboration for Professor Mike Reece at Queen Mary College, Dr Suelen Barg (Intra-European Marie Curie Fellow) is working on the development of bio-inspired ceramic composites. Natural composites like bone and nacre present unique combinations of strength and toughness and self-healing abilities that are in some cases unmatched by engineering materials. This is achieved through the formation of complex hierarchical architectures and molecular scale interfacial engineering in biological and natural materials. Freeze casting is a powerful technique to produce bio-inspired hierarchical structured composites mimicking the natural design of nacre. Despite promising preliminary results, many issues are still to be addressed and explored in order to take full advantage of freeze casting and understand the whole of bio-inspiration in the development of advanced synthetic structural composites. With regards to the structural control, a main challenge is to increase the freeze cast composites volume fraction of the ceramic phase (which is at ~80% now) to values nearer to the natural composites (~95%). The proteinous nano-layer in nacre has a key function in the multi-scale toughening mechanisms. However, we do not know yet how the properties of this thin layer should be to provide maximum energy dissipation and increased strength.



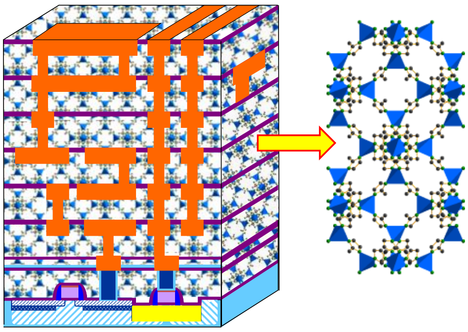
Silicon carbide scaffold fabricated by freeze casting

This Marie Curie fellowship is pursuing the design and fabrication of novel ceramic-based composites inspired by three key aspects of natural composite materials: complex hierarchical structures, combination of hard and soft phases and engineered interfaces. It is taking an integrated and multidisciplinary approach towards comprehending, processing and characterizing the materials with the following specific objectives:

- Combination of freeze casting and Spark Plasma Sintering as a novel approach for the fabrication of ceramic-based composites mimicking the hierarchical structures of nacre.
- Use soft phases on synthetic materials to truly replicate their role on natural composites.
- Multiscale interfacial engineering from micro to molecular level.

6.2.2 Metal-organic framework ZIF-8 films as low-κ dielectrics in microelectronics- *Dr Salvador Eslava and Prof. Eduardo Saiz*

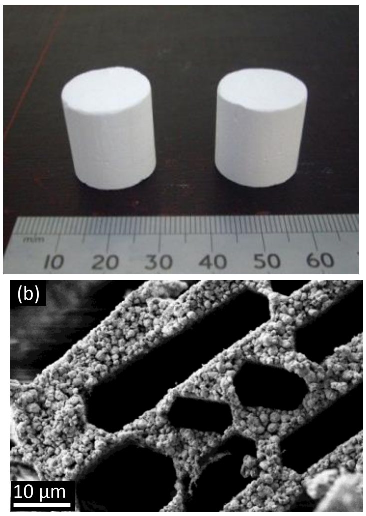
This project has found that metal-organic framework ZIF-8 films are promising candidates as future insulators (low-*κ* dielectrics) in microelectronic chip devices. Different characterization techniques show they offer low dielectric constant, high breakdown voltage, hydrophobicity, and sufficient thermal and mechanical stability for the microelectronics processing. This work is performed in collaboration with IMEC, a world-leading microelectronics research centre based in Belgium. The results have opened a new direction for research into the application of diverse metal-organic frameworks. Published in Chem. Mater., 2013, Vol:25, Pages:27-33



Sketch of a microelectronic chip including a metal-organic framework ZIF-8 as insulator in the on-chip interconnects

6.2.3 Preparation of zeolite monoliths with hierarchical porous structure by freeze casting- *Dr Salvador Eslava and Prof Eduardo Saiz*

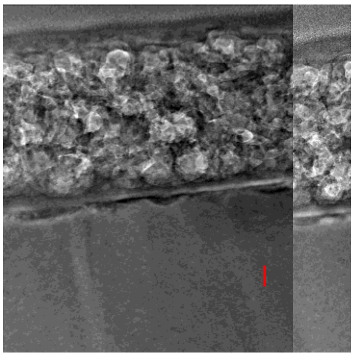
This project consists of fabricating porous zeolite monoliths using freeze casting. Freeze casting or unidirectional ice templating involves the formation of ice as a template of ceramic and/or polymeric materials. It has been used to create sophisticated porous and layered-hybrid materials, ceramic-metal composites, and porous scaffolds. This technique has not been exploited in the zeolite field. The use of freeze casting as a technique to prepare zeolite monoliths is being assessed and collaborators at Lulea University are examining their performance in catalysis.



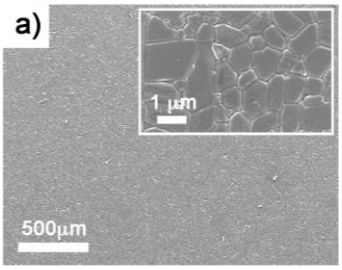
Images of zeolite monoliths and (b) internal structure

6.2.4 Calcium phosphate thin films and their interaction with the physiological environment- *Dr Salvador Eslava, Gil D. C. Machado, Dr. Na Ni and Prof. Eduardo Saiz*

The purpose of this project is to develop new *in situ* techniques based on attenuated total reflectance Fourier transform infrared spectroscopy for the analysis of protein adhesion on biomaterial surfaces, such as calcium phosphates. Films approx. 100nm thick of hydroxyapatite, tricalcium phosphate and mixtures of previous two have been successfully synthesised by sol-gel technique. This kind of films, coated on triangular silicon prisms, allow the in-situ monitoring of protein adsorption and description of the protein secondary structure. This project, framed in the initial training network for young researchers Biobone, involves collaboration with Professor Joël De Coninck at University of Mons, Belgium.



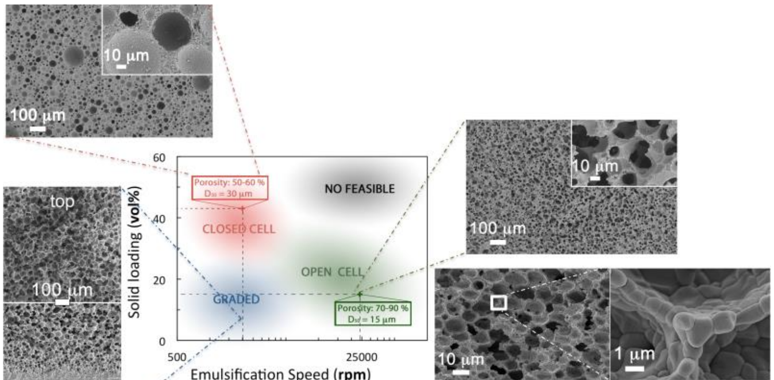
6.2.5 Assembling "smart" ceramic particles with responsive polymers to build complex ceramic structures - *Dr Esther Garcia-Tuñon and Prof Eduardo Saiz*



This project is developing a bottom up approach to fabricate complex ceramic structures with controlled morphological features from macro to nano levels. The design of 'smart' inorganic particles by surface functionalization with responsive polymers allows us to self-assemble ceramic suspensions or emulsified suspensions to form highly dense (a) and/or cellular ceramics.

The method is independent of the particle chemistry, versatile, reversible and simple, using surface functionalization with small additions of a single polymer to enable dispersion and trigger assembly. At high pH both, suspensions and emulsions, are very fluid, while under acidic conditions the BCS-functionalized surfaces "turn on" multiple links between the molecules functionalizing particles and droplets. A pH switch triggers a self-assembly process to form in-situ solid parts that can be easily handled and retain the complex shape of the mould. The rheological response of the suspensions can be manipulated to support a range of manufacturing techniques including the formulation of injectable ceramic inks for solid free form fabrication or injection moulding.

This project addresses two standing issues in the fabrication of highly porous materials: how to reliably form them into complex shapes and how to increase strength, opening new paths for the fabrication of lightweight structural components.



Long drying times lead to honeycomb structures as a result of thin film (walls) and plateau border (struts) formation between oil droplets in the emulsion.

By manipulating the emulsification conditions and the relative kinetics of self-assembly and drying, we can manufacture cellular ceramics with complex shapes and a broad range of microstructures ranging from closed-cell to highly interconnected open porosity or structures exhibiting graded architectures from dense to highly porous. These porous materials exhibit high compressive strengths that in the case of close-cell ceramics can be more than double of those previously reported for similar macro-porous. This extraordinary mechanical performance reflects the meso to macro scale structure of the materials and the efficiency of the process.

The potential for application is very broad including light filters, ceramic films with graded porosity, bulk thermal shock-resistant structures, thermal barrier coatings or temperature control membranes for auto thermal reforming, to mention a few. In particular, current research in our group is focusing on the use of closed cell ceramics as lightweight thermal insulators with structural capabilities and the application of open cell structures as catalytic supports and tissue engineering scaffolds.

6.2.6 Students Projects:

6.2.6.1 *High temperature deformation of age hardening coatings- Constantin Ciurea, supervised by Finn Giuliani and Neil Alford*

Traditional materials become softer as they are heated. The goal of this project is study a recently developed class of ceramics which increase their strength at high temperature (ternary nitrides e.g. $Ti_{1-x}Al_xN$). These have found widespread use as high temperature cutting tools but a fundamental understanding of the hardening mechanisms is lacking. This limits further optimization of the material system. Initial work has centred on accurately measuring the hardness of TiN and various $Ti_{1-x}Al_xN$ compositions over a range of temperatures and strain rates to extract fundamental deformation parameters such as activation volume and Peierls stress. In parallel the films have been carefully characterised by XRD and TEM.

A comparative study of the influence of temperature on the mechanical behaviour of bulk single crystal TiN and various $Ti_{1-x}Al_xN$ compositions deposited by two PVD techniques has been done. The influence of the grain boundary in TiN system and the addition of aluminium in TiN matrix on the mechanical properties have been examined. The hardness of bulk single crystal TiN is strongly affected by the increase in temperature. TEM analysis revealed that the plastic deformation of bulk single crystal TiN occurred along {011} slip plane at temperature up to 400°C.

Magnetron sputtered compositions close to the stoichiometric composition $Ti_{0.5}Al_{0.5}N$ exhibit significantly higher hardness than TiN and, more important, the hardness remains constant with temperature up to 350°C; this suggests that the addition of aluminium improves not only the room temperature hardness but also the mechanical stability with temperature. It is proposed that this mechanical behaviour is linked to the presence of stabilised cubic AlN phase in TiN matrix and this will be supported by XRD and TEM. Another area of focus has been to examine the influence of deposition parameters on mechanical properties of industrial cathodic arc evaporated $Ti_{1-x}Al_xN$ coatings. The deposition bias has a strong influence on the crystallography and morphology of these coatings. In addition, they do not exhibit a stabilised cubic AlN phase, compare to magnetron sputtered coatings. Therefore, the increase in temperature leads to a significant drop in the hardness of industrial cathodic arc evaporated $Ti_{1-x}Al_xN$ coatings, similar to the drop in hardness exhibited by TiN system.

6.2.6.2 *Polymer/Ceramic Self-healing Composites- Eleonora D'Elia supervised by Prof Eduardo Saiz and Dr Finn Giuliani*

The main aim of this project is to design a new family of self-healing hybrid materials by combining freeze casting of ceramic scaffolds with infiltration of selected organic phases and engineering of the organic/inorganic interfaces at the molecular level. The scaffold production has been controlled by optimisation of the freeze casting method reproducing the multi-scale structural features present in nacre. Optimum scaffolds have been infiltrated with specifically designed supramolecular polymers showing controlled rheological responses and self-healing properties. Basic studies of interfacial adhesion at the soft/hard interface have been carried out via DCB test in order to guide the development of new strategies for interfacial engineering. Those tests have resulted in the understanding and creation of completely self-healing organic/inorganic interfaces with shear responsive behaviour. Further studies on brick and mortar composite structures in tensile testing are being carried out to test the ability of self-healing of glass/polymer composites. Systematic structural and mechanical testing will be used to uncover the key parameters that govern the mechanical and healing response. The goal is to use nacre as the inspiration to create tough and resistant composites able to self-repair after impact or prolonged stress.

