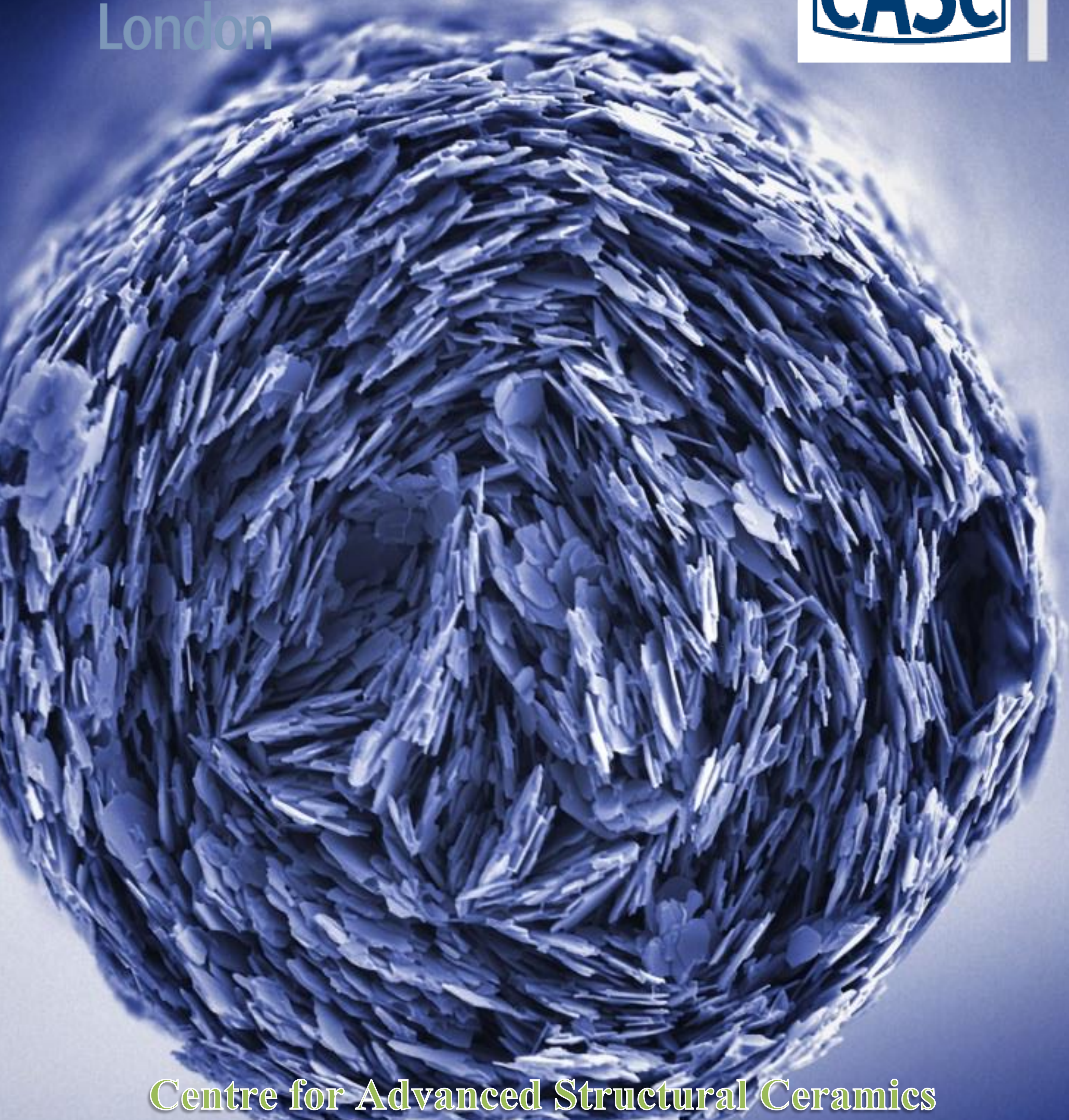
Imperial College London

CASC



Centre for Advanced Structural Ceramics
2016 Annual Report

Cover image by Ezra Feilden-Irving.

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Introduction

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

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

Our main goal is to continue these relationships and grow as a ceramics centre.

Professor Eduardo Saiz

CASC Director

MANAGEMENT

CASC was initially set up by Professor Bill Lee in 2008. In 2012, Professor Eduardo Saiz took over as Director.

Local Management Team (LMT)

The LMT is responsible for managing the centre's operations and meets monthly to oversee the pressing day-to-day issues of running the Centre. These issues include staff appointments, equipment purchase and building refurbishment, but are increasingly focussed on developing the Centre national and international profile, forging industrial links and achieving financial sustainability.

The LMT is chaired by Eduardo Saiz and other members are Finn Giuliani, Luc Vandeperre, Ainara Aguadero, Stephen Skinner, Daniel Balint, Julian Jones and Garry Stakalls.

The meetings are also attended by representatives of the Postdoctoral researchers (Laura Larrimbe) and PhD students (Jia Hui Theo) working on projects related to structural ceramics.

Industrial Consortium Group (ICG)

A key part of CASC's sustainability is the development of a consortium of companies with interest in structural ceramics. After the end of the EPSRC funding in 2013, an industry consortium scheme was set up to build on CASC's early success, to enable its sustainability and to support the long-term and fruitful relationships created between CASC-associated academics and UK's industry.

This was planned and presented in our first Industry Day meeting the 17th of May of 2011, where it was well received by the industry representatives and was developed by our Steering Group on July 4th 2011.

The Industrial Consortium started functioning in 2014 after the Steering Group meeting, held the 17th of January 2014.

The ICG develops the CASC Business Plan which contains the Centre's vision, objectives and an action plan to deliver such vision. It also acts as an advisory role to the Director and the Local Management Team, 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 undergraduate and postgraduate courses provided by the Centre.

The consortium has three levels of membership with a graduated annual fee and access to CASC facilities, people and projects as can be seen in the table in page 4.

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.
On the other hand, Sapphire and Ruby memberships are aimed at companies who want to collaborate with CASC on research and training.

All three levels of membership provide:

- Access to CASC equipment, at preferential rates, (including hot press, vacuum furnace, nanoindenter…) as well as the central facilities at the Materials Department (including X-ray Diffraction, Electron Microscopy, Secondary Ion Mass Spectroscopy and Thermal Analysis), with operator and interpretations.
  The degree of access will depend on the level of membership as seen in the table below.
- Access to CASC and CASC associated academics.
- Positions in the CASC Summer School.
- 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 and descriptions of such are needed by Easter previous year.
- Opportunity to propose research projects for students on Master Courses (Advanced Materials, Biomaterials & Nuclear), at differing levels depending on membership. Projects run from April to September, descriptions needed by May previous year.
- Opportunity to collaborate on out-of-term and industrial placements. Interviews can take place form October onwards.
- Receiving the CASC annual report and newsletter as well as 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 3 members signed up at Sapphire level (Morgan Advanced Materials, DSTL and Kerneos) and 3 members at Ruby level (Asahi Glass, Reaction Engines and John Crane) and we 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> or Alba Matas Adams < a.matas-adams@imperial.ac.uk – 020 7594 2053>

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

PEOPLE

Staff

Professor Eduardo Saiz

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

After graduating in Physics from Cantabria University in Spain he gained a PhD in Applied Physics from the Autonoma University of Madrid, working on the processing of ceramic superconductor thick films. In 1992 he became a Fulbright postdoctoral researcher at LBNL. He has worked extensively in the area of high-temperature capillarity and interfaces between dissimilar materials, developing new approaches to study spreading and adhesion in metal-ceramic systems and 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 his objectives is to develop high-temperature composites able to perform in extremely hostile conditions and increase efficiency in the transport and generation of energy. He is also working in the fields of biomineralization and the development of new ceramic-based biomaterials to enhance the osseointegration of orthopaedic implants and support the engineering of new bone and cartilage.

Professor Bill Lee

Professor Bill Lee was the founding Director of CASC from July 2008 until August 2012 and was the principal investigator of the EPSRC award. Bill is a Professor of Ceramic Engineering and was Head of the Department of Materials at Imperial College London from January 2006 to August 2010. After graduating in Physical Metallurgy from Aston University he gained a DPhil from Oxford University on radiation damage in sapphire, was a post-doc at Oxford and Case Western Reserve Universities, Assistant Professor at Ohio State University, USA, before becoming lecturer in ceramics at the University of Sheffield in 1989. While at Sheffield he was Manager of the Sorby Centre for Electron Microscopy and Director of the BNFL university research alliance the Immobilisation Science Laboratory. Bill was made a Fellow of the Royal Academy of Engineering in 2012 and his current research is focussed on ultra-high temperature ceramics for aerospace applications and ceramics for nuclear fuel and waste immobilisation applications.

Dr 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.

Finn has a PhD from the University of Cambridge where he examined small scale plasticity in multi-layered 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 projects in the area of boron carbide for amour applications.

Finally, he has an interest in novel in situ mechanical testing regimes whether in TEM, SEM or synchrotron.

Dr Luc Vandeperre

Dr Luc Vandeperre, currently a reader in the Department of Materials, joined the CASC academic staff in July 2010.

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 thermo-mechanical 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.

Dr Alba Matas Adams

Alba joined the Department of Materials as Technical Manager in November 2016. Prior to this she was a PhD student at ICIQ (Tarragona), researching on new materials for bio- and energy related applications. 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. She also engages herself in other programmes (XMAT, RESLAG, EPSRC) within the Department of Materials.

Garry Stakalls

Garry Stakalls started as technician for the Centre in July 2008. Prior to this he worked in the Materials Processing Group within the Department of Materials, where he commissioned and ran large experimental rigs and was involved in the processing of wide range of materials. His main activities have been to use and train new users on the use of the thermal analysis equipment as well as operating the hot press for sintering and pressing. He also maintains the equipment while liaising with Netzsch for thermal analysis and FCT for the hot press.

Researchers

Dr. Nasrin Al Nasiri	Junior Research Fellow
Dr Ayan Bhowmik	Research Associate
Dr. Eleonora D'Elia	Research Associate
Dr Esther García-Tuñón Blanca	Research Associate
Dr Daniel Glymond	Research Associate
Dr. Samuel Humphry-Baker	Research Associate
Dr Laura Larrimbe	Research Associate
Dr. Michael Rushton	Research Associate
Dr. Eugenio Zapata-Solvas	Research Associate

PhD students

Cyril Besnard	**Jindaporn Juthapakdeeprasert**
Eleonora Cali	**Alan Leong**
Gil Da Costa Machado	**Wirat Lerdprom**
Ezra Feilden-Irving	**Annalisa Neri**
Claudio Ferraro	**Kristijonas Plausinaitis**
Claudia Gasparrini	**Dimitri Pletser**
Tommaso Giovannini	**Giorgio Sernicola**
Yun-Hao Hsieh	**Jia Hui Teo**
Charles Hutchison	

Academic Visitors

Dr. Roberto Martin (CIDETEC)	**Dr. Alaitz Rekindo (CIDETEC)**
Dr. Cristina Botas (CIC Energygune)	**Dr. Eric Camposilvan (INSA, Lyon)**
Dr. Florian Bouville (ETH, Zurich)	**Dr. Florian Bouville (ETH, Zurich)**
Dr. Adam J. Stevenson (Saint-Gobain CREE)	**Mr Pedro Ivo Batistel Galiote Pelissari (ETH, Zurich)**
Ms Silvia Stella Ramirez Caballero (INSA, Lyon)	**Mr. Johanes Gabi (ETH, Zurich)**
Ms. Miriam Regue Griño (University of Bath)	

CASC Alumni

Suelen Barg	Lecturer in Structural Materials, University of Manchester, UK.
Miriam Miranda	Element Six, UK.
Salvador Eslava	Academic Staff, University of Bath, UK.
Na Ni	Junior Research fellow, ICL, UK.
Amanda Quadling	Morgan Advanced Materials, UK.
John Mitchell	Nexceris, UK.
Rui Hao	PDRA, University of Illinois, USA.
Vineet Bhakhri	PDRA, University of Western Ontario, USA.
Jianye Wang	Materials Technologist at John Crane, UK.
Philip Howie	PDRA, Cambridge University, UK.
Naeem Ur-Rehman	Research Engineer, Baker Hughes, USA.
Ben Milsom	Queen Mary University – Laboratory & Workshop Manager, UK.
Claudia Walter	IBM, UK.
Constantin Curea	Rolls-Royce, UK.
Bai Cui	Assistant Professor, University of Nebraska, USA.
Doni Daniel	Senior Lecturer, School of Aerospace and Aircraft Engineering, Kingston University, UK.
Victoria Garcia Rocha	Lecturer, Cardiff School of Engineering, UK.
Omar Cedillos Barraza	Assistant Professor, University of Texas, USA.
Hielz Zoltan	Junior Lecturer in Nuclear Related Technology at Gen2, UK.
Nasrin Al Nasiri	Junior Research fellow, ICL, UK.
Jonathan Phillips	Morgan Advanced Materials, UK.
Tingting Zhang	Assistant Professor, Dalian University of Technology, China.
Carsten Kuenzel	Modine Europe, GmbH, Germany.
Jenny Alex	Continental, Germany.
Robert Harrison	Research Fellow in Nuclear Materials at University of Huddersfield, UK.