6.2.6.3 Magnesium Phosphate cements for uranium encapsulation *- William Montague supervised by Dr Luc Vandeperre (PhD student, EPSRC-NNL Case studentship)*

The aim of this research is to determine whether magnesium phosphate cements can be used to encapsulate uranium metal arising from nuclear installations. A first part of the work was to investigate the relationship between cement formulation and processing properties as well as strength development. This lead to the selection of a limited number of recipes for corrosion trials of uranium metal encapsulated in magnesium phosphate cements at different temperatures to accelerate the corrosion. In parallel, cement samples without uranium were cured under the same circumstances to allow contrasting the evolution of the cement with and without uranium present. Currently the focus is on the decommissioning of a small number of the trials to understand the extent of corrosion and the corrosion products.

6.2.6.4 Development of high toughness mullite *-Daniel Glymond supervised by Dr Luc Vandeperre (PhD student, Office of Naval Research Global)*

Recent designs for light weight turbines for portable power require a high operating temperature and a recuperator to recover exhaust heat if reasonable efficiencies are to be obtained. Because of the high temperature design, high performance ceramics are needed for most of the engine components, including the heat exchanger, turbine blades, and other stationary components.

Mullite, $3Al_2O_3.2SiO_2$, is an attractive candidate material due to its low thermal conductivity, adequate thermal shock resistance, low cost, low density, thermodynamic stability, and reasonable strength at high temperatures. However, commercially available mullite has several undesirable characteristics. The first and most important is poor fracture toughness, typically in the 2.0-2.5 $MPa.m^{½}$ range. Such low fracture toughness severely limits the reliability and life time of mullite-based components. Second, there is concern about the creep resistance of mullite, which appears to be highly dependent on the processing method and variation of the alumina-to-silica ratio.

The aim of the work is to develop a mullite with properties, which would make it suitable for application in low power gas turbines.

6.2.6.5 Effects of impurities on phase formation in calcium aluminate cements - *Jenifer Alex (PhD student, Kerneos)*

Impurities play an important role in determining the high temperature properties of Calcium Aluminate Cements (CACs). High purity is desirable to guarantee a consistent and predictable performance of the specialty cements which are widely used for refractory applications. Most publications concerned with impurities in CACs focus on their effect on hydration and setting properties. This aims to provide a better understanding of the effect minor elements have on the high temperature properties of CACs. Approximately 0.5 wt% Na_2O is present in almost any industrially used alumina due to its introduction during the Bayer process. It is therefore that sodium containing compounds were chosen as a first case to examine the phase and microstructure evolution of CACs in their presence.

6.2.6.6 Degradation of zirconia refractories - *Amanda Quadling (PhD student)*

Refractories operate in challenging environments in which not only high temperatures are reached while in contact with corrosive media such as liquid metals but in which the temperature and the chemical environment also change rapidly. The aim of the work here is to understand better how subtle changes in the microstructure of the refractories influence the thermo-mechanical properties and resistance to corrosion and whether the combined effect of thermal shock and corrosion leads to worse degradation than when these occur separately.

6.2.6.7 Improving on ballistic performance of ceramics for armour - *Cyril Besnard (PhD student, DSTL)*

This project follows on from earlier work carried out at CASC on silicon carbide and boron carbide ceramics for armour. The aim is to improve the processing of these materials to yield enhance resistance to ballistic penetration.

6.2.6.8 Paper-plastic composites for re-use of difficult to recycle paper products- *Jonathan Mitchell (PhD student, EPSRC-KTN Case studentship)*

The aim of this project is to produce improved plastic products using the fibrous content of waste paper sources to reinforce the materials.

6.2.6.9 Layered double hydroxides for radionucleide anion removal and storage - *Jonathan Phillips (PhD student, EPSRC)*

In nuclear waste management radionuclide ions need to be separated from aqueous waste streams. Existing methods use precipitation and ion exchange membranes and subsequently immobilise the radionuclides in cement. In this project, a more integrated approach is being explored in which layered double hydroxides are first used for separating the radionuclides from water and then through thermal conversion also for long term storage.

6.2.6.10 Lightweight fillers from paper sludge ash - *Charikleia Spathi (PhD student, KTN-EPSRC Case studentship)*

This project aims to produce lightweight fillers by rapid sintering of glass-paper sludge ash composites. Results to date show that fillers with a density lower than 1 g cm^{-3} can be produced while retaining low water adsorption properties. Current efforts are focussed on understanding the critical attributes of the ash for the success of the process and developing a process model.

6.2.6.11 High value products from incinerator bottom ash - *Athanasios Bourtsalas (PhD student, Martin Gmbh)*

This project aims to extract value from incinerator bottom ash by creating sintered ceramic products of high strength.

6.2.6.12 Processing and characterisation of Simulant Non-oxide Fuels for Generation IV Reactors – *Robert Harrison with Bill Lee and 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 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.

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 is being assessed with the aim of producing 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-stoichiometry. Another area of interest is the effect of this non-stoichiometry on thermophysical properties such as thermal conductivity.

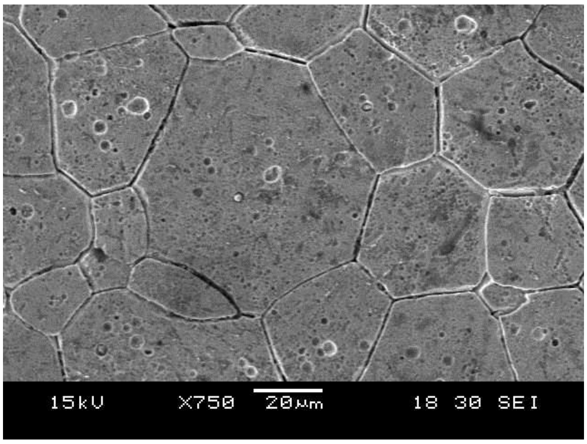


Figure 2; SEI image of ZrN sample produced by SPS

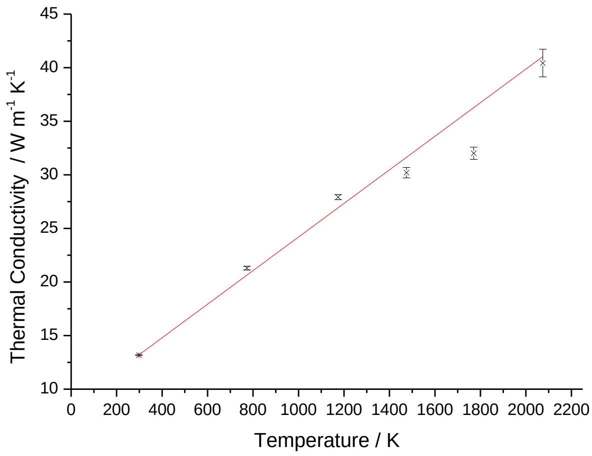


Figure 1; Thermal conductivity data for ZrN sample produced by SPS

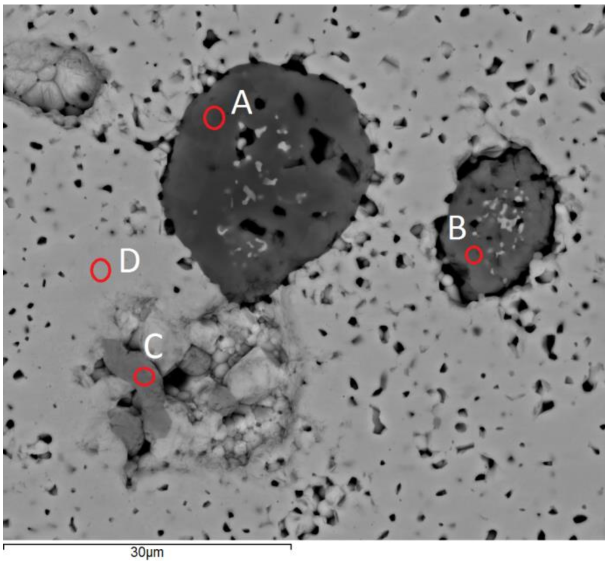
6.2.6.13 Simulating spent AGR fuel after various times- *Zoltan Hiezl with Bill Lee*

As the planet`s demand for energy increases, one solution is to extend the number and the life time of current nuclear power plants and build new ones. As a result more radioactive nuclear waste will be generated making its management crucial.

As part of the UK Spent Fuel Research Group, with members from Imperial, Cambridge University and Lancaster University, the work at Imperial involves fabricating UO_2 based simulant (SIMFuel) samples of spent Advanced Gas-cooled Reactor fuel. The aim is to develop a material that reproduces both core and rim microstructures of spent AGR fuels at various times after discharge from reactor (100, 1000, 10000 and 100000 years) containing nuclides predicted to be present.

Initially the type and amount of fission products have been calculated using the FISPIN programme. These fission products are then grouped and their atomic percentages are calculated within the spent AGR fuel. SIMFuel samples have been made in which inactive surrogate metal oxides are mixed with depleted uranium dioxide before sintering at 1700 °C for 5 hours in H_2 atmosphere then grinding and polishing the dense samples. Such samples are being characterised using optical microscopy, SEM, TEM and XRD and have been supplied to the other universities for further study.

To date, SEM-EDX analysis revealed metallic and oxide precipitate (grey phase) formation. The main components of the metallic precipitates are Mo, Rh, Ru and Pd, whereas in the grey-phase Ba, Zr and Sr can be found. Several fission product surrogates are dissolved in the UO_2 matrix, such as Ce and Nd. These results are in good agreement with atomistic modelling using empirical pair potentials calculated by Michael Cooper in the Centre for Nuclear Engineering at Imperial.



Different type of secondary phases in the SIMFuel samples

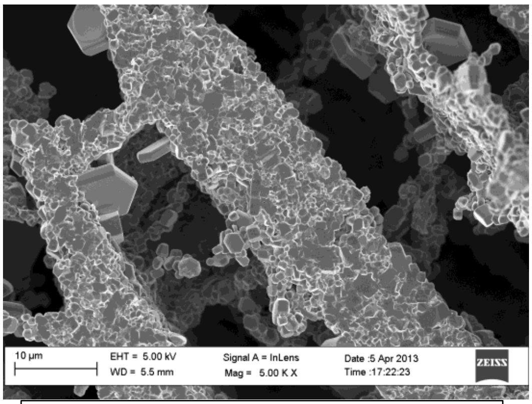
In the figure on the left two different secondary phases are visible, also there are two variations of the oxide precipitates. Submicron pores, that are distributed uniformly throughout the UO_2 matrix, also exist in the secondary phases. The light grey region is the UO_2 matrix. At the bottom of the image, C is a metallic precipitate which contains Mo, Ru and Pd. The dark region B is a $BaZrO_3$ containing oxide precipitate. The larger, darker region (A) is another type of precipitate, which contains mostly $SrZrO_3$. According to EDX, the UO_2 matrix (D) contains some Nd

With the help of SIMFuel, different properties, such as: thermal conductivity, oxidation, dissolution, radiation damage, leaching and corrosion can be studied without the danger of a high radiation field. These features would be extremely difficult and expensive to investigate using real spent nuclear fuel.