RESEARCH

PDRA Projects

- **Name: Dr. Ayan Bhowmik**
  Project title: Understanding Deformation Mechanics in Brittle Materials during Nano-indentation using in-situ Micro-Laue Technique.
  Supervisor: Dr. Finn Giuliani.
  Sponsor: EPSRC.

Developing a good understanding of the response of brittle materials, like ceramics and intermetallics under loading, especially during the initial stages of plastic deformation before failure, is crucial for the designing of engineering components out of such materials. This work investigates the deformation mechanisms in a [001]-oriented single crystal MgO.

To measure this we have carried out in-situ white beam micro-Laue diffraction while nano-indentation within synchrotron facilities in Diamond* and Advanced Photon Source†. This provides a unique protocol to study the fundamental operating mechanisms of deformation of material in small scale. Using a micro-focussed beam, both time and spatially resolved deformation map was obtained during nano-indentation. The Laue spots showed both rotation and streaking upon indentation that is typically indicative of both elastic lattice rotation and induced plastic strain in the material. Multiple facets of streaking of the Laue peaks suggested plastic slip occurring on almost all the {101}-type slip planes oriented 45˚ to the sample surface with no indication of slip on the 90˚ {110} planes. Owing to asymmetric slip beneath the indenter, as predicted by modelling results and observed through Laue analysis, sub-grains were found to nucleate with distinct misorientation. Tracking the Laue peak movement, a higher degree of lattice rotation was seen to occur in the material under the indent as compared to far field. Crystal plasticity finite element modelling was also applied to validate the experimental observations of plasticity.

* Diamond Light Source, Rutherford Appleton Laboratory, Didcot, UK
† Advanced Photon Source, Argonne National Laboratory, Argonne, Chicago, USA

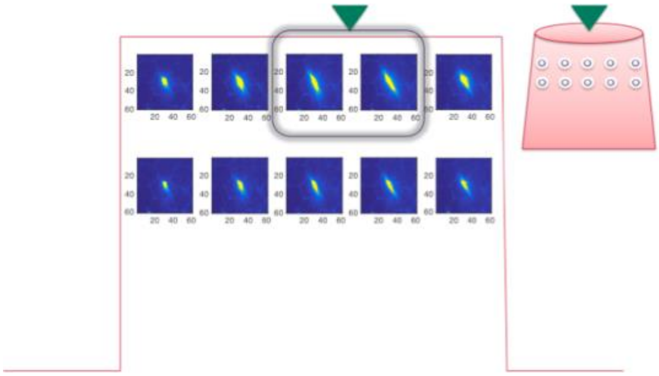


Figure 1. *Snapshot of the (1-13) peak obtained from the different locations of the pillar, as shown on the right with an exposure time of 3s. Also superimposed is the location of the indent with respect to the pillar axis based on the observation of the streaking of the peaks.*

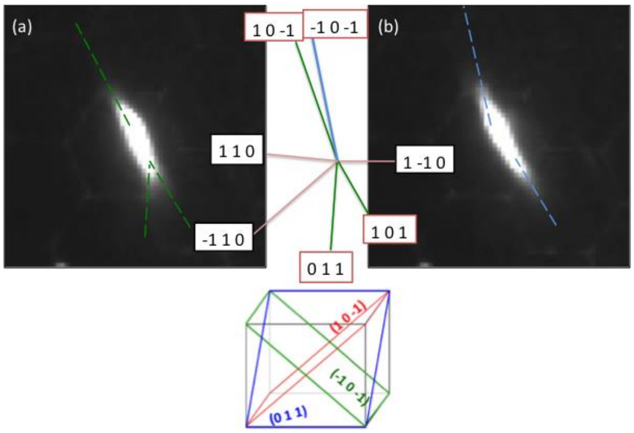


Figure 2. *The streaked reflections obtained from adjacent positions in the pillar under the indenter on which is superimposed the vectors denoting the direction along which the spot would streak given slip on various {110} planes.*

- **Name: Dr. Eleonora D´Elia**
  Project title: Living Materials.
  Supervisor: Prof. Eduardo Saiz.
  Sponsor: DARPA.

Smart materials have captivated the world of science and technologies for decades. The idea that a man-made material could sense the environment and respond to external stimuli such as light, temperature, or damage in an autonomous and programmed way is fascinating and, at the same time, closer than anticipated.

In this work we describe an approach for the fabrication of adaptive composite materials able to self-repair autonomously, sense mechanical stimuli such as pressure or flexion self-monitor their structural integrity and change their shape in response to external stimuli. These smart materials are based on the controlled integration of microscopic electrically conductive networks within polymeric matrices having self-healing or shape-memory capabilities. To realize this concept, we have taken advantage of the 2D nature of graphene combined with new processing techniques to design minimally-invasive networks able to provide a platform for inducing electrical stimuli in the composites. Superlight electrically conductive carbon-based networks with microscopic porosity obtained by freeze-casting have been infiltrated with a second polymeric phase. The networks are tailored to provide controlled and localized joule heating at relatively low voltages in order to stimulate the desired response in the polymeric matrix (healing or shaping). The resulting materials have graphene contents below 0.5 wt. %. Their mechanical response (strength and toughness) is evaluated and related to their microstructure.

Their healing ability is quantified in terms of recovery of these mechanical properties after damage. In parallel, their shape changing and mechanical sensing capabilities in response to electrical currents are also tested. Preliminary results on shape-memory compositions show strengths up to 60 MPa and complete shape recovery through joule heating in 10 seconds. Furthermore, the composites are able to record, through a conductivity change, the initiation and progression of a crack, providing damage monitoring capabilities.

The work brings together the fields of construction, materials science, robotics, energy and bioengineering in an innovative way, opening new paths for the design of smart actuators and adaptive composites.

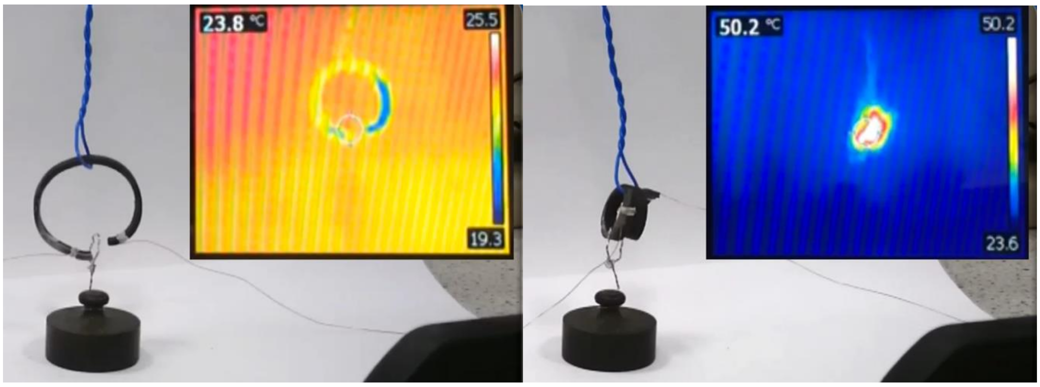


Figure1. *Joule heating effect in a shape-memory conductive sample showing the sample curling up and grabbing a weight due to current being passed through it.*

- **Name: Dr. Eleonora D'Elia**
  Project title: RESLAG.
  Supervisor: Prof. Eduardo Saiz.
  Sponsor: HORIZON 2020.

The European steel industry generated about 21.4 million tons of slag in 2012 resulting from steel making. About 24% is not being reused, representing a severe environmental problem in Europe, but also a huge amount of available material for potential recycling. RESLAG will face this environmental problem by providing 4 eco-innovative industrial alternative applications to valorise the steel slag.

The main objective of RESLAG project is to valorise the steel slag that is currently not being recycled (right now it is partially landfilled and partially stored in the steel factories) and reuse it as a raw material for 4 innovative applications that contribute to a circular economy in the steel sector with an additional cross-sectorial approach. These applications will be demonstrated at pilot level and led by end-user industries. Altogether open enormously the range of possibilities of taking profit from slag not only for the steel sector but also for many other sectors.
In this project, Imperial College is a fundamental partner involved in the mechanical, thermal and optical characterization of the slag pebbles as receive and the produced refractories used in the steel industry.

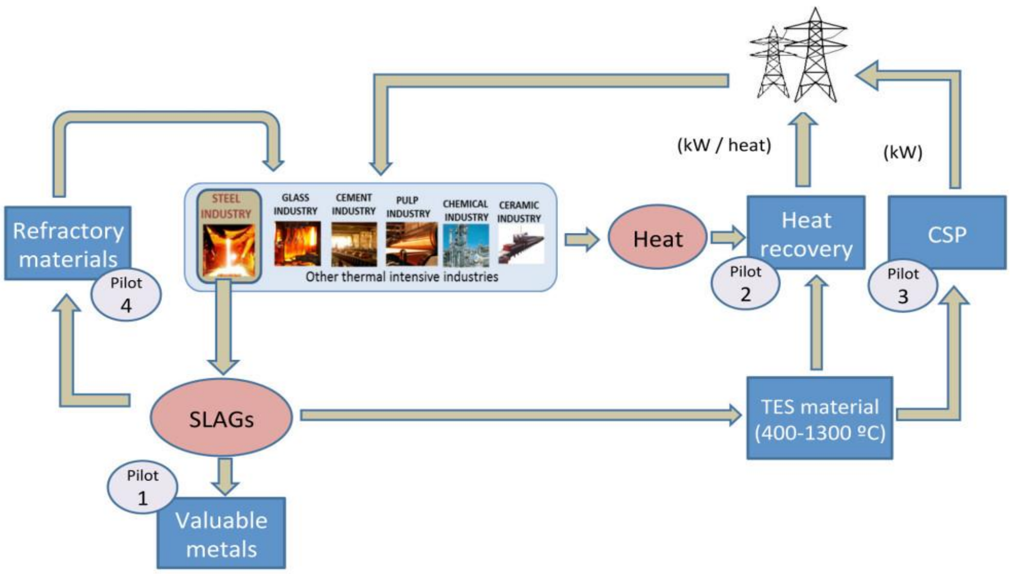


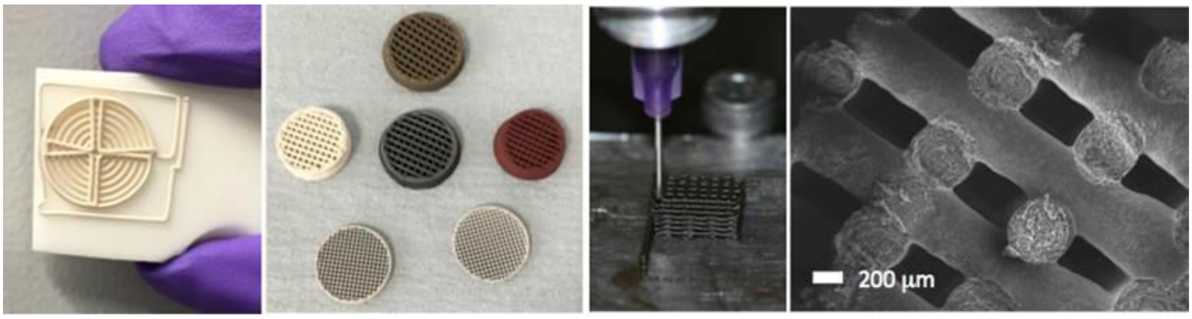
Figure 1 *– RESLAG Project Main Concept design.*

- **Name: Dr. Esther Garcia-Tuñon Blanca**

Project title: Responsive Processing Approaches for Direct Ink Writing.
Supervisor: Prof. Eduardo Saiz.
Sponsor: EPSRC.

As new technologies in key areas such as energy and medicine develop, the demand for state-of-the art fabrication to create complex multifunctional structures and devices also grows. Additive Manufacturing promises a revolution on how things are made, bringing freedom to create completely new designs and more efficient devices. But making all of these a reality demands a major effort in material development, since the commercial applications in AM are now mostly limited to a number of metals and polymers.

In or group, we have been developing a range of water-based formulation based on 'responsive' building blocks[1-3] for direct ink writing. These formulations are flexible and easily scalable up. They allow us to design 3D-inks for different materials, from oxide and non-oxide ceramics and metals to chemically modified graphene, enabling the printing of multi material devices. Using these pH and thermo responsive blocks we are able to build 3D scaffolds and devices for a wide range of applications, from calcium phosphates for bone replacement to graphene based materials for energy storage and mechanical sensors.



References:
1. *Designing Smart Particles for the Assembly of Complex Macroscopic Structures*. E. García-Tuñon, S. Barg, R. Bell, J.V.M. Weaver, C. Walter, L. Goyos, E. Saiz. Angew. Chem. Int. Ed., 52, p: 7805–7808, 2013.
2. *Printing in Three Dimensions with Graphene*. E. García-Tuñon, S. Barg, J. Franco, R. Bell, S. Eslava, E. D'Elia, R. C. Maher, F. Guitian, E. Saiz. Adv. Mat., 27(10), p: 1688-1693, 2015.
3. *Robocasting of structural ceramic parts with hydrogel inks*. E. Feilden, E. García-Tuñon, F. Giulianni, E. Saiz, L. Vandeperre. J. Eur. Ceram. Soc, 36 (10), p: 2525–2533, 2016.

❖ **Name: Dr. Daniel Glymond**
Project title: Ceramic Materials and Shaping Technologies for Short Life Propulsion Systems.
Supervisor: Dr. Luc Vandeperre.
Sponsor: Microturbo.

Powder pressing is industrially established but not well suited to the production of complex shaped turbine blades and components. However, pressing followed by green machining is applied successfully in space components and could potentially offer a way to produce intricate shapes while taking advantage of the well-developed pressing technology. Alternative shaping methodologies find their origin in clay based ceramics and are based on suspensions of ceramic powders: wet processing or colloidal techniques. A wide range of variants, often differing only in a limited way, exist. From these a number appear promising.

In gel-casting a gel former is added to the ceramic suspension so that it can be cast and subsequently gelled in a mould. The shape can then be demoulded, dried and sintered. Omatate, from the Oak Ridge National Laboratory in the USA, developed this methodology and used a radial-vane turbine rotor made from silicon nitride as a key example component[1]. However, drying of gel cast components can be cumbersome especially if the dimensions increase. Nevertheless, it seems obvious that this methodology must be part of the mix.

In later years, the use of binders from the food industry such as gelatine have been investigated and these have clear advantages over the polymer monomers in terms of toxicity[2]. A family of similar techniques are termed coagulation casting, in which a fluid suspension is made to solidify by removing the interparticle repulsive forces (for example by an homogeneous change in the suspension pH) once the object has been cast. An alternative is to engineer responsive particle surfaces that will promote particle dispersion in a suspension and subsequent assembly in response of an external trigger (e.g. pH). This could be done, for example, by grafting the particle surfaces with a pH responsive polymer such as a BCS polymer.

Finally, another way to produce ceramic parts with complex shapes is the use of solid-free-form fabrication techniques in which the part is printed in three dimensions following a computer design. We will focus on robotic assisted deposition, a continuous extrusion technique that can be used to print a sample layer by layer employing colloidal ceramic inks. The inks have to be pseudoplastic so they flow in the printing nozzle under pressure and after printing they can sustain the weight of the part without deformation. This can be achieved by, for example, using inks based on thermally reversible hydrogels that are fluid at low temperature allowing the homogeneous dispersion of ceramic particles and pseudoplastic at room temperature, allowing printing.

References:
1. *Development of Low-Toxicity Gelcasting Systems*. M.A. Janney, O.O. Omatete, C. A. Walls, S. D. Nunn, R.J. Ogle, G. Westmoreland. Journal of the American Ceramic Society, 81(3): p. 581-91, 1998.
2. *Gelatin gelcasting of ceramic components*. L.J. Vandeperre., A.M. De Wilde, and J. Luyten, Journal of Materials Processing Technology 135: p. 312-316, 2003.

- **Name: Dr. Samuel Humphry-Baker**
  Project title: Reliability of Fuel Cells.
  Supervisors: Dr. Luc Vandeperre and Prof. Alan Atkinson.
  Sponsor: 7th EU Framework.

Fuel cells offer efficient and small-scale conversion of fuel-to-electricity. However their high operation temperatures render some thermal stability challenges. Specifically, when a device is turned on and off, it is repeatedly cycled from room temperature to several hundred degrees Celsius. Such temperature cycling can induce stresses at the interface between components of differing thermal expansion coefficient. We are using X-ray diffraction to characterise the nature of residual stresses in joints between metal and ceramic components, and thus guide strategies for stress minimisation in future generations of device.

- **Name: Dr. Laura Larrimbe**
  Project title: Transpiration Cooling Systems for Jet Engine Turbines and Hypersonic Flight.
  Supervisors: Dr. Luc Vandeperre and Prof. Bill Lee.
  Sponsor: EPSRC.

Thermal protection systems for hypersonic flights are expected to have to operate with component temperatures in excess of 2000 ºC, leaving only a small group of materials with sufficient high melting points. Ultra High Temperature Ceramics (UHTC) have become the lead candidates for the development of such protection systems also due to their high thermal conductivity which enables heat to be conducted laterally thus reducing the maximum temperatures of the sharp leading edge. The basis of transpiration cooling is the introduction of a cool layer of gas between the component and the hot freestream flow, reducing the heat flux to the material (Figure 1).

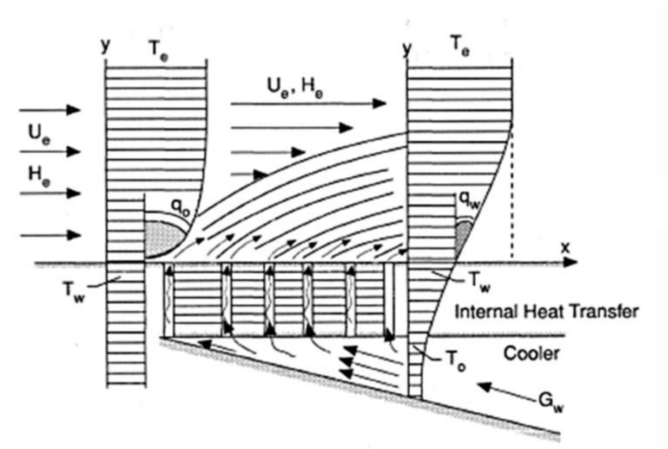


Figure 1. *Transpiration cooling system*

UHCTs with controlled porosity are suitable for application in transpiration cooling systems. This work addresses the manufacturing of innovative porous UHTCs by establishing a densification route which does not require pressure and allows producing the components in the correct shape without requiring extensive machining or large amounts of material loss. Samples of ZrB_2 with homogenous porous structures were manufactured by partial sintering or by addition of different volume fractions of fugitive inclusions, using starch as a pore former (Figure 2).

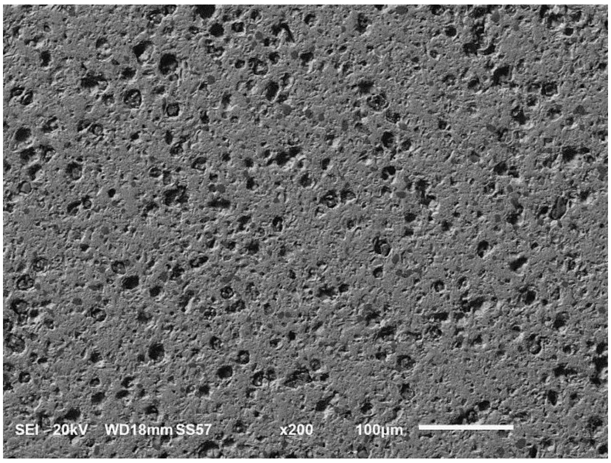


Figure 2. *Pressureless sintered ZrB_2 using starch as a fugitive agent*

Characterization of the sintered porous UHTCs was focussed on measuring systematically the relationship between pore structure, porosity and some properties such as thermal conductivity, strength or flow. All this information enables to select the most relevant candidate which capable to maintain excellent thermal and structural properties whilst moving to a high porosity.

Future research will focus on the study of pores generated by 3D printing organic channel structures, followed by gel casting of ceramic around these preforms.

- **Name: Dr. Michael Rushton**

Project title: Modelling of Heat Flow in Fukushima Wasteforms.
Supervisors: Dr. Luc Vandeperre and Prof. Bill Lee.
Sponsor: EPSRC.

One of the main problems facing the remediation of the Fukushima Daiichi site is the treatment of the effluent cooling water from Units 1 – 3. Large volumes of water were injected into the reactor cores and the spent fuel pools which were subsequently treated in a series of sophisticated systems. These have left large quantities of highly contaminated adsorbent, termed High Dose Spent Adsorbents (HDSAs) and are currently stored on-site while a suitable method of long term disposal is developed.

To this end, a low temperature processing route is being developed at Imperial College by which the HDSAs may be immobilised in a low melting point glass.

To support this activity, the current project aims to develop a model across finite element and microstructural length scales to help underpin the assessment of wasteform options, including the feasibility of using the decay heat to drive self vitrification. A radiolytic heat generation tool is being developed to calculate the temperature distributions in HDSA bearing wasteforms and to provide predictions for possible wasteform thermal/stress damage which will aid in the optimization of processing conditions. The project is in collaboration with the Immobilisation Science Laboratory at Sheffield University and with partners in Japan at the universities of Kyushu and Tohoku and at Hitachi-GE Nuclear Energy and is part of a recentlyawarded EPSRC grant “Advanced Waste Management Strategies for High Dose Spent Absorbents”.

- **Name: Dr. Eugenio Zapata-Solvas**
  Project title: Carbides for Future Fission Environments.
  Supervisor: Prof. Bill Lee.
  Sponsor: EPSRC.

  The aim of this project is to develop new Zr-based carbides, including Zr-based MAX phases, for coating Zr-alloys cladding in fission reactors of future nuclear power plants. The synthesis, sintering by hot press and spark plasma sintering and microstructural characterization by XRD, SEM and TEM of the different Zr-based carbides is done at Imperial College. The research has been focused on the effect of processing and of the impurities in the synthesis of sub-stoichiometric ZrC_{1-x}, and $Zr_{n+1}AlC_n$ and $Zr_{n+1}SiC_n$ MAX phases, being able to synthesize Zr_3AlC_2 with the highest yield reported till date.

PhD Projects

- **Name: Cyril Besnard**
  Project title: Si Doping of Boron Carbide.
  Supervisor: Dr. Luc Vandeperre and Dr. Finn Giuliani.
  Sponsor: DSTL.