6.2.6.14 ***<u>Tough, Bio-Inspired Hybrid Materials for implants. Claudio Ferraro with Eduardo Saiz.</u>*** Natural composites, such as seashells or bone, have strength and toughness far in excess of hose of their constituents. A key feature of these natural materials is the combination of hierarchical structures, with characteristic dimensions spanning multiple size-scales and carefully engineered interfaces. Although the notion of biomimicry is not new, we know of no engineering materials which utilize structure at so many different length-scales to derive specific mechanical properties.

This project will investigate the use of freeze casting, based on the freezing of suspensions to develop and tough ceramic-based implant materials.

Freeze casting uses the controlled freezing of ceramic suspensions to create strong porous ceramics with complex hierarchical structures controlled at multiple length scales from the atomic to the macro levels by controlling the composition of the suspension and the freezing conditions. Composites can be built by filling the porosity of the scaffolds with a second "soft" phase (polymer or metal). The project focuses on issues such as increasing the ceramic content and refining the microstructure of layered composites or the manipulation of the properties of the "soft" phase and the adhesion and roughness at the "soft-hard" interface in order to enhance strength and toughness. This project is part of the initial training network for young researchers Biobone



Structure of a freeze cast SiC scaffold

6.2.6.15 Freeze casting of porous calcium phosphate scaffolds. Gil Machado with Eduardo Saiz. The goal is to use the directional freezing of ceramic suspensions to create strong porous calcium phosphate scaffolds to support bone regeneration on load bearing situations. The goal is to combine the freeze casting technique with a systematic analysis of sintering of calcium phosphates as a function of their composition such that scaffolds with controlled architecture (from nano to macro levels) and improved mechanical response can be fabricated. This project is part of the initial training network for young researchers Biobone

6.3 External PhDs

CASC funds two external PhD studentships, at QMUL and Sheffield. The CASC funded research student at Cambridge has submitted his PhD thesis.

6.3.1 Preparation and characterisation of novel carbon materials for refractory applications – University of Sheffield

Jianke Ye, a final-year PhD student, co-supervised by Shaowei Zhang (Sheffield/Exeter) and Bill Lee (CASC) is working on surface modification of carbon materials for refractory castable applications. He has continued to make good progress during the past 12 months. He has investigated the controllability of TiC and SiC coating thicknesses and their effects on the rheological behaviour of carbon black/graphite. In addition he has cast some model carbon-containing castables with the help of industrial partners to further investigate the behavior of TiC or SiC coated carbons in real castable systems. The main findings from these studies are: 1) the TiC or SiC coating thickness could be readily controlled/tailored to meet practical requirements *via* simply adjusting the ratio between Ti or Si and carbon (Fig. 1); 2) with increasing the coating thickness, the absolute value of zeta potential increases (Fig. 2); 3) TiC or SiC coated carbons show much improved water-wettability and water-dispersivity, thus performing much better in real castables than their uncoated counterparts. The water demand for castable placement can be considerably reduced by using them as carbon sources; 4) mechanical strength of a model castable containing coated graphite/carbon black after drying and firing at 1500^{o}C is 2-3 times higher than that in the case using uncoated carbon.
Jianke has already started writing his PhD thesis recently and is expected to finish by this June/July.

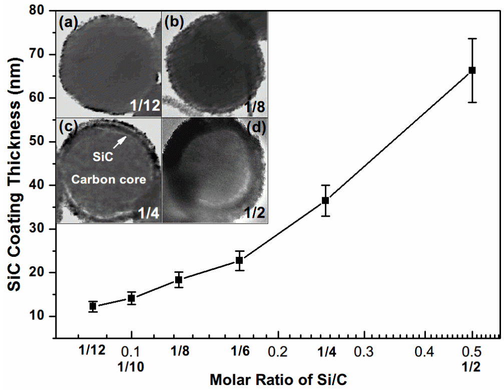


Fig. 1. SiC coating thickness as a function of Ti/C ratio

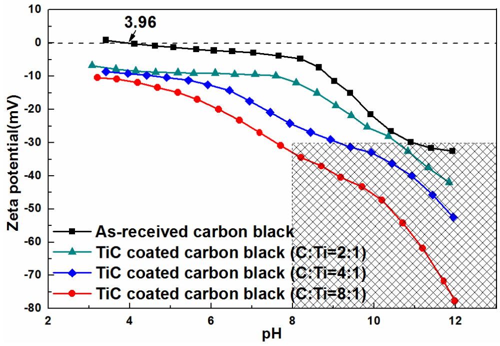
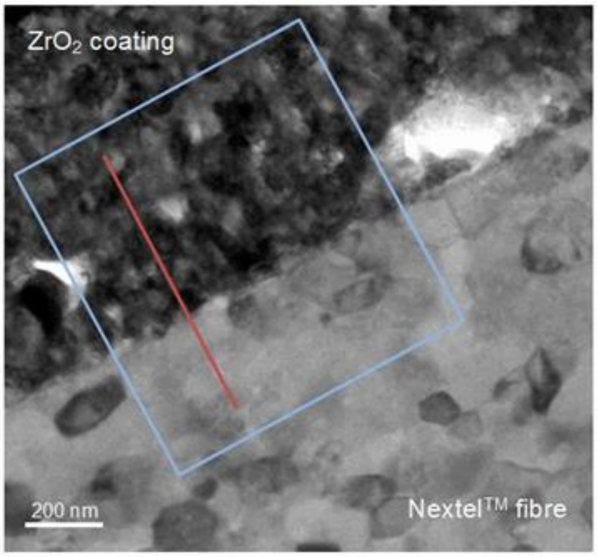


Fig. 2. Zeta potential as a function of pH and Ti/C ratio. Si/ carbon black molar ratio.

6.3.2 Development and characterisation of transparent glass matrix composites

Bo Pang with Aldo Boccaccini and David McPhail



TEM image of the interfacial region between ZrO_2 coating and NextelTM 610 alumina fibre. The red line indicates the position of EDS line analysis; the blue square indicates the position for EDS area analysis

Glass matrix composites based on alumina fibre reinforced borosilicate glass were fabricated. A novel processing technique, called “sandwich” hot-pressing, was developed. It consists of arranging the reinforcing fibres in two directions with a periodic interspacing between glass slides, and submitting the material to a heat-treatment for consolidation into highly dense and transparent composites, which were characterised by XRD analysis and SEM observations. The composites’ mechanical, optical and microstructural properties were studied and compared to those unidirectional fibre reinforced borosilicate glass composites and unreinforced glass matrix produced under the same conditions. Furthermore, a hybrid sol-gel technique was developed for coating the fibres with a smooth and crack free ZrO_2 interfacial layer to provide a weak bonding at the fibre/matrix interface to promote fibre pull-out during fracture.

It was shown that multi-directional fibre reinforced glass matrix composites retained at least 50% of the light transmittance and exhibited high flexural strength compared with the unreinforced glass matrix. The highest measured flexural strength value of these composites was 56 ± 7 MPa. The composites reinforced by ZrO_2 coated fibres had higher flexural strength (approx. 36%) and lower standard deviation (approx. 47%) compared with those reinforced by uncoated fibres. The introduction of a ZrO_2 interfacial layer led to higher composites’ integrity, which was proved by observations of fibre pull-out and crack deflection upon failure during mechanical tests. The developed composites show potential for applications where optical transparency and mechanical competence are requirements, e.g. in special machinery requiring strong transparent windows and in construction.

6.3.3 Other structural ceramics research projects

Other structural ceramics research projects at Imperial are listed below. Further information and contact details are available in the Department of Materials *Annual Report-Research in Progress* document, which can be downloaded from the Department of Materials website at www.imperial.ac.uk/materials.

- **3D microstructures and mechanical properties of LSCF-based SOFC cathodes,** Professor Alan Atkinson and Dr Finn Giuliani – Zhangwei Chen
- **Alternative phosphate based cements for reactive metal encapsulation,** Dr Luc J Vandeperre, Dr Martin Hayes (National Nuclear Laboratory UK) - William Montague
- **Cathode materials for low temperature protonic oxide fuel cells,** Professor John A Kilner - Matthew Sharp
- **Chromium poisoning of LSCF cathode in SOFCs,** Professor Alan Atkinson and Professor John A Kilner – Soo-Na Lee
- **Constrained sintering of fuel cell electrolytes,** Professor Alan Atkinson – Dr Xin Wang
- **Corrosion of spent advance gas reactor (AGR) fuel cladding in trace aqueous electrolyte environments,** Professor Bill Lee and Dr Mary P Ryan – Chin Heng Phuah
- **Crystallisation studies of fluorapatite glass-ceramics,** Professor Robert G Hill (Queen Mary, University of London) – Adam Calver
- **Deposition and characterisation of layered Ruddlesden-Popper phases for solid oxide fuel cell cathodes,** Dr Stephen J Skinner and Dr Yeong-Ah Soh – Kuan-Ting Wu
- **Design of new engineered oxide thin films with tailored properties,** Professor John A Kilner – Dr Mónica Burriel
- **Determination of the composition and interfacial characteristics of multilayer heterostructured oxides as potential high performance solid oxide fuel cell electrolytes,** Professor John A Kilner – Stuart Cook
- **Durability studies of radioactive wasteforms,** Professor Bill Lee and Dr Julian R Jones – Nor Ezzaty Ahmad
- **Effect of interfaces on the ionic conductivity of solid oxide fuel cell materials,** Professor David W McComb, Professor John A Kilner and Dr Stephen J Skinner - George Harrington
- **Glass ceramic matrix composites containing carbon nanotubes,** Professor Aldo R Boccaccini, (University of Erlangen-Nuremberg), Professor Bill Lee and Dr Milo SP Shaffer (Department of Chemistry) – Tayyab Subhani
- **Glass corrosion: parameter estimation in reaction diffusion problems involving ionic species with limited data,** Dr Paul Tangney and Professor Bill Lee – Xin Yang
- **High temperature deformation of age hardening coatings,** Dr Finn Giuliani and Professor Neil McN Alford – Constantin Ciprian Ciurea
- **High-temperature oxidation mechanisms of MAX phase ceramics,** Professor Bill Lee – Bai Cui
- **High toughness mullite development,** Dr Luc JM Vandeperre and Dr Finn Giuliani – Daniel Glymond