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

- **Name: Gil Da Costa Machado**
  Project title: Calcium Phosphate Scaffolds with Controlled Properties for Biological Applications.
  Supervisor: Prof. Eduardo Saiz.
  Sponsor: Marie Curie ITN-FP7

After the initial characterization of the starting powders, the thermal behaviour of the materials with a biphasic composition (from pure Hydroxyapatite to pure β-Tricalcium Phosphate) was assessed and the optimal sintering conditions were established. Furthermore, an innovative emulsion-based soft templating method was used for the purpose of controlling structural features (porosity, pore size and interconnectivity) at the micrometric scale. The biological behaviour of such materials was studied in vitro by incubating them with human mesenchymal stem cells in an osteogenic medium.

Specific differentiation markers were measured to assess the osteogenic potential of the Calcium phosphate flat substrates with varying roughness profiles. Three-dimensional scaffolds were also produced through the robocasting of periodical structures with the emulsion based slurries. Printing conditions were optimised for different compositions and their bioactivity was evaluated through standard incubation tests in simulated body fluid.

An important goal of this work was to fabricate three-dimensional scaffolds with these materials - i.e., incorporating the microporosity and roughness that results from the emulsification process – while controlling structural features at a macrometric scale, such as pores with hundreds of micrometers where cells can penetrate and proliferate. For such processing to be possible, it is paramount to understand the rheological behaviour of these materials.

Fig. 1 shows how the apparent viscosity of the ceramic suspension and emulsion at different steps of the processing route varies with the shear rate. At basic pH (early in the process), the materials are very fluid. However, in order to be used in 3-D shaping techniques such as robocasting, they must simultaneously be fluid enough to flow through a nozzle during extrusion and be stiff enough to keep their shape after that. Therefore, the coagulation step (pH switch) previously mentioned is necessary, as it increases the viscosity of the materials roughly three orders of magnitude, making them suitable for 3D printing.

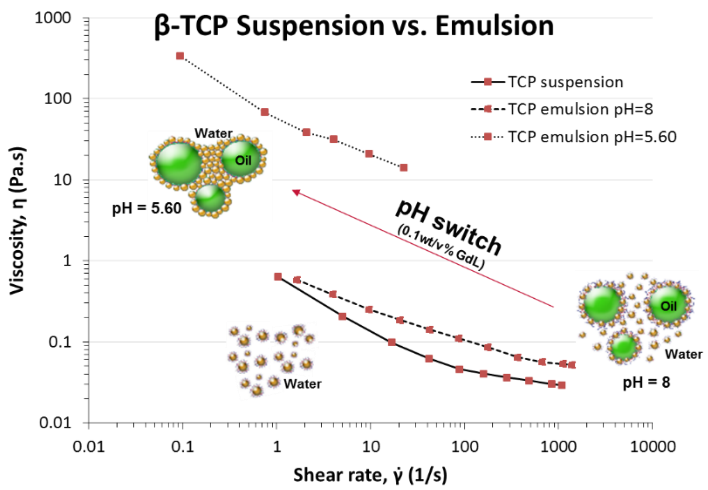


Figure 1. *Apparent viscosity of both initial (TCP suspension) and emulsified (TCP emulsion) ceramic suspensions, and coagulated (TCP emulsion pH=5.60) emulsion after pH switch*

At this point, it is possible to make large scaffolds with controlled structures and geometries by extruding these particle stabilized emulsions. Fig. 2 shows a piece prepared through such method, on which it is possible to see the microporosity that results from the oil droplet templating and how it reflects of the final surface roughness of each printed rod.

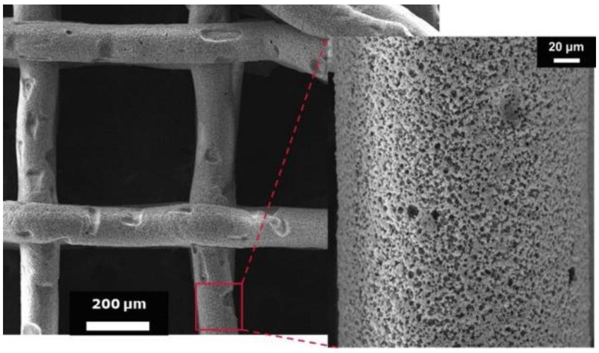


Figure 2*. Robocasted scaffold by extruding particle stabilised emulsion with HA.*

These levels of structural control allow for an extremely versatile method of production of calcium phosphate scaffolds with varying chemical composition.

- **Name: Eleonora Cali**

Project title: Magnetic Nanoparticles for Uranium Sensing and Removal from Solution.
Supervisors: Dr. Luc Vandeperre and Prof. Mary Ryan
Sponsor: EPSRC, DISTINCTIVE Consortium.

The development of magnetic nanoparticles for separation technologies in liquid systems is well-developed and already in use in medical testing. The challenge is to develop surface functionalization to target the species of interest.

This project will investigate the potential for core-shell magnetic-sorbent structures to be used in waste form separation, or removal of RNs from liquid streams. Particle development and characterisation will be carried out at Imperial and active sorption work at Loughborough.

- **Name: Ezra Feilden-Irving**

Project title: Additive Manufacturing of Ceramics and Composites.
Supervisors: Dr. Finn Giuliani, Prof. Eduardo Saiz and Dr. Luc Vandeperre.
Sponsor: CASC Industrial Consortium.

Additive manufacturing is reasonably well established for the production of conventional ceramic parts with complex geometries, but little attention has been given to more exotic ceramics and ceramic composites. It is highly desirable to print a number of these materials, as many of their applications require short production runs of small batches of parts. In the present work we use a 3D printing technique known as robocasting, which consists of continuous extrusion of pastes, to print a range of ceramic materials, ceramic matrix composites, and polymer matrix composite parts. The shear forces in the nozzle during printing can be tuned to give highly textured microstructures when the paste consists of anisotropic particles (such as short fibres, platelets), which heavily effect the strength, toughness and other mechanical properties of the materials. These have been measured using a new in-situ SEM DCB method, and compared to conventionally produced material.

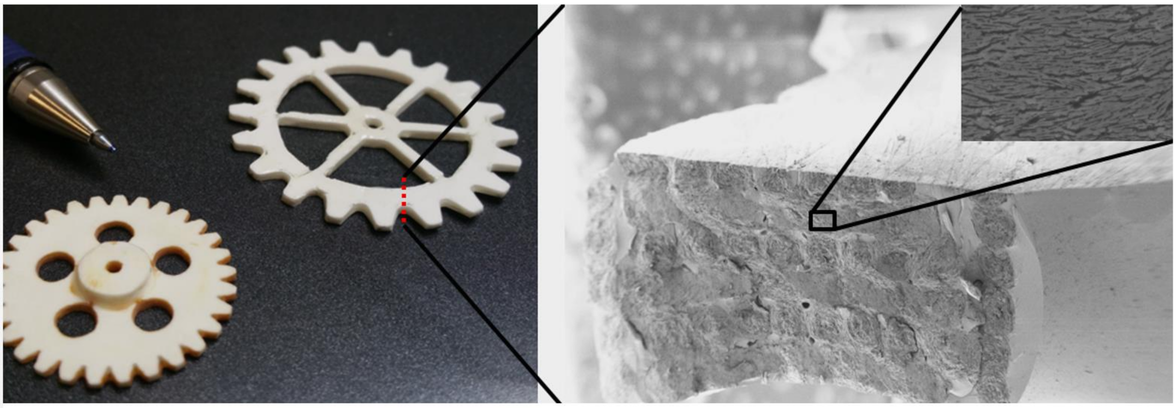


Figure 1. *A pair of ceramic composite parts produced by robocasting, consisting of a network of highly aligned* Al_2O_3 *platelets infiltrated with epoxy.*

- **Name: Claudio Ferraro**
  Project title: Bio-Inspired Ceramic/Metal Composites.
  Supervisor: Prof Eduardo Saiz.
  Sponsor: FP7.

The progress of a wide range of strategic fields from aerospace, construction, transportation or medicine depends on our ability to develop new light weight composites with outstanding mechanical properties. In this respect, natural materials such as bone, silk or nacre offer clear examples of how enhanced mechanical performance can be reached in low density materials through structural manipulation. Much attention has been paid to the idea of applying the design principles observed in nature to the fabrication of synthetic composites. One of the common design features in natural composites seems to be the use of layered and brick-and-mortar structures in which stiff layers or bricks are joined by thin soft interlayers. An interesting possibility is the replication of these designs using technical ceramics as the stiff phase and metallic alloys as the mortar. However, the challenge still remains on how to effectively translate natural principles to synthetic metal-ceramic materials and how to develop effective fabrication technologies to implement them in practical dimensions.

In this project we have used a combination of freeze-casting and reactive presureless infiltration to fabricate layered alumina/Al_4Mg composites. By using ceramic particles with different aspect ratios it is possible to manipulate the layer thickness at the microscopic scale between few microns up to 50 µm and to control the structure of the ceramic layer (grain size and porosity). The resulting composites are lightweight, strong and tough. We have characterized their mechanical response as a function of their architecture. The composites can exhibit high flexural strengths and initiation fracture toughness (up to 800 MPa and 16 MPa.$m^{1/2}$). More interestingly, these materials exhibit several toughening mechanisms that result in a unique R-curve behaviour with fracture resistance values that can reach up 100 MPa.$m^{1/2}$. Crack propagation has been investigated with different techniques (optical microscope, in-situ SEM and x-ray tomography) to analyse the key toughening mechanisms. The observations have served to identify the role of phenomena such as crack propagation or bridging and to propose strategies to enhance their contribution. We also investigated the best approaches towards the characterization of the mechanical response of this kind of bio-inspired materials.

- **Name: Claudia Gasparinni**
  Project title: Oxidation of Carbides for Fast Breeder Fuel.
  Supervisors: Prof. Bill Lee and Dr. Luc Vandeperre.
  Sponsor: EPSRC DISTINCTIVE Consortium/NDA/NNL.

Oxidation of ZrC and UC was investigated via experiments on ZrC hot pressed specimens and on depleted UC pellets and fragments in a furnace and with an in situ technique: High Temperature Environmental Scanning Electron Microscopy (HT-ESEM).

The Maltese cross shape of the oxide formed during ZrC oxidation was investigated with HT-ESEM experiments at 1073 K in 200 Pa O_2 atmosphere. Its formation mechanism is found to be comprised of three steps: edges delamination, crack formation at corners and crack propagation towards the inner core with formation of microcracks parallel to the interface. Microcracks are formed due to debonding of the interface which occurs when the oxide reaches approximately 20 µm thick. High Resolution TEM revealed the oxide/carbide interface to be comprised of a 2 µm thick amorphous carbon matrix with nanocrystals of ZrO_2 embedded in it.

The influence of temperature on the oxidation mechanism of UC was investigated with fragments oxidised in air in a furnace and in a HT-ESEM in an oxygen atmosphere from 673 – 1173 K. Oxide morphology, conversion and specific surface area (SSA) were significantly affected by temperature, e.g. oxidation at 873 K gave a product with greater SSA and conversion compared to higher temperature of oxidation. Samples oxidised at 873 K in the HT-ESEM showed instantaneous oxidation on the entire sample surface after insertion of oxygen, while samples oxidised at T > 873 K showed partial sintering of the oxide which acts as a diffusion barrier and limits the occurrence of oxidation of UO_2 to U_3O_8 to cracked surfaces.