- **In situ dissolution measurements of CeO_2 , PuO_2 and UO_2 thin films using XAS spectroscopy and AFM,** Professor Bill Lee and Dr Mary P Ryan – John O'Neill
- **Investigation of the oxygen cathode of SOFC by nonlinear EIS,** Dr Jason Riley, Professor John A Kilner and Professor David W McComb – Ning Xu
- **Investigation of perovskite related $La_2NiO_{4+\delta}$ electrodes and novel electrolytes for solid oxide electrolysis cells (SOECs),** Dr Stephen J Skinner and Professor John A Kilner – Lydia Fawcett
- **Investigation of ZrC coatings for ceramic nuclear fuels for generation IV very high temperature reactor,** Professor Bill Lee and Professor Robin W Grimes (part of collaborative project with University of Manchester) – Edoardo Giorgi
- **Ionic mobility in superstructured oxides,** Dr Stephen J Skinner – Ryan Bayliss
- **Magnesium phosphate cements for uranium encapsulation,** Dr Luc J Vandeperre and Dr Martin Hayes (NNL) – William Montague
- **Making light aggregates from paper sludge ash**, Professor Christopher R Cheeseman and Dr Luc J Vandeperre – Charikleia Spathi
- **New materials from extruded plastic paper laminates,** Professor Christopher R Cheeseman (Department of Civil and Environmental Engineering), Dr Luc J Vandeperre and Professor Aldo R Boccaccini, (University of Erlangen-Nuremberg) – Jonathan Mitchell
- **New research directions for solid oxide fuel cell science and engineering,** Professor Alan Atkinson, Professor John A Kilner, Dr Stephen J Skinner and Professor Nigel P Brandon (Department of Earth Science and Engineering)
- **Novel metakaolin-derived geopolymer binders for radioactive wastes,** Professor Christopher R Cheeseman (Department of Civil and Environmental Engineering) and Professor Aldo R Boccaccini, (University of Erlangen-Nuremberg) – Carsten Kuenzel
- **Oxyfuel combustion – Academic programme for the UK (OxyCAP),** Dr Andreas M Kempf (Department of Mechanical Engineering), Dr Paul S Fennell (Department of Chemical Engineering and Mr Fraser Wigley
- **Materials for Wound Repair (funded by Welland Medical).** Dr. Miriam Miranda, Prof Eduaro Saiz, Mrs Diane Chircop
- **Predicting in service thermo-mechanical performance of ultra-high temperature ceramics,** Dr Luc J Vandeperre, Professor Neil McN Alford and Dr Finn Giuliani – Jianye Wang
- **Radiation damage and gas accumulation in nuclear ceramics,** Professor Bill Lee – Dr Matthew Gilbert
- **Solid oxide fuel cells – Integrating degradation effects into lifetime prediction models (SOFC-Life),** Professor Alan Atkinson and Professor Nigel P Brandon (Department of Earth Science and Engineering) – Dr Xin Wang
- **Synthesis and in-situ studies of cathodes for solid-oxide fuel cells,** Dr Stephen J Skinner and Professor John A Kilner – Russell Woolley
- **The effect of transition metal oxide doping on ceria based electrolyte materials,** Professor Alan Atkinson and Professor John A Kilner – Samuel Taub
- **Ultra-high temperature ceramics (UHTCs) for aerospace applications,** Professor Bill Lee – Dr Doni J Daniel

6.4 Completed Research Projects

In this section we report projects, such as reports for industry and PhD's that have been successfully completed.

6.4.1 The processing and deformation of ZrB_2 based ceramics - Jianye Wang (CASC funded PhD),

Zirconium diboride, ZrB_2, based materials have been proposed for structural applications at ultra-high temperatures (>2000 °C). However, their mechanical behaviour at such temperatures is only poorly documented. In this work, the processing and the deformation behaviour at temperatures up to 2000 °C of ZrB2, was investigated.

Densification of zirconium diboride based materials is difficult and most reported routes use a combination of high pressures and high temperatures to obtain a high density. However, it had been reported that with the aid of carbon, boron carbide and silicon carbide, pressureless sintering of ZrB_2 is possible. Further work in this thesis shows that the key factor to obtain successful sintering is to limit the oxidation of the raw materials. It is shown also that dense materials can be obtained from relatively coarse powders with only carbon as the sintering additive. Adding silicon carbide or boron carbide does allow the grain growth at the sintering temperature to be limited.

Mechanical characterisation of these materials was performed firstly using small-scale hardness measurements by nano-indentation at moderate temperatures (25-300°C). The indentations were carried out at strain rates in the range 10^{-4} and 10^{-1} s^{-1}. An analysis to extract the Peierls stress (6.6 ± 0.7 GPa) and activation energy (2.56 ± 1.6 10^{-19} J) for lattice resistance controlled plastic flow was developed. Additional mechanical characterisation consisted in measuring the self-contact hardness at temperatures from 900-2000 °C. These measurements clarify that the initial rapid decrease in hardness at room temperature is followed by a region of more or less constant hardness before further decreases in hardness become apparent at the highest temperatures. A TEM investigation of the deformation mechanisms shows that near room temperature, extensive dislocation flow occurs underneath indentations, whereas at the highest temperatures measured in this work, dislocations either anneal out or do not partake in the deformation. The available data was then summarised through proposing a deformation mechanism map for ZrB2.

6.4.2 Metakaolin based geopolymers to encapsulate nuclear waste - Carsten Kuenzel (EPSRC funded PhD student)

The use of geopolymers to encapsulate intermediate level waste (ILW), particularly Magnox swarf contaminated with Al metal and Cs/Sr-loaded clinoptilolite was investigated. Both wastes have different interactions with the encapsulation matrix. For Magnox swarf waste containing trace Al metal, the pH of the encapsulating matrix is a key factor that controls corrosion and release of hydrogen. Cs and Sr can leach from contaminated clinoptilolite into the encapsulating geopolymer and therefore the chemical interactions of these ions with the matrix have been investigated.

A fundamental understanding of the geopolymer system used for encapsulation studies was developed. This involved studying the influence of different precursors on the mechanical properties. It was shown that metakaolin based geopolymers are unstable at room temperature when in contact with an atmosphere with a low relative humidity and that excessive drying shrinkage occurs. This shrinkage can be reduced by adding inert fillers which have low impact on the mortar viscosity and mechanical strength.

Magnox waste and Al-metal have been encapsulated in metakaolin based optimised geopolymers mortars and surface interactions studied using SEM-EDX and XRD. In addition the corrosion rates were determined. Magnox swarf does not react with the geopolymers matrix, while Al-metal rapidly corrodes. However, by using a metakaolin with a low molar Si:Al ratio and controlling the molar Al:Na ratio in geopolymers the corrosion can be significantly reduced and this allows encapsulation of this difficult waste stream.

Surface reactions of Cs/Sr-contaminated clinoptilolite and geopolymers were also studied. Simulated wastes containing Cs^{+} and Sr^{2+} salts were mixed with geopolymers and the influence of the cations on the geopolymer microstructure and leaching were investigated. Mixing Cs/Sr-contaminated clinoptilolite with activation solutiongeopolymers causes surface dissolutionpozzolanic reaction of clinoptilolite with release of Cs and Sr ions into the matrix. Leaching of Cs contaminated geopolymers showed that Cs+ ions can be immobilised at concentrations up to 10 wt.%. Sr^{2+} reacts with the activating solution and dissolved metakaolin and is build chemically into the structurethis causes relatively high Sr leaching.

The research has resulted in a number of key conclusions related to the stability of metakaolin derived geopolymers and their interactions with the selected wastes.

6.4.3 The effect of carbon nanotubes on the sintering behaviour of hard and ultra-high temperature ceramics – QMUL Ben Milsom (CASC funded PhD),

The effect of carbon nanotubes on the sintering behaviour

Ben Milsom is supervised by Mike Reece (QMUL) in collaboration with Eduardo Saiz (CASC).

Over the last year his project has focussed on refining the experimental method and analytical model for the calculation of the activation energy of ZrO2 as well as ZrO2-CNT composites. The results show that the addition of a percolating network of CNTs significantly reduces the activation energy, but does not change the dominant sintering mechanism of grain boundary diffusion. The sintering activation energy for boron carbide (B4C) is being studied to determine whether the effects observed for the ZrO2 are consistent with other systems.

Mechanical testing has been carried out on B4C and ZrO2 CNT samples. This has shown the hardness is significantly reduced by the presence of even a small quantity (<1 vol %) of CNTs and drops off rapidly as the CNT content exceeds 2 vol %. On a recent research visit to the Polytechnic University of Catalunya, Spain, scratch tests on ZrO2, SiC and B4C-carbon composites were performed with varying CNT quantities from 0-2 vol % as well as ceramic-carbon black composites for comparison. Wear properties of the materials have been examined across a wide range of distances from 0.1-100m for all samples and measured the depth across the tracks using profilometry. The presence of carbon and in particular CNTs was shown to reduce the wear rate for B4C but not the ZrO2, this could be due to some reaction between the carbide and the CNT during sintering that does not occur in the case of the oxide, but further analysis is needed to confirm this.

This year a paper has been submitted entitled: the effect of carbon nanotubes on the sintering behaviour of zirconia, to the Journal of the European Ceramic Society. Data on the grain growth activation energy of ceramic CNT composites will be presented at the European Materials Research Society meeting in Krakow, Poland in September. The figure shows the effect of sintering temperature on density and grain size of ZrO2 and ZrO2 CNT composites. It shows that the presence of CNTs aids the sintering of the ZrO2, producing an increased density at any given temperature and that with increasing CNT content there is a reduction in grain size even at temperatures above that required to achieve full density in the case of ZrO2 2 vol % CNT.

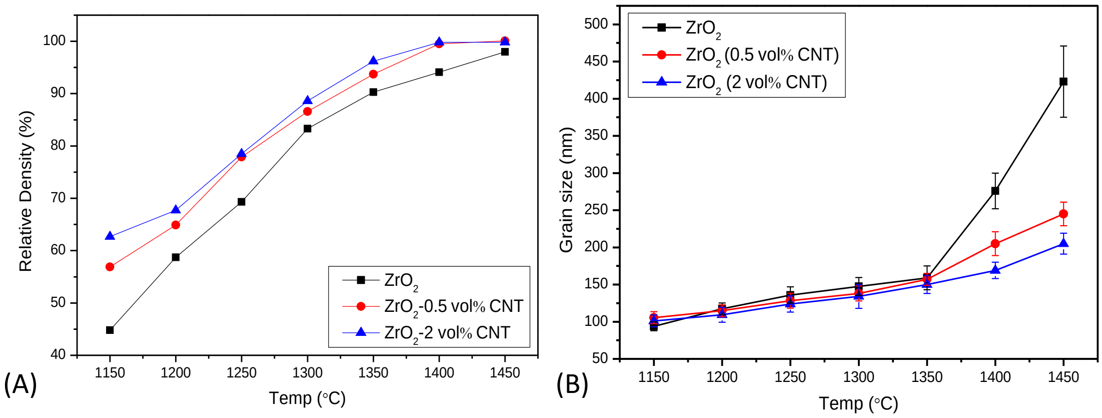


Figure 1 (A) Relative density and (B) grain size, of ZrO_2 and ZrO_2-CNT composites across the temperature range 1150-1450˚C sintered for 8 min with 16MPa uniaxial pressure and a heating rate of 200˚C/min

Figure 1 (A) Relative density and (B) grain size, of ZrO2 and ZrO2-CNT composites across the temperature range 1150-1450˚C sintered for 8 min with 16MPa uniaxial pressure and a heating rate of 200˚C/min

This year we have worked on two collaborations with students from Imperial College London. I have assisted Miriam Miranda Fernandez in the preparation of ZrO2 graphene composites to determine the effect of graphene on the sintering behaviour of ZrO2 as well as the mechanical and electrical properties of the composites. We have also continued to assist in the project on freeze casting Al2O3-C composites whilst maintaining the unique structure, initially with Dr Claudia Walter and more recently with Dr Suelen Barg.

Over the next six months the electrical properties of ZrO2, SiC and B4C CNT composites will be studies at temperatures up to 800˚C and the results compared with the monolithic materials as well as carbon black composites of the same loading. The thermal diffusivity of the various composites up to 1500˚C will also be examined.

1.1.1 Development and characterisation of bioactive coatings based on biopolymer and bioactive glass obtained by electrochemical means

Fatemehsadat Pishbin with Aldo Boccaccini and Mary Ryan

Bioactive glass coatings are candidates for improving biological adhesion between metallic orthopaedic implants and human tissue. Such glass coatings can be mechanically improved by using biocompatible polymers forming composite coatings. The biopolymer can also act as carrier of drugs and other bioactive molecules. This research focuses on the development of “soft” coatings based on natural biocompatible and biodegradable polysaccharides (chitosan) and bioactive glass (45S5 Bioglass®). Electrophoretic deposition (EPD) has been employed to develop such composite coatings. EPD is a promising technique for co-deposition of organic and inorganic components at low temperatures on complex shaped substrates. Kinetics of deposition of chitosan and 45S5 Bioglass®

from aqueous solutions on both planar and 3D porous metallic structures have been investigated. Additionally, EPD has been applied to fabricate novel multifunctional coatings with drug release capability. Antibacterial agents have been incorporated in the composite films. To evaluate biological behaviour of the coatings preliminary drug release and in vitro cellular and microbiological tests have been conducted

7 Impact and Sustainability

With the appointment of academic and then research staff, publicity has focussed on staff presenting at and taking part in discussions at conferences and on overseas visits. Memoranda of understanding have been signed with prestigious ceramics research centres including Erlangen, Bremen in Germany, Lyon and Limoges in France, Nagoya Institute of Technology in Japan and Florida in the USA. A newsletter is produced two to three times a year and circulated to our email list (about 350 members) and at conferences we attend. The website continues to make information available including upcoming conferences and how to join our industry consortium. In addition we are publicising the national Richard Brook prize for best ceramics PhD (Section 7.8).

We have published 49 papers, given around 44 lectures and obtained £14.00M in research funding.

7.1 Lectures and Visits

Omar Cedillos Barraza

- *Fabrication of TaC-HfC ceramics for ultra-high temperature applications.* Poster presentation. Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications II, 13th - 18th May, Hernstein, Austria.

Dr Vineet Bhakhri

- *Understanding the high-pressure phase transitions in silicon-doped boron carbide.* F Giuliani, V Bhakhri, JE Proctor, T Scheler, E Gregoryanz and SG Macleod, Oral presentation, 34th International Conference and Exposition on Advanced Ceramics and Composites, Dayton Beach, Florida, January 2012

Dr Doni Daniel

- Oxidation behaviour and microstructural evolution of HfB2 – based ceramics from 1600C to 2000^{o}C, Imperial College London, UK, IWAC 05, Sept. 9-12, 2012.
- The effect of chemical composition on the densification, thermal and oxidation behaviour of different stoichiometries of zirconium and hafnium oxycarbides, 37th ICACC, Daytona Beach, FL, USA, 27th Jan-1st Feb, 2013.
- Development of ultrahigh temperature ceramics (UHTCs) for hypersonic applications, Invited lecture, 2nd ICAMP, Anna University, Chennai, India, Feb. 6- 8, 2013.
- Materials for extreme environments, Distinguished guest lecture, The Indian Ceramic Society, Anna University, Chennai, India, 5, Feb. 2013.

Dr Salvador Eslava

- *Zeolite monoliths with controlled internal structure prepared by freeze casting,* Eslava S, Hartmann C, Saiz E, 3rd International Conference on Multifunctional, Hybrid and Nanomaterials (Elsevier), 2013. Oral presentation
- *Metal-organic framework ZIF-8 films: low-κ dielectrics for future microelectronic chip devices* Eslava S, Zhang L, Esconjauregui S, Yang J, Vanstreels K, Baklanov MR, Saiz E, 3rd International Conference on Multifunctional, Hybrid and Nanomaterials (Elsevier), 2013. Poster presentation
- *Metal-organic framework ZIF-8 as low-k dielectrics in microelectronics,* Eslava S, Zhang L, Vanstreels K, Baklanov MR, Saiz E, 3rd International Conference on Metal-Organic Frameworks and Open Framework Compounds, 2012, Edinburgh, UK, 2012. Oral presentation

Miranda Fernandez

- *Influence of graphene oxide on the sintering behaviour of a ceramic material* E-MRS 2012 Conference, Strasbourg, May 14-18, 2012

Dr Finn Giuliani

- High Temperature deformation of TiN and TiAlN. Oral Presentation. ICMCTF, 29thApril-3rd May, San Diego, USA

Zoltan Hiezl

- *Preparation and characterization of UO_2 based SIMFuel.* Poster presentation. Fifth International Workshop on Advanced ceramics, 9-11 September 2012, London, United Kingdom
- The 2nd International Seminar on Global Nuclear Human Resource Development for Nuclear Safety, Security and Safeguard. Invited participant. 18-26 February 2013, Tokyo, Japan

Dr Julian Jones

- *Regenerative synthetic bone grafts etc*. Cavendish Laboratory, University of Cambridge, 26 October 2012
- *Glass bones and toughened scaffolds for regenerative medicine.* Centre European de la Ceramique (CEC) University of Limoges, 25 September 2012

Professor Bill Lee

- *Advanced ceramics and composites in the nuclear sector, and possible future applications of ceramics in the nuclear sector.* Summer School on Inorganic Materials for Energy Conversion and Storage, University of California at Santa Barbara, USA, 27-28 August 2012
- *Microstructural stability of HfB_2-based ceramic composites on laser testing at high heat flu.* 5th Intl. Workshop on Advanced Ceramics, Imperial College London, 11 September 2012
- *Developments in ceramic and glass composite material (GCM) wasteforms for difficult radioactive wastes.* University of Limoges, France, 25 September 2012

- *Fabrication, microstructural characterisation, oxidation and laser testing of ultra high temperature ceramics.* Materials Science and Technology Conference, Pittsburgh, Pennsylvania, USA, 10 October 2012
- *Materials needs for storage and geological disposal of the UK's radioactive wastes.* Materials UK Energy Materials Conference and Exhibition, Loughborough University, 16 October 2012
- *CoRWM's continuing role in the UKs managing radioactive waste safely programme.* OECD Nuclear Energy Agency Radioactive Waste Management International Forum on Stakeholder Confidence (FSC 13), Prague, Czech Republic, 23 October 2012
- *Fabrication, microstructural characterisation, oxidation and laser testing of ultra high temperature non-oxide ceramics.* Plenary Lecture, 6th Intl. Conf. on Advanced Materials and Nanotechnology (AMN6), Auckland, New Zealand, 12 February 2013
- *Fabrication, microstructural characterisation, oxidation and laser testing of ultra high temperature non-oxide ceramics.* Industrial Research Ltd., Wellington, New Zealand, 18 February 2013
- *Managing radioactive waste safely: the balance between social and technical issues.* Australian Institute of Nuclear Science and Engineering (AINSE) Public Lecture, Lucas Heights, Sydney, Australia, 21 February 2013
- *Working with DSTL: The good, the bad and the summary.* DSTL National PhD Scheme Conference, Kassam Stadium, Oxford, 27 February 2013
- *Managing Radioactive Waste Safely, the Delicate Balance between Technical and Social Issue.* UK protect on Nuclear issues meeting on Nuclear futures: Linking Policy and Technology, Bristol University, 26 March 2013
- *Imperial Engineering and AWE: Opportunities Through the Centre for Engineering and manufacturing Studies*, AWE-Imperial Strategic Alliance Showcase, Aldermarston, 15 April 2013
- *Fabrication and Microstructural Characterisation, Oxidation and Laser testing of Ultra High Temperature Ceramics (UHTCs).* Department of Materials, Oxford University, 9 May 2013
- *Characterisation and Simulant UK Higher level Wasteforms*, 1st meeting of IAEA Coordinated Research project on Processing Technologies for HLW, Formulation of Matrices and Characterisation of Wasteforms, St Ptersburg, Russia, 30 may 2013
- *Current and Planned Research on UHTCS at Imperial College*, Wright=Patterson Air Force Base, Dayton, Ohio, USA. 7 June 2013.

Dr Esther García-Tuñón

- Assembling "smart" ceramic particles with responsive polymers to build complex ceramic structures', Esther García-Tuñón, Suelen Barg, Robert Bell, Jon Weaver, Eduardo Saiz, MACAN, CapStone Meeting: April 20-26, 2013, Haifa, Israel.
- Ceramic Foams by Emulsion Templating, Esther García-Tuñón, E., Bell, Robert, Barg, S., Weaver, J., Saiz, E., 37th International Conference and Expo on Advanced Ceramics and Composites, (American Ceramic Society), Jan 27 – Feb 1, 2013, Daytona Beach, Florida USA.

Professor Eduardo Saiz

- Hirarchical Scaffolds and Composites with Practical Dimensions, Invited talk, MRS Spring Meeting, San Francisco, USA, April 2012,

- Building Hierarchical Ceramic-Based Materials Colloqium, Department of Materials, Oxford University Oxford, UK, May 3 2012
- Building Hierarchical Ceramic-Based Materials, Colloqium, Department of Materials, EPFL, Laussane , Switzerland, May 21 2012
- Segregation of Metals on Ceramic Surfaces, Invited talk, First Annual ONR Program Review for MURI topic “Tailoring of Atomic-Scale Interphase Complexions for Mechanism-Informed Material Design,” Leghigh University, USA, 8 June 2012.
- The Role of Interfacial Structure on Spreading, Invited talk. International Workshop on Interfaces at Bear Creek. Bear Creek USA, October 2012
- Bioinspired Ceramic/Carbon Composites, Invited seminar. Army Research Labs Aberdeen Proving Grounds, USA, 9 October 2012.
- Kinetics of High-Temperature Spreading, Invited talk. International Workshop on Wetting and Capillarity in Complex System, Dresden, Germany, February 2013.
- The Challenge of Fabricating Porous Materials, Department Seminar, Laboratoire de Physique des Surfaces et des Interfaces Centre de Recherche en Modélisation Moléculaire, University of Mons-Hainaut, Mons, Belgium, 22 February 2013.
- CVD of Graphene on Cu. PICS workshop. University of Marseille, 27-30 May 2013.

Dr Luc J Vandeperre

- *Design and verification for Ceramics : the State of the Art*, European Space Agency workshop, ESTEC, Noordwijk, Invited lecture 24^{th}-25^{th} May 2012
- *Deformation mechanism map for ZrB_2,* 2^{nd} Ultra-high Ceramics Conference, Presenter Vienna, 14^{th}-18^{th} May, 2012
- *A deformation mechanism map for ZrB_2* , Plenary lecture 5^{th} International Workshop on Advanced Ceramics, IWAC05, London, 10^{th}-11^{th} September, 2012
- Nuclear waste encapsulation in geopolymers, Applications of Geopolymers, invited lecture, Stoke-on-Trent, UK, 4 December 2012
- The influence of microstructure and grain boundary chemistry on slow crack growth in SiC, invited lecture, 2nd Int. Symposium on Ceramics Nanotune Technology, ISCeNT-2, Nagoya, Japan, 6-8 March 2013
- Pressureless Sintering of SiC-B4C composites, Oral presentation, 37th International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, USA, 28 January-1st February, 2013
- The influence of microstructure and grain boundary chemistry on slow crack growth in SiC, Oral presentation, 37th International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, USA, 28 January-1st February, 2013
- The effect of addition of ceria stabilised zirconia on the creep of mullite, Daniel Glymond, oral presentation, 37th International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, USA, 28 January-1st February, 2013
- Strength-formulation correlations in magnesium phosphate cements for nuclear waste encapsulation, Oral presentation, W. Montague, 37th International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, USA, 28 January-1st February, 2013
- Magnesium phosphate cements for nuclear waste encapsulation, oral presentation, W. Montague, University Nuclear Technical Forum 2013, London, 23-25 April 2013

Jianke Ye

- *Molten salt preparation of aluminium oxide coated graphite flakes for castable applications*. Presentation at 55th International Colloquium on Refractories. Aachen, 19-20 September 2012

Michele Pettinà

- *Modelling damage and failure in structural ceramics at ultra-high temperatures*, Conference presentation, 37th International Conference and Exposition on Advanced Ceramics and Composites, Jan. 27-Feb.1, 2013, Daytona Beach, FL, USA.
- *Modelling damage and failure in structural ceramics at ultra-high temperatures*, Poster presentation, DSTL National PhD Scheme Conference, Feb. 27, 2013, The Kassam Stadium, Oxford, UK.
- *Modelling of oxidation effects, crack growth, crack density and creep behaviour for SiC/SiC ceramic matrix composites*, Conference presentation, 37th International Conference and Exposition on Advanced Ceramics and Composites, Jan. 27-Feb.1, 2013, Daytona Beach, FL, USA.