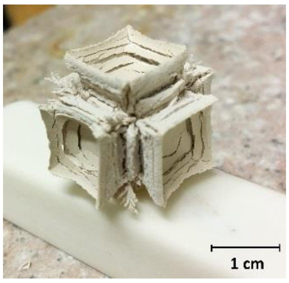


Figure 1. *Details of the Maltese cross shape of the oxide formed when a 1cm cube specimen of ZrC is oxidised in air at 1000°C for 4h.*

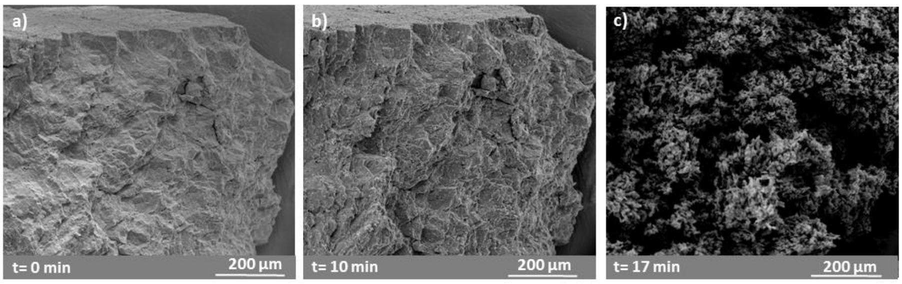


Figure 2. *a) SEI showing in situ oxidation of a UC fragment at 600 °C in 50 Pa O_2 atmosphere at t=0 min:, b) a) SEI showing in situ oxidation of a UC fragment at 600 °C in 50 Pa O_2 atmosphere at t=10 min: c) details of the typical popcorn like transformation due to oxidation from UO_2 to U_3O_8*

❖ **Name: Tommaso Giovannini**

Project title: Optimising Coating Design by Experimental Investigation and Microstructural Modelling Techniques.
Supervisors: Dr. Finn Giuliani and Dr. Daniel Balint.
Sponsor: SECO Tools.

Machining operations are an integral part of manufacturing chains for numerous different industries. The cutting tools which perform these machining operations are subject to extremely harsh operational environments due to the high thermal and mechanical loads they are subjected to. Cutting tools are composed of a bulk substrate material, usually a cemented carbide, which is covered by a thin (~10 µm) ceramic based coating used to improve both the toughness and the wear resistance of the tool.

Improving the mechanical response of these ceramic coatings is of crucial importance to improve overall cutting tool performance. These improvements depend of a thorough understanding of the microstructural mechanisms which govern their deformation. These include the dependence of the coatings mechanical properties on parameters such as temperature, coating thickness and grain structure as well as the quality of adhesion between the coating and the substrate and in between layers, in multilayer coatings. One aspect which is particularly relevant, and has received little attention, is the understanding of the effect that these properties have on the plastic deformation behaviour of the coatings. Through the use of experimental work and microstructural modelling techniques the project aims to obtain a thorough understanding of these mechanisms and how they affect overall coating response.

Having obtained this understanding the aim is then to propose coating design alterations aimed at improving overall coating performance.

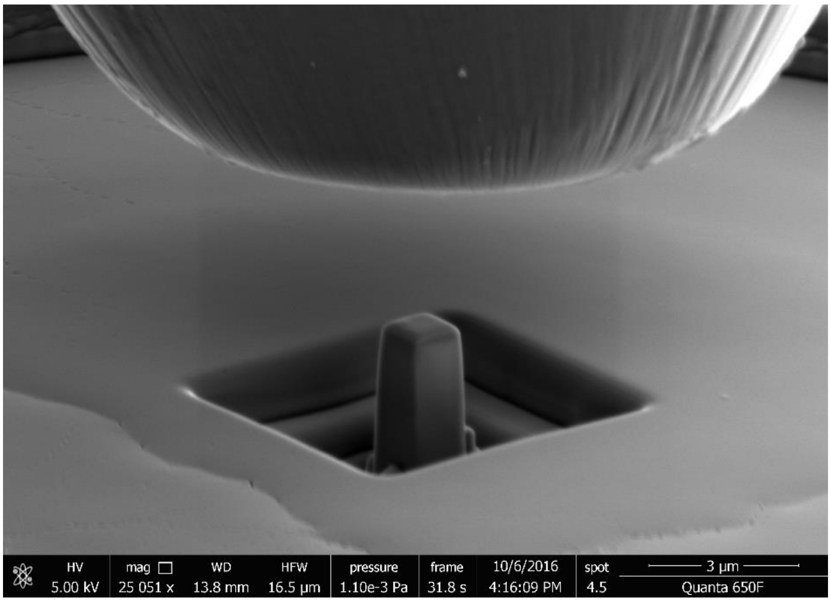


Figure 1. *Micropillar compression experiment performed on a single grain in a highly textured Al_2O_3 coating.*

- **Name: Yun-Hao Hsieh**

  Project title: Ceramic Wasteforms for Advanced Fuel Cycle Reprocessing.
  Supervisors: Prof. Bill Lee and Prof. T.D. Waite (UNSW, Sydney, Australia).
  Sponsor: The UNSW Tyree Scholarship.

Many advanced reprocessing technologies have been designed and developed to meet the future nuclear waste policies and further separate waste. One of the most promising advanced reprocessing methods, EURO-GANEX (Group Actinides Extraction), is nowadays being developed and aim to further separate both major (U, Pu) and minor (Np, Am, and Cm) actinides together from fission products. In that context, new advanced immobilization matrices capable of accommodating such modified waste streams have to be investigated[1, 2].

Synroc and borosilicate glass are potential wasteforms that have proven themselves to be efficient to immobilize high-level nuclear wastes (HLW) [3]. In this project, a new composition of Synroc, “Synroc-Z”, is designed and characterized. The primary modification is to reduce the amount of zirconolite phase, which acts as the main host for actinides.

Synroc-Z has been prepared via hot uniaxial pressing (HUP), with optimized process conditions to obtain dense samples. A well-known borosilicate glass, R7T7, was melt to compare with HUPed Synroc-Z. In both wasteforms, their durability via the MCC-1 test at 90^{o}C and microstructure after corrosion was tested.

The mass loss before and after leaching test for Synroc-Z was negligible (< 0.02%), while for the R7T7 glass it was relatively larger (>0.35%). Nano TiO_2

particles (~50 nm) were formed on the perovskite-rich surface. The thickness of TiO_2 skin was determined via AFM which was ~60 nm. In the leached sample, which were polished to 1 μm, it can be clearly observed that TiO_2 particles were assembled on the brighter contrast area while the TiO_2 particles were dispersed on the rougher (15 um polishing) Synroc-Z surface but dense on the edge of holes. The leached R7T7 glass formed Al, Zn and Si rich layer on the surface. The ratio of Al, Zn and Si of layer on the surface is ~1: 2: 4 while the composition of unleached R7T7 glass is ~2: 1: 18.

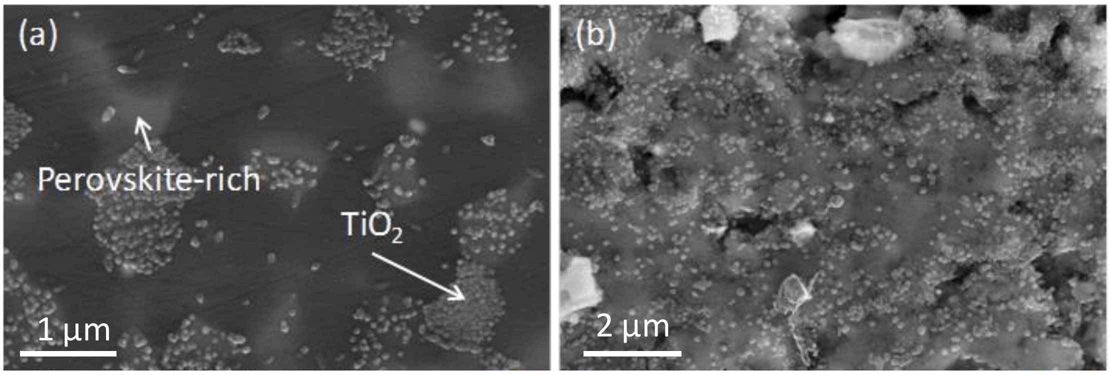


Figure 1. *SEM images of 20 wt.% waste loading HUPed Synroc-Z samples with (a) 1 μm and (b) 15 mm polishing finish. The TiO_2 particles compact on perovskite-rich regions. Samples with 15 μm polished shows dispersed TiO_2 skin but dense in some edges of holes.*

References:
1. *Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment* K. L. Nash and G. J. Lumetta, . Elsevier Science, (2011).
2. *Development of a New Flowsheet for Co-Separating the Transuranic Actinides: The "EURO-GANEX" Process*. M. Carrott, K. Bell, J. Brown, A. Geist, C. Gregson, X. Hères, C. Maher, R. Malmbeck, C. Mason, G. Modolo, U. Müllich, M. Sarsfield, A. Wilden, R. Taylor. Solvent Extraction and Ion Exchange, 32[5], p: 447-67, 2014.
3. *Radioactive waste forms for the future*. W. Lutze and R. C. Ewing. North-Holland, 1988.

- **Name: Charles Hutchison**

Project title: Glass Composite Materials for Radioactive Waste Immobilisation.
Supervisor: Prof. Bill Lee.
Sponsor: EPSRC and Sellafield.

This project examines Glass Composite Materials (GCMs), which may contain several crystal phases, as wasteforms for some of the Difficult Intermediate level Wastes from the Legacy Ponds and Furloes at Sellafield. The GCMs have been made by Plasma Vitrification and Joule Heated In-Container Vitrification (JHICV). Standard characterisation techniques such as XRD, SEM and EDX are being used to determine the phases in GCMs before and after leach studies, in varying conditions.

This will allow tracking of how crystalline components affect the durability and ultimately whether these GCMs can be safely disposed of.

- **Name: Jindaporn Juthapakdeeprasert**
  Project title: Development of Multifunctional Cement Kiln Refractory Coatings.
  Supervisor: Prof. Bill Lee.
  Sponsor: SCG Cement-Building Materials.

To produce OPC Clinker, cement industry has to consume a high amount of fuel; lignite, coal… each year. Approximately 10-15% of the energy is lost to the atmosphere through refractories and external surface. Developing a coating with low thermal conductivity could prevent the heat loss from the cement kiln. However, if the coating is to be used at a riser duct, cyclone, kiln lining and cooler of the cement kiln, other functions must also be taken into consideration. The coating must also have high mechanical, thermal and chemical stress resistance to be able to withstand high temperatures (>1500^{o}C), clinker dust abrasion and chemical corrosion of alkaline, sulphur or chloride gases. Therefore, this multifunction coating would not only reduce energy usage but also protect the refractories surface and decrease restoration coat and time which lead to an extraordinary cost saving.

- **Name: Alan Leong**
  Project title: Graphene Coatings for Pipelines.
  Supervisors: Prof. Eduardo Saiz and Dr. Cecilia Mattevi.
  Sponsor: Petronas, Malaysia.

Graphene is a 2D material with unique functional and mechanical properties, from tuneable electrical and optical response to high intrinsic stiffness and strength, chemical versatility, controllable permeability or extremely high specific surface area. It has the potential to revolutionize a wide range of technologies from batteries to composites and membranes. However, to achieve this goal we need to develop ways to integrate graphene into fabrication technologies and to develop approaches to synthesize large quantities of material tailored for specific applications.

Graphene is a very appealing reinforcing phase for polymer pipeline liners/coatings. The addition of graphene can provide controlled permeability, enhanced mechanical properties and even sensing capabilities. However, neither mechanical exfoliation nor chemical vapour deposition are amenable to the large-scale synthesis of graphene needed for this application. We will address this need by using chemically modified graphene (CMG) that can be fabricated in bulk quantities. CMG intrinsic surface area, permeability and mechanical properties are comparable to pristine graphene and combined with its unique chemical versatility it opens exciting possibilities for the development of novel composites.

- **Name: Wirat Lerdprom**
  Project title: Impact of Fast Firing on Phase Evolution in White-ware Ceramics.
  Supervisor: Prof Bill Lee.
  Sponsor: Cementhai Ceramics Co., Ltd, Thailand

Porcelains are clay based materials, used extensively in household, scientific and engineering applications, which are produced via viscous flow sintering. The sintering process of porcelains is not only to densify the green body, but also to induce mineralogical phase changes. Densification and phase evolution are influenced by sintering conditions i.e. heating rate, dwell time, atmosphere, and temperature.