7.2 Publications

Dr Vineet Bhakhri

- *Instrumented indentation investigation into mechanical behaviour of ceramics at moderately elevated temperatures.* V Bhakhri**,** J Wang, N Ur-rehman, C Ciurea, F Giuliani, LJM Vandeperre, Journal of Materials Research (Focus Issue on Instrumented Indentation) 27, Issue 1, 2012

Dr Jianye Wang

- Instrumented nanoindentation investigation into the mechanical behavior of ceramics at moderately elevated temperatures. Bhakhri, V., J. Wang, N. Ur-rehman, C. Ciurea, F. Giuliani and L. J. Vandeperre, Journal of Materials Research **27**(01): 65-75, 2012
- The Hardness of ZrB_2 between 1373 K and 2273 K. Wang, J., E. Feilden-Irving, L. J. Vandeperre and F. Giuliani, Advanced Ceramic Coatings and Materials for Extreme Environments II, John Wiley & Sons, Inc.**:** 187-195, 2012.

Dr Doni Jayaseelan Daniel

- Mechanical properties of ZrB_2- and HfB_2-based ultra-high temperature ceramics fabricated by spark plasma sintering, E. Zapata-Solvas, DD Jayaseelan, HT Lin, P Brown and WE Lee, J. Europ. Ceram. Soc., 2013 (in print)
- In situ formation of oxidation resistant refractory coatings on Sic-reinforced ZrB_2 ultra high temperature ceramics, DD Jayaseelan, E Zapata-Solvas, P Brown and WE Lee, J. Am. Ceram. Soc., 95, 1247-1254, 2012, Issn:0002-7820
- Microstructural evolution during high-temperature oxidation of spark plasma sintered Ti_2AlN ceramics, B Cui, R Sa, DD Jayaseelan and WE Lee, Acta Mat., 60, 1079-1092, 2012. ISSN:1359-6454

Dr Salvador Eslava

- *Synthesis and optimization of the production of millimeter-size hydroxyapatite single crystals by Cl--OH- ion exchan.* Garcia-Tunon E, Franco J, Eslava S, Bhakhri V, Saiz E, Giuliani F, Guitian F, J. Am. Ceram. Soc., 2013
- *A two-scale Weibull approach to the failure of porous ceramic structures made by robocasting: Possibilities and limits.* Genet M, Houmard M, Eslava S, Saiz E, Tomsia AP, J. Eur. Ceram. Soc., 2013, Vol 33, Pages:679-688(doi)
- *Metal-organic framework ZIF-8 films as low-k dielectric in microelectronics.* Eslava S, Zhang L, Esconjauregui S, Yang J, Vanstreels K, Baklanov MR, Saiz E, Chem. Mater., 2013, Vol 25, Pages 27-33(doi)

Dr Finn Giuliani

- Synthesis and optimization of the production of millimeter-size hydroxyapatite single crystals by Cl--OH- ion exchange, Garcia-Tunon E, Franco J, Eslava S, Bhakhri V, Saiz E, Giuliani F, Guitian F J. Am. Ceram. Soc., 96, 759-765, 2013

Dr Julian R Jones

- *Bioactive glass foam scaffolds are remodelled by osteoclasts and support the formation of mineralized matrix and vascular networks in vitro.* Midha S, van der Bergh W, Kim TB, Lee PD, Jones JR, Mitchell CA, Advanced Healthcare Materials, DOI: 10.1002/adhm.201200140
- *A review of bioactive glass - from Hench to hybrids.* Jones JR, Acta Biomaterialia, 9, 4457–4486, 2013
- *Effect of calcium source on structure and properties of sol-gel derived bioactive glasses.* Yu B, Turdean-Ionescu CA, Martin RA, Newport R J, Hanna JV, Smith ME, Jones JR, Langmuir, 28, 17465-17476, 2012
- *Transesterification of functional methacrylate monomers during alcoholic copper-catalyzed atom transfer radical polymerization: Formation of compositional and architectural side products.* Connell LS, Jones JR, Weaver JVM. Polymer Chemistry, 3, 2735-2738, 2012
- *Preparation of electrospun poly(lactic acid)-based hybrids containing siloxane-doped vaterite particles for bone regeneration.* Fujikura K, Obata A, Lin S, Jones J R, Law RV, Kasuga T. Journal of Biomaterials Science, Polymer Edition 23-10, 1369-1380.se, 2012
- *Induction of hydroxycarbonate apatite formation on polyethylene or alumina substrates by spherical vaterite particles deposition.* Obata A, Hasegawa D, Nakamura J, Jones JR, Kasuga, Materials Science and Engineering C32, 1976 – 1981, 2012
- *Influence of strontium for calcium substitution in bioactive glasses on degradation, ion release and apatite formation.* Fredholm Y, Karpukhina N, Brauer DS, Jones JR, Law RV, Hill RG, Journal of Royal Society Interface, 2012, 9, 880-889
- *Sintering and crystallization of phosphate glasses by CO_2-Laser irradiation on hydroxyapatite ceramics.* Obata A, Jones JR, Akiyoshi S, Kasuga T. International Journal of Applied Ceramic Technology, 9, 541-549, 2012
- *Bioactive silica / poly(γ-glutamic acid) hybrids for bone regeneration: effect of covalent coupling on dissolution and mechanical properties and fabrication of porous scaffolds.* Poologasundarampillai G, Yu B, Tsigkou O, E Valliant, Yue S, Lee PD, Hamilton RW, Stevens MM, Kasuga T, Jones JR. Soft Matter, 8, 4822 – 48322012

- *Characterising the hierarchical structures of bioactive sol-gel silicate glass and hybrid scaffolds for bone regeneration.* Martin RA, Yue S, Hanna JV, Lee PD, Newport R J, Smith ME, Jones JR. Philosophical Transactions of the Royal Society A, 370, 1422-1443 2012
- *Role of pH and temperature on silica network formation and calcium incorporation into sol-gel derived bioactive glasses.* Valliant EM, Turdean-Ionescu C, Hanna JV, Smith ME, Jones JR. Journal of Materials Chemistry, 22, 1613 – 1619 2012

Professor Bill Lee

- *In-situ formation of oxidation resistant refractory coatings on SiC-reinforced ZrB_2 ultra high temperature ceramics,* DD Jayaseelan, E Zapata-Solvas, P Brown and WE Lee, J. Am. Ceram. Soc. 95 [4] 1247-54 2012
- *TEM Study of the early stages of Ti_2AlC oxidation at 900^oC,* B Cui, DD Jayaseelan and WE Lee, Scripta Mat. 67 [10] 830-33 2012
- *High-temperature oxidation behaviour of MAX-phase ceramics,* B Cui and W E Lee, Refractories Worldforum 5 [1] 105-112 (2013). Winner of 3rd place in Gustav Eirich Award 2012
- *Microstructure and high-temperature oxidation behaviour of Ti_3AlC_2/W composites,* B Cui, E Zapata-Solvas, MJ Reece, C Wang and WE Lee, J. Am. Ceram. Soc. 2013
- *Mechanical properties of ZrB_2- and HfB_2-based ultra-high temperature ceramics fabricated by spark plasma sintering,* E Zapata-Solvas, DD Jayaseelan, HT Lin, P Brown and WE Lee, J. Euro Ceram. Soc. 33 [7], 373-86 (2013)
- *Thermal properties of La_2O_3-doped ZrB_2-HfB_2-based ultra-high temperature ceramics,* E.Zapata-Solvas, DD Jayaseelan, PM Brown and WE Lee, accepted for J Euro. Ceram.Soc., 2013

Professor Eduardo Saiz

- *Role of molecular chemistry of degradable pHEMA hydrogels in three-dimensional biomimetic mineralization.* Huang JJ, Liu G, Song CY, Saiz E, Tomsia AP, Chemistry of Materials, 24, 1331-1337, 2012
- *Sol-gel method to fabricate CaP scaffolds by robocasting for tissue engineering.* Houmard M, Fu Q, Saiz E, Tomsia AP, Journal of Materials Science-Materials in Medicine, 23, 921-930, 2012
- *Activation energy paths for graphene nucleation and growth on Cu.* Kim H, Mattevi C, Calvo MR, Oberg JC, Artiglia L, et al, ACS Nano 6, 3614-3623, 2012
- Metal-Organic Framework ZIF-8 Films As Low-kappa Dielectrics in Microelectronics, Eslava, S., L.P. Zhang, S. Esconjauregui, J.W. Yang, K. Vanstreels, M.R. Baklanov, E. Saiz, , Chemistry of Materials, **25**(1): 27-33, 2013
- Soda-lime glass-coating containing silver nanoparticles on Ti-6Al-4V alloy, Esteban-Tejeda, L., B. Cabal, F. Malpartida, R. Lopez-Piriz, R. Torrecillas, E. Saiz, A.P. Tomsia, J.S. Moya, Journal of the European Ceramic Society, **32**(11): p. 2723-2729, 2012.
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- Synthesis and Optimization of the Production of Millimeter-Sized Hydroxyapatite Single Crystals by Cl--OH- Ion Exchange, Garcia-Tunon, E., J. Franco, S. Eslava, V. Bhakhri, E. Saiz, F. Giuliani, F. Guitian, Journal of the American Ceramic Society, **96**(3): p. 759-765, 2013.
- A two-scale Weibull approach to the failure of porous ceramic structures made by robocasting: Possibilities and limits, Genet, M., M. Houmard, S. Eslava, E. Saiz, A.P. Tomsia, (vol 33, pg 679, 2013), Journal of the European Ceramic Society, **33**(8): p. 1393-1393, 2013.
- A two-scale Weibull approach to the failure of porous ceramic structures made by robocasting: Possibilities and limits, Genet, M., M. Houmard, S. Eslava, E. Saiz, A.P. Tomsia, , Journal of the European Ceramic Society, **33**(4): p. 679-688, 2013.
- Sol-gel method to fabricate CaP scaffolds by robocasting for tissue engineering, Houmard, M., Q. Fu, E. Saiz, A.P. Tomsia, Journal of Materials Science-Materials in Medicine, **23**(4): p. 921-930, 2012.
- Role of Molecular Chemistry of Degradable pHEMA Hydrogels in Three-Dimensional Biomimetic Mineralization, Huang, J.J., G. Liu, C.Y. Song, E. Saiz, A.P. Tomsia, Chemistry of Materials, **24**(7): p. 1331-1337, 2012.
- Biocomposites of pHEMA with HA/beta-TCP (60/40) for bone tissue engineering: Swelling, hydrolytic degradation, and in vitro behavior, Huang, J.J., E. Ten, G. Liu, M. Finzen, W.L. Yu, J.S. Lee, E. Saiz, A.P. Tomsia, Polymer, **54**(3): p. 1197-12, 2013.
- Combinatorial design of hydrolytically degradable, bone-like biocomposites based on PHEMA and hydroxyapatite, Huang, J.J., D.C. Zhao, S.J. Dangaria, X.H. Luan, T.G.H. Diekwisch, G.Q. Jiang, E. Saiz, G. Liu, A.P. Tomsia,Polymer, **54**(2): p. 909-919, 2013.
- Perspectives on the role of nanotechnology in bone tissue engineering, Dental Materials, Saiz, E., E.A. Zimmermann, J.S. Lee, U.G.K. Wegst, A.P. Tomsia, **29**(1): p. 103-115, 2013.
- E. Garcia-Tunon, S. Barg, R. Bell, J. Weaver, C. Walter, L. Goyos, E. Saiz, Designing 'Smart' Particles for the Assembly of Complex Macroscopic Structures", Accepted for Publication in Angewandte Chemie. DOI: 10.1002/anie.201301636 and 10.1002/ange.201301636
- A novel approach for the fabrication of carbon nanofibre/ceramic posrous structures, Caludia Walter, Suelen Barg, Na Ni, Robert C. Maher, Esther Garcia-Tunon, Muhammad Mezzafar Zaiviji Ismail, Flora Babot, Eduardo Saiz, Accepted for Publication Journal of the European. Ceramic Society

- **Patents**
- G. Liu, D. Zhao, **E. Saiz**, A. P. Tomsia, Biodegradable Synthetic Bone Composites, United States Patent 8,344,042, January 1 2013.

Dr Luc Vandeperre

- C. Kuenzel, L.M. Grover, L. Vandeperre, A.R. Boccaccini, and C.R. Cheeseman, Production of nepheline/quartz ceramics from geopolymer mortars. Journal of The European Ceramic Society, **33**, 2013, p251-258.
- C. Kuenzel, L.J. Vandeperre, S. Donatello, A.R. Boccaccini, and C.R. Cheeseman, Ambient Temperature Drying Shrinkage and Cracking in Metakaolin-Based Geopolymers. Journal of the American Ceramic Society, **95**(10), 2012, p3270-3277.
- T. Zhang, L.J. Vandeperre, C.R. Cheeseman, Magneisum-silicate-hydrate cements for encapsulating problematic aluminium containing wastes, Journal of Sustainable Cement-Based Materials, **1**(1-2), 2012, p34-45.

- V. Bhakhri, J. Wang, N. Ur-rehman, C. Ciurea, F. Giuliani and L. Vandeperre, Instrumented nanoindentation investigation into the mechanical behaviour of ceramics at moderately elevated temperatures, Journal of Materials Research, **27**(1), 2012, p65-75.
- W. Montague, M. Hayes, L.J. Vandeperre, Strength-formulation correlations in magnesium phosphate cements for nuclear waste encapsulation, accepted for proceedings of the 37th International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, USA, 28 January- 1st February, 2013
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- L.J. Vandeperre & J. Teo, Pressureless sintering of SiC-B4C composites, accepted for proceedings of the 37th International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, USA, 28 January- 1st February, 2013

Book chapter

- J. Wang & L.J. Vandeperre, Variation of Mechanical Properties of UHTCs with Temperature, submitted to W. Fahrenholz, E. Wuchine, W.E. Lee & Y. Zhou, editors, Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications, to be published by ACerS in collaboration with Wiley.

Jianke Ye

- *Molten salt synthesis and characterization of SiC coated carbon black for refractory castable applications,* J Ye, S Zhang, W E Lee, J. Euro. Ceram. Soc, 2013 (accepted, in press)
- *Microstructure and Rheological Properties of Titanium Carbide Coated Carbon Black Particles Synthesised from Molten Salt,* J. Ye, R. Thackray, W E Lee and S Zhang, Ceram. Int. (under review), 2013

7.3 Memoranda of understanding

To provide a framework for future collaboration and as a supplement to existing framework agreements at institution level with Imperial College, CASC has signed Memoranda of Understanding (MoUs) with the following research centres:

- Institute of Nuclear and New Energy Technology, Tsinghua University, China
- Institute of Ceramics Research and Education, Nagoya Institute of Technology, Japan
- Energy Research Institute @ NTU, Nanyang Technological University, Singapore
- Institute of Biomaterials at University, Erlangen-Nuremberg, Germany
- Advanced Ceramics Group, University of Bremen, Germany
- Materials Science and Engineering Department, University of Florida

7.4 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 October 2012, covering additional CASC research and equipment, visitors to the Centre and the second summer school on ceramics.

7.5 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.

7.6 Submitted and funded proposals

7.6.1 Proposals submitted

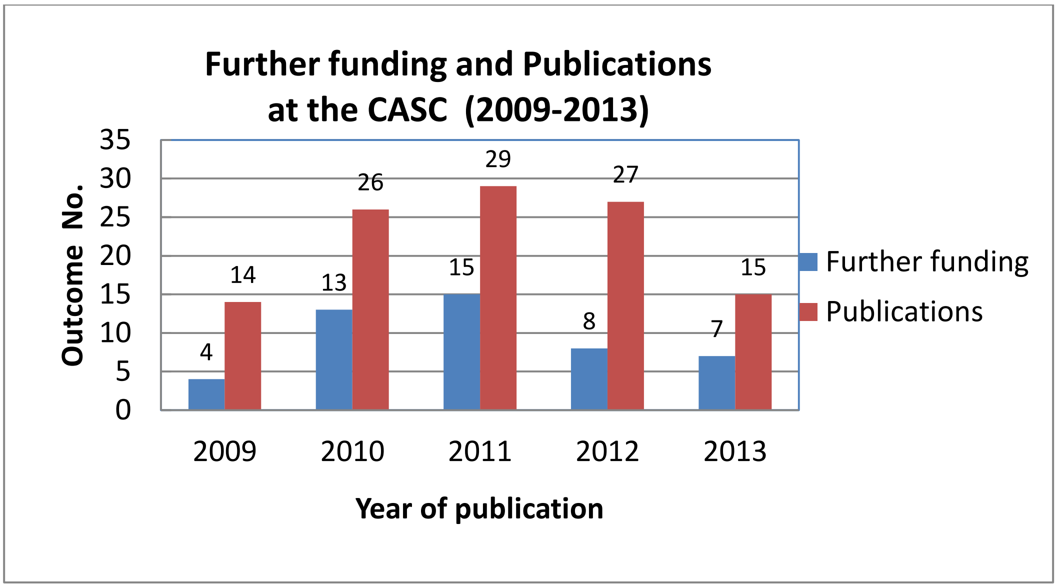
- Deformation of Alumina Coatings, SECO Tools AB, FEB 2013, Principle Investigator, F.Giuliani
- *Ceramic materials and shaping technologies for short life propulsion systems*, LJ Vandeperre, F. Giuliani, E. Saiz and WE Lee, in collaboration with Microturbo, awaiting outcome
- *Verification and design methodologies for ceramics – part II*, LJ Vandeperre in collaboration with Astrium and Thales, asked to resubmit with revised budget
- *SiC fibre reinforced glass ceramic composites for Skylon*, LJ Vandeperre in collaboration with Reaction Engines, KT partnership application, awaiting outcome

7.6.2 Proposals funded

- Major EPSRC Grant of £5.8M has been funded to a research project for 5 years (2013-2017) to Develop Materials for Extreme Environments. It is a collaborative project between Loughborough University (PI, J Binner), Imperial College and Queen Mary University of London (Prof Bill Lee, Prof Mike Finnis and Prof Mike Reece) as the Co-Investigators. A team of four researchers will develop the required understanding of how the processing, microstructures and properties of materials systems operating in extreme environments interact to the point where materials with the required performance can be designed and then manufactured.
- Major European Council –FP7 project of €3.6 M was funded towards the initial training network for young researchers in the strategic area of bioceramics for bone repair. It is a Marie Curie Initial Training Networks (ITN) funded by FP7. The Principal Investigator & coordinator is Eduardo Saiz. This is a European Framework Programme 7 for four years from March 2012. The ultimate objective of the BioBone network is to train young researchers to fill this demand in the strategic area of bioceramics for bone repair.
- *Calcium aluminate refractories,* Kerneos, £125K, 2012-14, WE Lee
- *Glass composite materials,* Sellafield Sites , £40K, 2012-14, WE Lee
- *Support for Workshop on Predictive Multi-scale Modelling of Structural Materials,* US ONR Global, EOARD and ERDC, $20K, 2012, WE Lee
- *Processing of C Fibre UHTC composites,* US Navy and ONR Global, $300K, 2012-15, WE Lee and D Daniel
- *William Penney Fellowship,* AWE and Imperial College, £300K, 2013-15, WE Lee
- Deformation of Polycrystalline Diamond. Element six, £60K, May 2013, F.Giuliani
- *MAST STC Core Programme, Work Package 3.1.7 - Ceramic Composites*, LJ Vandeperre, in collaboration with Morgan AM&T, NP Aerospace, CERAM, University of Oxford, Loughborough University, and Surrey University, funded £300k (£75k to CASC)

- *Further ceramics for armour*, DSTL, LJ Vandeperre, F Giuliani, funded £100K, *PhD studentship to investigate mechanisms of uptake to cement-based materials*, LJ Vandeperre & M. Ryan in collaboration with AMEC, funded
- *Amelogenin Degradation by MMP20 and KLK4 in Enamel Biomineralization,* Co-I, NIH (USA), $ 1.4 M, Eduardo Saiz
- *Glass-ceramic Interfaces, Asahi Glass Company,* £150K, Principal Investigator, Eduardo Saiz
- *Biomimetic organic-inorganic hybrid structural materials,* Marie Curie Intra-European Fellowships, Principal Investigator, 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, Principal Investigator, Eduardo Saiz.
- *Graphene 3D networks,* EPSRC, 1 February 2013-31 January 2017, £2.2M, Principal Investigator, Eduardo Saiz
- *Engineering with Graphene for Multi-functional Coatings and Fibre-Composites,* EPSRC, 1 February 2013-31 January 2017, £1.3M, Co-Investigator, Eduardo Saiz
- *Graphene Enhancement of the Photocatalytic Activity of Semiconductors,* Marie Curie Intra-European Fellowships, 1 November 2013-30 October 2015. €300K, Eduardo Saiz.
- Silicon stabilisation of Boron Carbide, £650 K, EPSRC September 2012, Principle Investigator, F. Giuliani

The summary on further funding and publications obtained between 2009 and 2013 is shown below which shows a positive outcome. It is expected that by the end of 2013, the number of outcome would reach the trend.



2009	2010	2011	2012	2013
£ 3.7 M	£2.7 M	£14.5 M	£1.0 M	£7.0 M

7.7 Other evidence of esteem

Omar Cedillos Barraza

- Best Poster Prize. Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications II, 13 -18 May 2013, Hernstein, Austria.

Dr Salvador Eslava

- Best oral presentation awarded at the Postdoctoral Researcher Symposium in the Materials Department, Imperial College London, 2012.

Dr. Suelen Barg

•Advanced composites inspired by nature FP7-PEOPLE-2011-IEF, Intra-European Fellowships (IEF),

Dr Miranda Fernandez

- *BIOHYMAT: Biomimetic organic-inorganic Hybrid structural materials*, FP7-PEOPLE-2011-IEF, Intra-European Fellowships (IEF)

Dr. Na Ni

EPSRC postdoctoral prize

Dr Finn Giuliani

- Editor of the American Ceramics Society Bulletin

Dr Julian Jones

Fellowships of learned societies

- FIMMM

Editorships

- 2011 – present: Ceramics International
- 2011 – present: Journal of Biomaterials and Tissue Engineering (Regional Editor -Europe)
- 2010 – present: International Materials Reviews
- 2009 – present: The Open Biomedical Materials Journal
- 2008 – present: The Open Medical Devices Journal

Professor Bill Lee

- Board of Directors of the American ceramic Society (2010-13)
- Member Board of Directors of Technology Strategy Board’s materials Knowledge Transfer Network
- Member Tokamak Solutions Scientific and Environmental Advisory Board
- Kingery Award of American Ceramic Society 2012
- Mellor memorial Lecture of Ceramic Society of the Institute of Materials 2012
- Fellow of the Royal Academy of Engineering 2012
- AWE William Penney fellow 2013

Professor Eduardo Saiz

- Member of the International Editorial Committee of the Boletin de la Sociedad Española de Cerámica y Vidrio
- Editor of Advances in Applied Ceramics
- Ad-hoc member of several National Institute of Health (NIH) special emphasis panels
- Vice Chair Basic Science Division American Ceramic Society
- Member of the international advisory committee of the 7th Conference on High Temperature Capillarity (HTC 2012)

Dr Luc Vandeperre

- Organiser, 1 Day Research Meeting on Advanced Ceramics, Imperial College London, 28th May 2013
- Organiser, Symposium on materials for extreme environments at the 37th International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, USA, 28 January-1st February, 2013

7.8 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. Five nominations were received for the 2012 prize, which was won by Dr Bai Cui. Bai's research on *Microstructural Evolution and Oxidation Behaviour of Spark Plasma Sintered MAX Ceramics* was supervised by Professor Bill Lee at Imperial College London. The award took place on 4 December 2012 in New York, when Dr Andrew Hosty (Morgan Ceramics) presented Bai with a certificate, plaque and £1000 cheque.