New advanced sintering processes have been introduced aiming to improve product quality and energy usage efficiency such as conventional fast firing (CS), spark plasma sintering (SPS), flash sintering (FS) and microwave sintering (MWS), each of which has different process parameters.

The aim of this work is to investigate microstructural and physico-mechanical property changes (apparent bulk density, water absorption, Vickers hardness, and fracture toughness) in a porcelain body sintered using the 4 techniques and consider energy, financial and other aspects to determine which is most likely to find industrial application. The study involves investigation of mullitization, glass formation, and quartz dissolution from the different sintering techniques using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive spectroscopy (EDS). Finally, the ultimate goal of this work is to develop understanding of process parameters i.e. heating rate, pressure, atmosphere, electric field, and microwave radiation on mineralogical composition and densification in porcelains.

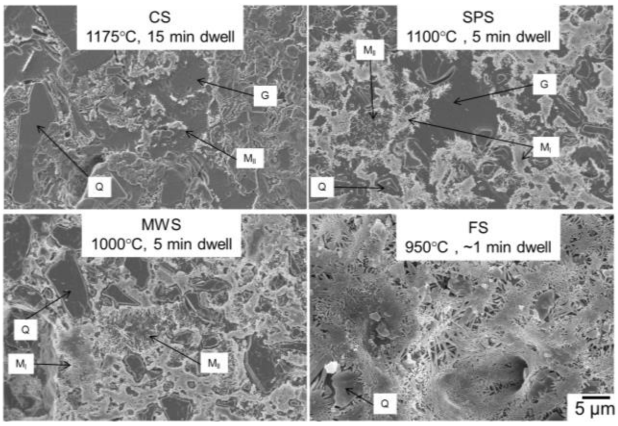


Figure 1. *SEM-SE images of conventional sintered (CS), spark plasma sintering (SPS), microwave sintering (MWS), and flash sintered (FS) porcelain samples; showing etched samples using 20% HF (MI=primary mullite, MII=secondary mullite, G=glass, and Q =Quartz).*

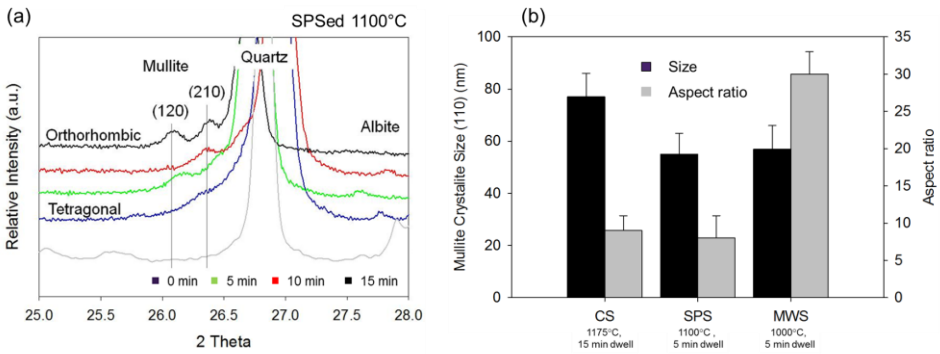


Figure 2. *(a) XRD patterns of the SPSed samples showing different mullite crystal structure as a function of dwell times, (b) mullite crystallite size and aspect ratio of the porcelains sintered using different techniques.*

- **Name: Annalisa Neri**
  Project title: Development of a Novel Wound Management Dressings.
  Supervisor: Prof. Eduardo Saiz.
  Sponsor: Welland Medical Ltd.

Wound management represents a challenging field, not only in research and product development but also in clinic, where patients present an array of wound types. In particular, infection is a common problem in wound healing: this can result in reduced healing rates, prolonged hospitalization time and increased care costs.

The focus of this study is to develop and characterise a novel dressing comprising collagen and honey which is able to actively promote healing while preventing infection in a variety of wound types.

Collagen presents several properties that are desirable for a wound dressing: strong biocompatibility, weak antigenicity, biodegradability and in addition it can terminate the chronic state of a wound. The honey component exhibits anti-inflammatory and anti-bacterial properties, while also allowing for manipulation of the wound pH. Herein the combination of collagen and honey is investigated for the design of a novel bioactive wound dressing film able to actively promote healing. This material is intended to adhere and conform to the wound site and to degrade in contact with wound exudate. The collagen-honey films produced (Fig. 1) are being characterised in terms of chemical homogeneity, degradation rate, mechanical properties, antibacterial activity and cells response.

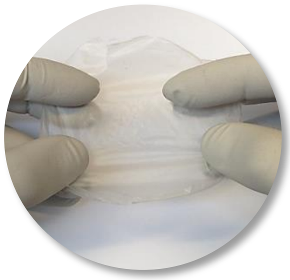


Figure 1. *Collagen-honey based films*

- **Name: Kristijonas Plausinaitis**
  Project title: Adsorption of Heavy Metals and Radionuclides on Cement Phases.
  Supervisors: Dr. Luc Vandeperre and Prof. Mary Ryan.
  Sponsor: Amec Foster Wheeler.

Lead (Pb) is one of the constituents in intermediate level radioactive waste. Due to its high toxicity, it is of particular importance to understand the behaviour of soluble Pb ions, in particular their sorption on and migration within the cement backfill, one of the main proposed engineering barriers for geological waste disposal.

Of particular interest for understanding the long term safety of these engineered barriers is how the evolving cement matrix may affect efficacy of capture of mobile species by sorption and /or precipitation processes.

In this work, batch sorption analysis of Pb on to hydrated Nirex Vault Reference Backfill (NVRB) cement powder indicates a Langmuir like process: a linear uptake followed by a plateau due to saturation at increasing concentrations. Leaching experiments were also carried out and suggested that the sorption process is reversible.

The homogeneity of surface interaction was analysed using spatially resolved chemical analysis. In particular we have used scanning electron microscopy (SEM), energy dispersive X – ray spectroscopy (EDS) and secondary ion mass spectrometry (SIMS) to provide information on surface concentrations. These data indicated that the uptake of Pb is relatively homogenous across the cement surface with no sites with much higher concentration observed. This suggests that lead is primarily uptaken into the calcium silicate hydrate (C – S – H) gel since this is the most abundant phase in the cement. In addition localized and unique crystal clusters were also observed on samples exposed to higher concentrations of Pb in solution.

The results indicate that a number of previous studies where the Pb was introduced during cement hydration and where Pb was found not to be released significantly are misleading from a geological waste repository perspective where the Pb will only come in contact with the cement after hydration is completed.

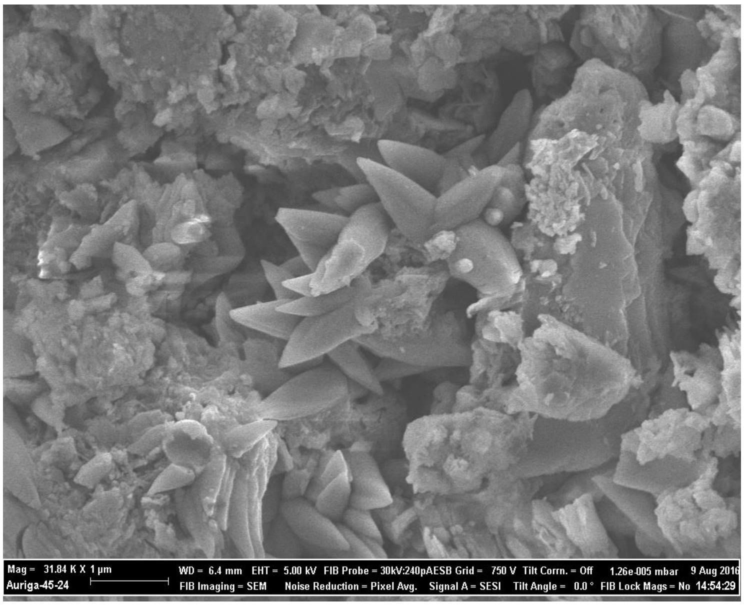


Figure 1. *SEM figure displaying unique crystal cluster formed on the NVRB cement sample exposed to Pb.*

- **Name: Dimitri Pletser**
  Project title: Low Temperature Immobilisation of Spent Adsorbents from Fukushima.
  Supervisors: Prof. Bill Lee and Dr. Luc Vandeperre.
  Sponsor: Hitachi Ltd.

The clean-up of the Fukushima Daiichi site continues to generate large volumes of spent adsorbents which need to be disposed of permanently. One of the candidates is a low temperature immobilisation process to avoid volatilising radioactive Cs and Sr species. Detailed radionuclide volatilisation experiments were performed at Hitachi Research Laboratories in Japan, to investigate possible Cs volatilisation behaviour from commercial zeolitic adsorbents. Cs volatilisation was shown to be negligible, in most cases below detection limits, at temperatures below 600ºC, with volatilisation starting at 700 ºC and strongly increasing above 800ºC.

To minimise Cs loss in the final waste treatment an immobilisation process with a maximum temperature of 600ºC was developed by sintering model waste with glass frit to form a dense Glass Composite Material (GCM) wasteform. A zeolitic model wasteform, chabazite, was loaded with between 8-12 wt % Cs waste loading and was sintered with two lead-based glass compositions, lead borosilicate (PBS) and a lead borate (PB) glass composition, at a maximum temperature of 600ºC.

Full encapsulation of the zeolitic model wasteform was achieved for waste loadings up to 50 wt.% in PBS and 40 wt.% in PB in all cases, with both GCM systems showing dense microstructures. PBS GCM formation was successful at a maximum of 500ºC, while the PB GCM formation was shown to be possible at a maximum temperature of 400ºC. Sintering optimisation undertaken has shown that the microstructure of the final wasteform can be finely tuned by controlling composition, sintering profiles and thermal treatment regimes. Sintering behaviour was shown to be independent of Cs waste loading of the adsorbent, but was shown to be strongly influenced by thermal treatment of the wasteform during sintering.

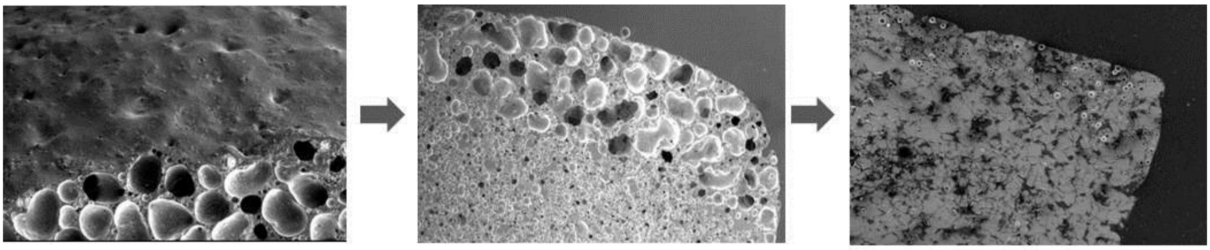


Figure 1. *Cross-sectional SEM images of PBS wasteforms. Show the progressive densification of three generations of wasteforms with increasingly optimised sintering profiles*

- **Name: Giorgio Sernicola**

Project title: Understanding the Role of Interfaces and Local Residual Stresses on the Failure of Polycrystalline Metal-Ceramic Composites.
Supervisors: Dr. Finn Giuliani and Dr. T. Ben Britton.
Sponsor: Element Six.

Opening ceramics up to a wider range of applications needs for us to understand and improve their fracture properties. This will enable increased exploitation of ceramics in applications such as space, deep well drilling and other extreme environments, where their high temperature stability, high hardness and high strength are required.

In the last three decades, improvements in fracture performance have been achieved through the developing of new understanding of the toughening mechanisms, typically involving microstructure control that focuses on crack deflection at grain boundaries and interfaces. Typically these improvements are difficult to engineer, as changing microstructural processing (e.g. through heat treatment / chemistry or powder processing) does not result in a one-to-one correlation with performance, as the influence of microstructure on crack path is varied and complex. We wish therefore to use and improve on recent developments of characterisation at the micro-scale to improve our understanding of performance at the macro-scale.