Nominations have been invited for the third award of this prize in 2013. Five PhDs on the topic of ceramic science or engineering that have been awarded at a UK university in the twelve months before 31 May 2012 have been nominated by their supervisor. The recipient of the prize will be decided by the external members of the CASC Steering Group; it is hoped that this award will be presented at a one-day research on advanced ceramics (1-DRAC) meeting in autumn 2013.

7.9 Industrial Consortium

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:

Membership	Focus	Cost (£k + VAT pa)	Steering Group	Access to CASC academics	Preferential access to facilities	Summer School places
Diamond	Strategic	50	Yes	Yes	Yes	5
Sapphire	Research and Training	15	No	Yes	Yes	2
Ruby	Research and Training	5	No	Yes	Yes	1

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

8 UK Meetings and Networks

CASC has continued its role of co-ordinating UK structural ceramics meetings. We have become more visible at international meetings and are expanding our role in organising these meetings. Part of CASC's plan is to raise the international profile of the UK's structural ceramics research. To this end we are targeting key conferences and also helping with organisation of some conferences in London so we can show off CASC to the attendees.

8.1 CASC Summer School on Ceramics

The third CASC summer school on ceramics took place at Imperial College London from 12 to 14 September 2012. Thirty two attendees, with a wide range of backgrounds and an even mix of industrial and academic experience, gathered at Imperial for tutorials and practical demonstrations focussed on current developments in ceramic synthesis, processing and mechanical characterisation. Presenters from several European and American institutions covered a wide range of topics such as vapour powder synthesis, wet processing of ceramics - including freeze casting and electrophoretic deposition - and mechanical testing at nano to macro scales. The school also provided a forum for dialogue and networking.

The Summer School is now an annual event directed towards ceramic engineers and researchers who wish to enhance their ceramics background or keep abreast of the more recent developments. Our aim is to provide a forum for the industrial and academic community to meet in a setting that encourages open communication and the discussion of practical problems.

Attendees at the CASC Summer School 2012

Following the success of the first three Summer Schools, this is now an annual event directed towards ceramic engineers and researchers – working in universities or industry – who wish to enhance their ceramics background or keep abreast of the more recent developments. The fourth ceramic summer school will be held during 18-20th September 2013. Presenters at the fourth CASC Summer School 2013 will include:

- 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)
- *Dr Mike Williams (Kennametal—Sintec, UK)*
- Prof John Fernie (AWE, UK)

Topics for the summer school will include:

- Suspension based processing methodologies
- Pressure assisted densification
- Ceramic membranes for gas separation and filtration
- Tailoring ceramics for electro-discharge machining

- Joining of ceramics
- Micro-mechanical behaviour of thin films and experimental testing
- Simulation of the mechanical behaviour of ceramic matrix composites

8.2 1-DRAC

These 1-Day Research Meeting on Advanced Ceramics meetings, coordinated by Luc Vandeperre on behalf of the Ceramic Science Committee of the IoMMM, provide opportunities for young researchers to present their work to the UK ceramic community. After a successful 1DRAC meeting in Birmingham in 24 November 2011, 1-DRAC travelled south again for this academic year. It was held at Imperial College on 28th May 2013 with a programme of 9 talks and was attended by about 50 people. The next 1-DRAC meeting will be held at Loughborough University with Bala Vaidhyanathan as host.

8.3 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.

8.4 CASC seminar series

CASC has organized a seminar series in the department of materials at Imperial College with the participation of internationally recognized speakers (see below). The seminars are open to the public.

- *Prof. Helmuth Cölfen,* University of Konstanz, Germany - **Bio-Inspired Organic-Inorganic Hybrid Materials**
- *Prof. Wayne Kaplan,* Israel Institute of Technology Haifa, Israel **Interfacial Complexions & Thermodynamic Transitions at Interfaces**
- *Dr. Nicholas Dunne,* Queens University, Belfast, UK **Potential of fibre reinforced calcium phosphate cements for load bearing orthopaedic applications**
- *Prof. Paolo Colombo,* Department of Mechanical Engineering, University of Padova, Italy **Porous Ceramics and Advanced Ceramic Components from Preceramic Polymers**
- *Prof. Andreas Mortensen,* Éccole Polytechnice Fédérale de Lausanne, Switzerland **Capillarity in infiltration**

8.5 Workshop on Predictive Multi-scale Modelling of Structural Materials

In December 3-4 2012 CASC helped organise and host a workshop at Imperial College funded by the US military to bring together world-leading groups in predictive modelling of relevance to the defence sector. This high level invitation-only meeting had 60 attendees and will continue in 2013 entitled Research Advances in Structural Materials: Theory, Simulation and Experiments, Dec 9-11 at

Imperial under the auspices of the Thomas Young Centre for Materials Theory and Simulation. The workshop includes the following list of speakers presented their talk on different topics:

Bill Lee (Imperial)	Welcome and Introduction to Workshop
Chair Arthur Heuer (CASE)	FUNDERS PERSPECTIVE
Julie Christodoulou (US ONR)	Integrated Computational Materials Engineering: A Perspective from the US Office of Naval Research.
John Beatty (US Army)	Multi-scale Research in Materials for Extreme Dynamic Environments
Andrew Heaton (DSTL)	Multi-scale Materials Modelling in DSTL
Chair Lorenzo Iannucci (Imperial)	IMPACT & FRACTURE
Bryn James (DSTL)	The Physics of Impact and Blast: Interaction on Many Scales
Vikram Deshpande (Camb)	Micro-mechanics of Ceramic Impact
Richard Todd (Oxford)	Multi-scale Experiments for Modelling the Deformation and Fracture of Ceramics
Chair Alessandro di Vita (KCL)	CERAMIC SYSTEMS
Jun Shi (Rolls Royce)	Multi-scale Modelling of Ceramic Matrix Composites
Dietmar Koch (DLR)	Limits of Experimental Based FE-modelling for Ceramic Matrix Composites
Frank Abdi (Alpha Star)	Environmental Degradation and Micro-Crack Formation in Ceramic Matrix Composites Using Multi-Scale Progressive Failure Modeling
Kamran Nikbin (Imperial)	Continuum Damage Modelling to Predict Structural Integrity of Cracked Ceramic Components
Chair Kamran Nikbin (Imperial)	OTHER SYSTEMS
Antoinette Tordesillas (Melbourne)	Measurement, Characterisation and Modelling of Granular Materials: a Possible Road-map
John Yates (Manchester)	Developments in Multi-scale Fracture Modelling for Engineers
Endel Iarve (UDRI)	Discrete Damage Modelling Methods for Structural Composites
Ferri Aliabadi (Imperial)	Multi-scale Modelling of Material Degradation and Fracture
Lorenzo Iannucci (Imperial)	Multi-scale Modelling in Armour Design
Chair Mike Finnis (Imperial)	MATERIALS DESIGN
Joerg Neugebaur (MPI)	Materials Design-based Predictive Ab initio Thermodynamics
David Porter (Oxford)	Analytical Structure-Property Relations for Multi-scale Engineering Simulation and Material Design
Frank Zok (UCSB)	Lattice Materials: Designing for Strength and Energy Absorption
Chair Alex Shluger (UCL)	METALS
Y-J Kim (Korea University)	Numerical Ductile/creep Fracture Simulations of Cracked Structural Components using Meso-scale Damage Models
Noel.O'Dowd (Limerick)	Simulation of Deformation and Failure of Structural Steels at the Microscale
Ralf Drautz (ICAMS)	Bond-Order Potentials for Modelling Phase Stability in Complex Alloys

Fionn Dunne (Imperial)	Facet fatigue: modeling microstructure for component performance
David Dye (Imperial)	Materials discovery and alloy design: using fundamental insight to achieve the accelerated insertion of materials
Daniel Balint (Imperial)	Dislocations Under Shock Loading
Chair Bill Lee (Imperial)	OTHER SYSTEMS
Tap A Parthasarathy (AFRL)	Modeling oxidation kinetics of SiC-MeB2 and predicting behavior under hypersonic flight conditions
Bill Troha (Alpha Star)/Frank Abdi (Alpha Star)	Foreign Object Impact Damage to Ceramic Matrix Composites and the Validation of Multi-Scale Progressive Failure Modeling
Ron Winter (AWE)	Plate-impact loading of cellular structures formed by selective laser melting
Alan Cocks (Oxford)	A Variational Modelling Approach to Bridge the Micro and Macro Scales

8.6 BioBone workshop on structural characterisation at multiple length scales

CASC will participate on the organisation of a workshop on materials characterisation at multiple length scales (3-5 July 2013). The workshop is organized in the framework of BioBone an initial training network funded by the EU. The objective is to introduce young scientist to the state of the art of several characterization techniques relevant in the field of bioceramics. It will feature several internationally recognized speakers and it is open to scientists outside the network. The programme on the workshop includes the following speakers on different topics:

Imperial College London

BioBone Meeting & Workshop

3-5 July 2013 — Imperial College London

BIOBONE

3rd July – Wednesday (Afternoon) - Room G04A	
2.30-4.00	Registration for BioBone researchers + 1st part of BioBone ESRs&ERs meeting
4.00-4.30	*Coffee break*
4.30–6.00	Lab Tour + 2nd part of BioBone ESRs&ERs meeting
4th July – Thursday	
8.30-9.00	Registration
9.00-9.15	**Prof. Eduardo Saiz** - Introduction
9.15-10.00	**Dr. Sergio Bertazzo-** *"The State-of-the-Art of Electron Microscopy and the Characterization of Biominerals"*
10.00-10.45	**Dr. Alexandra Porter -** *"Analytical Electron Microscopy of Bone"*
11.10-11.55	**Dr. David Payne-** *"Photoelectron Spectroscopy of Biomaterials – New Opportunities at 'High' Pressure"*
11.55-12.40	**Prof. Philip Withers -** *"Time Lapse CT of Bone Failure"*

2.00-2.45	**Dr. Wolfgang Wagermaier -** *"Imaging of Bone Structure and Properties During Mineralization and Healing with Materials Science Methods"*
2.45-3.30	**Prof. Mark Smith***"An Introduction to the Application of Solid State NMR Techniques to the Characterisation of Biomaterials"*
4.00-4.30	**Dr. Katia Biotteau** (BioBone ER from Ceramtec)
4.30-5.00	**Dr. Yann Fredholm** (BioBone ER from Keramat)
5.00-5.30	ESRs Poster session
5th July – Friday (Morning)	
9.00-9.45	**Dr. Sarah Fearn-***"Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Its Application to Bone Analysis"*
9.45-10.30	**Prof. Joël De Coninck-***"IR and Wetting Surface Analysis for Biomaterials Characterization"*
11.00-11.45	**Dr. Ada Cavalcanti-***"Cells at Interfaces: Regulating Cellular Functions with Nanoscale Spacing of Extracellular Ligands"*
11.45-12.30	**Dr. Iain Dunlop-***"Mechanical Characterisation of Polymeric Biomaterials"*
12.30-1.00	Final Debate/Discussion – Concluding remarks