To investigate the fracture properties of individual features (i.e. individual crystallographic planes, individual grain boundaries or interfaces), we have developed an innovative fracture testing method. This approach is based on the double cantilever wedging to measure the fracture energy evolution with crack length during stable fracture and was successfully applied at the micro-scale inside a SEM (Fig. 1). This method enables direct view of the crack growth in our sample and direct measurement of the energy absorbed during fracture, without use of load-displacement data. This is afforded through the generation of a new stable geometry test, combined with an in-situ testing and image based analysis strategy that affords direct correlation of stable opening of a crack with the energy released in the test sample.

In addition to these precise tests, we have targeted characterisation at understanding how microstructure influences crack paths in polycrystalline metal-ceramic composites. Our focus has been on using high angular resolution EBDS combined with microindentation, to focus on how the local gradient of residual stresses (Fig. 2) due to thermal expansion mismatches change during an indentation based fracture test.

Exploitation of these novel techniques allows us to gather new insights on the mechanical properties of advanced ceramics that can usher in a new way of engineering the microstructure to obtain tougher ceramics.

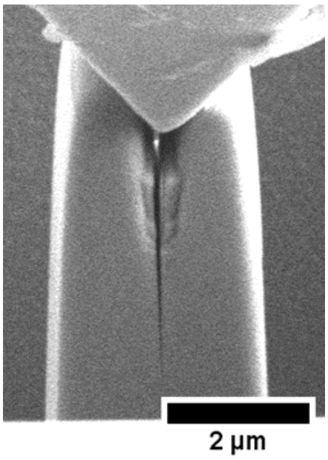


Figure 1. *In situ wedging of a DCB of SiC*

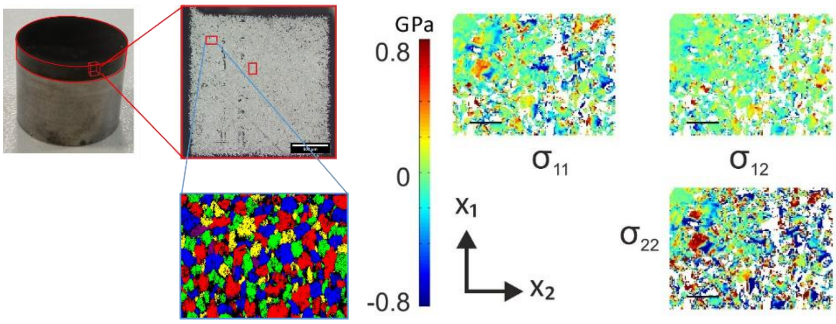


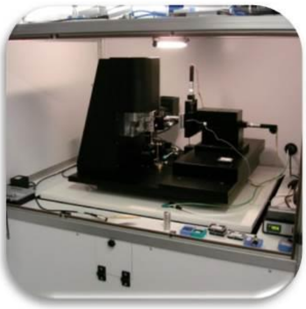
Figure 2. *In plane stress gradient maps measured via HR-EBSD on a polycrystalline diamond sample*

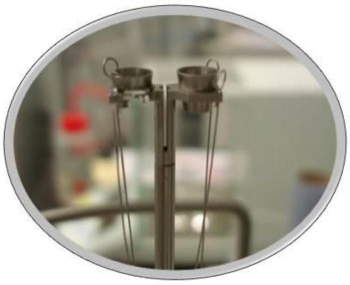
- **Name: Jia Hui Teo**

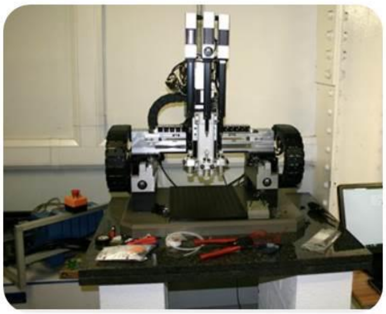
  Project title: Designing Ceramic Matrix Composites for Ceramic Armour.
  Supervisors: Dr. Luc Vandeperre and Prof. Eduardo Saiz.
  Sponsor: DSO National Laboratories.

Ceramics are hard materials, which makes them ideal for armour but their brittleness and weakness in tension is detrimental to performance. It is generally understood that impedance mismatches are bad for any armour systems as they are points of reflection, generating tensile stress waves which should be avoided. In this work, varying microstructures will be created using materials with different impedances to understand the reflection of waves at such interfaces on the microstructural level. Consequently, a better understanding of how the microstructures can be tailored to create materials that are able to reflect compressive waves progressively across the entire thickness instead of generating a large tensile wave at the rear end of the ceramic which will likely cause the ceramic to shatter. Delaying the failure of the ceramic gives it more time to defeat the ceramic, allowing sustained projectile erosion which could help improve the ballistic performance of the ceramic.

CAPABILITIES AND FACILITIES



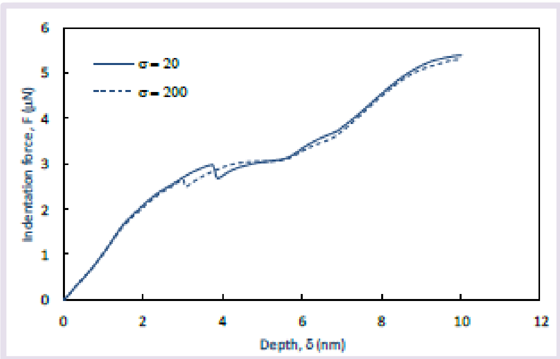




Although the purchasing and installation of large items of equipment by the Centre from the original CASC project is now completed, we continue to improve our experimental capability in this area using funds from other sources.

All equipment is available to the UK ceramics community. Here you will find a list of some of the equipment that we have, and if you wish to use any of these facilities, or have any question, please contact Garry Stakalls (g.stakalls@imperial.ac.uk, 020 7594 6770) or Alba Matas Adams (a.matas-adams@imperial.ac.uk, 020 7594 2053).

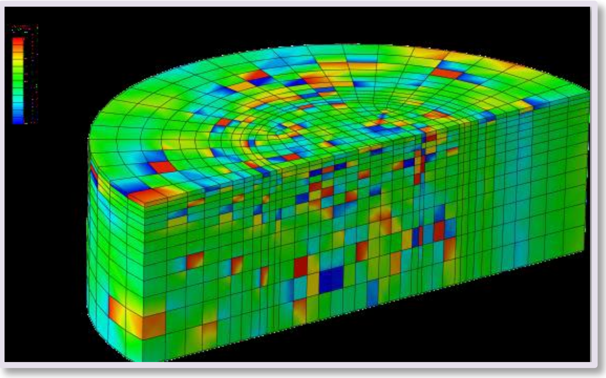
Nano-indenter



The high temperature nano-indenter manufactured by Micro Materials is located in the Structural Ceramics laboratory, on the ground floor of the Royal School of Mines (RSM), taking advantage of the better control of air temperature and the reduced vibration levels.

As well as being fully instrumented, the nano-indenter operates at temperatures up to 750^{o}C. Usage of the nano-indenter is high, and results obtained have been reported at international meetings including the Third International Workshop on Mechanical Behaviour of Systems at Small Length Scales (Kerela, India), the Fall MRS conference (Boston), the American Ceramics Society meeting (Daytona Beach) and at the ICMCTF (San Diego).

Server



CASC's multiprocessor server allows solving complex and node rich finite element simulations such as a crystal plasticity simulation including soft and hard slip systems in MgO. Three dimensional crystal plasticity simulations are being carried out using parallel processing on the CASC cluster. It has been used to simulate the relation between primary and secondary slip systems activation and hysteresis, and the softening observed in the indentation force displacement response. A normal random distribution of the critical resolved shear stress results in a lower 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.

Freezer 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 of eliminating solvents by keeping the material structure intact for further processing like sintering.

We currently use this process for drying freeze-cast materials like alumina, zirconia, zeolites and graphene oxide.

Thermodynamic software

We purchased the FactSage version 6.1 from GIT Technologies, together with three substance databases.

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

Thermal analysis

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

The equipment comprises:

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

Crucibles of the high temperature combined TGA DTA

Netzsch have provided multiple training sessions, and all three items of the equipment are up and running.

The facility is heavily used and starting to attract external users.

The **dilatometer** has two set-ups:

1. An alumina tube and pushrod for measurements up to 1600°C.
2. A graphite set-up for measurements up to 2400°C.

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 are the measurement of the thermal expansion of refractory materials to estimate the risk of thermal shock damage, the characterisation of a wide range of ultra-high temperature ceramics, the study of mullite sintering and the analysis of residual stresses in mullite zirconia composites, hardness measurements of ZrB_2 and Al_2O_3 and the analysis of cracking due to shrinkage in geopolymers and sintering of silicon carbide-boron carbide composites.

Measurements for industrial partners such as Rolls Royce have also been carried out.

Induction-heated thermo-mechanical test rig

The **combined TGA-DTA** has been used to quantify mass loss during drying of geopolymers, to analyse the decomposition of magnesium phosphate and magnesium silicate cements for nuclear waste treatment, to study silicon carbide or mullite sintering, to perform analysis of UHTC oxidation, to determine carbon yield from various ceramic additives and for characterisation of raw materials in general. Usage for third parties included work with Professor Jon Binnner (Birmingham University), Loughborough University and Dr Bai Cui (University of Illinois), as well as characterisation of derivative products from commercial paper mills and work with Morgan Technical Ceramics.

The equipment to measure **thermal diffusivity via laser flash** has been extensively used to characterise a wide range of ultra-high temperature ceramics and carbon-ceramic composites as well as in collaborations with Rolls Royce, Morgan Technical Ceramics and Professor Mike Reece at Queen Mary College (thermo-electric materials).

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^{o}C, the second frame has induction heating up to 1200^{o}C.

The equipment is used in work with diverse industrial partners such as Seco Tools AB (Sweden). In the last years, it has been used for a range of projects including measuring the properties of commercial cutting tools near the service temperature, studying mullite creep, and measuring high temperature strength of UHTCS's and commercial refractories.

Vacuum hot press

The vacuum hot press from FCT Systems is fully operational.

The press operates at temperatures up to 2400^{o}C for sintering and 2100^{o}C for hot pressing with a maximum force of 250 KN at atmospheric pressure or under vacuum. We can use dies with diameters as large as 8 cm allowing for the fabrication of large samples.

Its use in CASC projects includes the preparation of a wide range of materials such as silicon carbide, boron carbide and composites, aluminium nitride alloys, zirconium carbide, tantalum and hafnium carbide, joining of UHTC's, glass ceramic-SiC composites, ultra-light SiC structures and mullite.


Vacuum hot press

Its unique high-temperature capability has enabled the fabrication of 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.

It is also used by other university groups to perform tests on forging of functional ceramics for Professor Alford (Imperial College London) and for treatment of UHTC precursors for Professor Binner (Loughborough University).

Vacuum furnace

The vacuum furnace from Thermal Technology is fully operational. The furnace is capable of heating a volume of 5 cm in diameter and 15 cm tall to temperatures up to 2500^{o}C under vacuum or under a mixture of gasses.

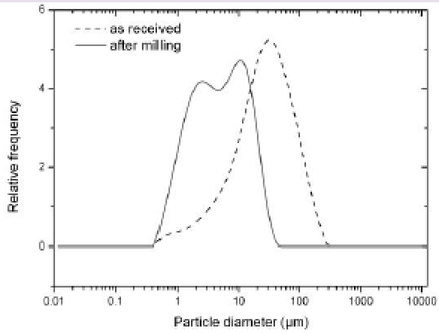
Opposed viewing ports allow observation of the sample during heating, and a sample elevator and cooling chamber allows for exchange of samples whilst the furnace is at temperature. The equipment has been used in the sintering of ceramics and metal-ceramic composites as well as for the analysis of glass and metal wetting on ceramic substrates.

Wet grinding mills

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

Particle Size Analyser

The Department provided funds to acquire a laser particle size analyser. The equipment is able to determine size distribution using scattering of light by particles in dilute solutions and has the ability to measure particles with diameters ranging from 10^{-2} to 10^{-4} μm without changing any optics.



Examples of powder particles = distributions

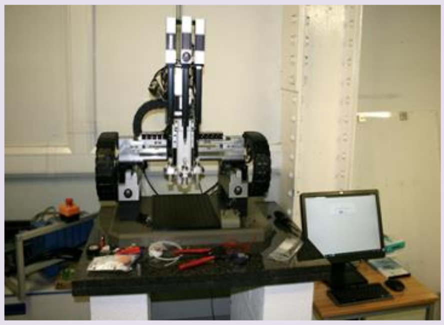
High Temperature elastic properties by impulse excitation


Figure Set-up for room temperature measurements.

In 2013 we installed a piece of equipment to determine the Young and shear modulus as well as the Poisson ratio of different materials. The measurement principle is based on the relationship between shape, density and stiffness and the natural vibration frequencies of a sample.
For example, to determine the Young modulus, typically a bending vibration mode is excited by hitting a sample supported on the nodes of the vibration with a small projectile in the centre. The resulting vibration is picked up with a microphone and analysis of this signal using the Fourier transformation yields the frequency of the vibration.
The software also analyses the decay in amplitude of the vibration with time to determine a value for the damping of the vibration.

The model installed at CASC comes with a furnace capable of operating to 1750°C in air or inert atmosphere. Hardware and software enables fully automated excitation and measurement, making it possible to investigate the variation of the elastic properties with temperature, the hopping of oxygen vacancies bound to dopants in response to stress at low temperature in doped zirconia, and the softening of grain boundary glassy phases in sintered silicon nitride.

3D Printer



Another important piece of equipment at CASC is a robotic assisted deposition system from 3D Inks (USA). This system can print 3D structures using continues extrusion, with submicron reach submicron-printing precision. The printer allows the combination of three different inks to fabricate multiphase structures.

Optical Microscope Axio Scope A1

Optical microscope with reflected and transmitted light, bright and dark field, DIC, camera and software for image acquisition and analysis was also installed in 2013.
The microscope has a modular design that facilitates the installation for different set-ups to allow *in-situ* experiments like mechanical testing or freezing of colloids.

Rapid prototype (CNC) milling machine

Rapid prototyping is the dramatically transformation of the design and manufacturing processes and this milling machine has answered the call for a cost-effective, high precision and compact solution.

It is used to create realistic models, functional prototypes and moulds and is compatible with a wide range of materials. It is able to produce highly accurate parts including those for complex snap-fits from an extensive range of non-proprietary materials including Acetal, ABS, chemical woods, acrylic, plaster, nylon, styrene and many medical grade materials including PEEK.

It offers a number of significant advantages over additive rapid prototyping (ARP) or "3D orienting" systems, making a combination of the two technologies the perfect prototyping solution.

Elemental Mass Gas Analyser

An Oxygen-nitrogen-hydrogen Elemental Mass Gas Analyser (Horiba, EMGA – 830 series) was installed at CASC in 2015.
This includes Carbon-sulphur Elemental Mass Induction Analyser (EMIA series) and a Glow Discharge-Optical Emission Spectroscopy (GD-OES) setup.

Graphene reactor

A one of a kind modular system for large-scale synthesis of chemically modified graphene based on chemical graphite exfoliation is in use. This system is flexible and allows for “on demand” fabrication of materials with tailored properties.

The rig consists of two jacketed glass reactors of up to 5L mounted on a bench standing framework (*Radleys, Essex, UK*). Overhead stirrers (*Heidolph*) with PTFE propeller stirring paddles placed at different heights ensured vigorous mixing in the reactors. Oil in jackets is connected to a *Huber Unistat* recirculating chiller.

The manipulation of liquids (e.g. addition of concentrated acids or transfer of slurry between vessels) is carried out using a software controlled peristaltic pump with acid resistant tubing (Marprene).

AVA software allows for online control of the temperature in the jacket oil or the reacting mixture, mas addition and stirring. The component parts of the system are a computer controlled reactor system with two chambers to perform the chemical exfoliation of graphite at controlled temperature, stirring speed… and a purification system based on centrifugation at controlled temperature.

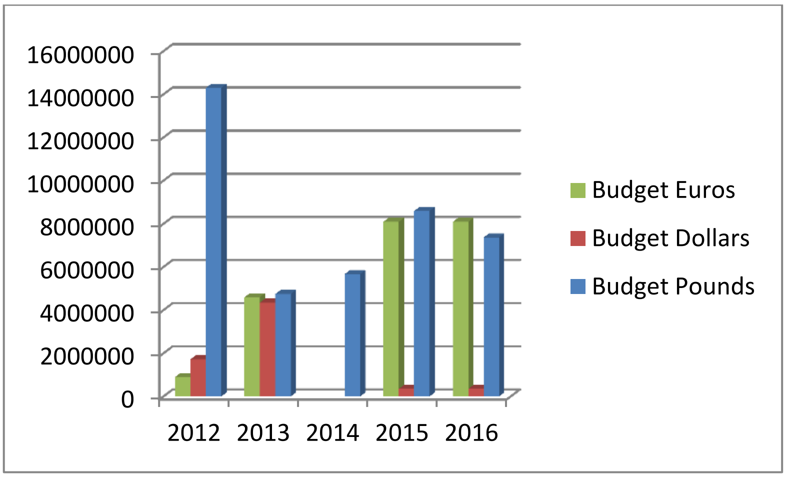
This unique modular approach allows us the flexibility to synthesize materials on demand for different applications.

Other equipment

Other equipment like a new polishing machine and a glove box were installed.

An additional set up has been installed with the TG/DTA analyser to measure the specific heat capacity. This is a high accuracy rhodium furnace and the temperature can go up to 1450^{o}C.

CASC RESEARCH PORTFOLIO



Funded proposals, in different currencies, over the last 5 years

Current Projects (Jan-Dec: 2016)

- **Understanding and Designing Materials Systems for Extreme Environments.**
  Funder: Engineering and Physical Science Research Council (EPSRC).
  Project start date: 2013.
  Budget (£): 2,600,000.

- **Engineering with Graphene for Multi-Functional Coatings and Fibre-Composites.**
  Funder: Engineering and Physical Science Research Council (EPSRC).
  Project start date: 1st of February 2013.
  Budget (£): 286,893.

- **Graphene-Three Dimensional Networks.**
  Funder: Engineering and Physical Science Research Council (EPSRC).
  Project start date: 1st of February 2013.
  Budget (£): 1,257,620.

- **Wound Care Materials.**
  Funder: Welland Medical.
  Project start date: 1st of April 2014.
  Budget (£): 41,766.

- **Graphene-Based Composites for Pipeline Liners.**
  Funder: Petronas Research Sdn Bhd.
  Project start date: 1st of June 2014.
  Budget (£): 479,863.

- **Carbides for Future Fission Environments (CAFFE).**
  Funder: Engineering and Physical Science Research Council (EPSRC).
  Project start date: 1st of July 2015.
  Budget (£): 603,917.

- **Bio-inspired Self-Healing Materials Based on Ceramic- Polyurethane Hybrid Composites.**
  Funder: DARPA-USA.
  Project start date: August 2015.
  Budget ($): 348,069.

- **RESLAG: Turning Waste from Steel Industry into Valuable Low Cost Feedstock for Energy Intensive Industry.**
  Funder: European Commission.
  Project start date: 1st of September 2015.
  Budget (€): 8,092,712.

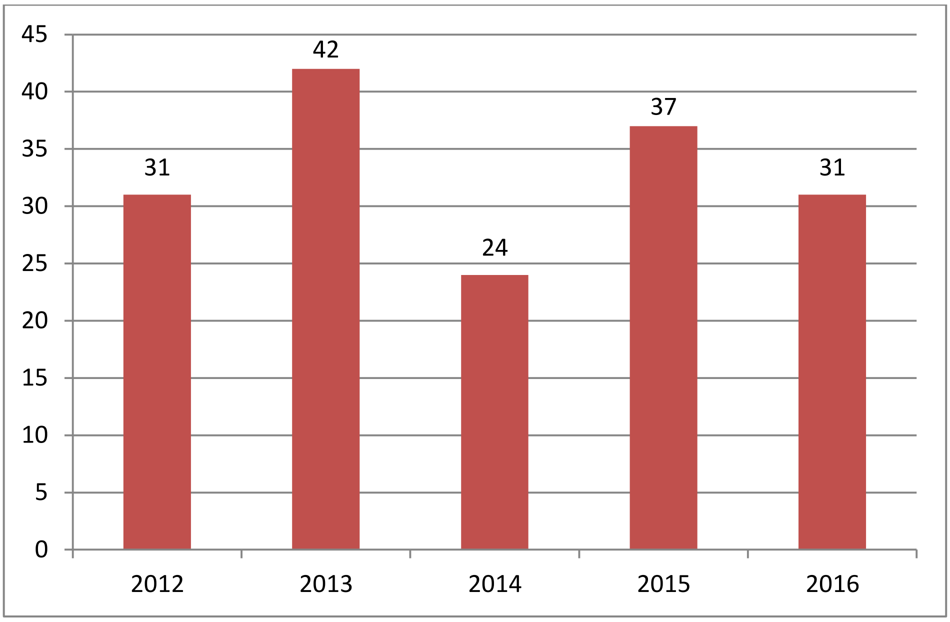
- **Advanced Waste Management Strategies for High Dose Spent Adsorbents.**
  Funder: Engineering and Physical Science Research Council (EPSRC)
  Project start date: 30th of November 2015.
  Budget (£): 191,687.

- **High Emissivity Coatings for Furnace Linings.**
  Funder: SCG Thailand.
  Project start date: 2015.
  Budget (£): 497,381.

- **Mechanical Properties of CMC's.**
  Funder: Rolls Royce.
  Project start date: 2016.
  Budget (£): 150,000.

- **Ceramic Armour from Rice Husk Ash.**
  Funder: DSTL.
  Project start date: 2016.
  Budget (£): 260,000.

- **Transpiration Cooling Systems for Jet Engine Turbines and Hypersonic Flight.**
  Funder: Engineering and Physical Science Research Council (EPSRC).
  Project start date: 18th of August 2016.
  Budget (£): 1,000,000.



CASC's number of publications over the last 5 years

Publications: Journal Papers (Jan-Dec: 2016)

1. *Processing and properties of ZrC, ZrN and ZrCN ceramics: a review*. R.W.Harrison, W.E.Lee. Advances in Applied Ceramics, **115**, p: 294-307, 2016.
2. *Synthesis and Oxidation Testing of MAX Phase Composites in the Cr–Ti–Al–C Quaternary System*. D. Horlait, S. Grasso, N. Al-Nasiri, P. A. Burr, W. E. Lee. Journal of the American Ceramic Society, **99** (2), p: 682-690, 2016.
3. *Thermal Properties of Rare-Earth Monosilicates for EBC on Si-Based Ceramic Composites*. N.Al Nasiri, N. Patra, D. Horlait, D. D. Jayaseelan, W. E Lee. Journal of the American Ceramic Society, **99**(2), p: 589-596, 2016.
4. *Low-temperature solution synthesis of nanosized hafnium carbide using pectin*. N. Patra, N. Al-Nasiri, D. D. Jayaseelan, W. E. Lee. Ceramics International, **42** (1), p: 1959-1963, 2016.
5. *Effect of Sodium on Microstructures and Thermoelastic Properties of Calcium Aluminate Cement–Bonded Refractories*. J. Alex, L. Vandeperre, W. E..Lee, B. Touzo, C. Parr. Journal of the American Ceramic Society, **99** (3), p: 1079-1085, 2016.
6. *Synthesis and DFT investigation of new bismuth-containing MAX phases*. D.Horlait, S. C. Middleburgh, A. Chroneos, W. E. Lee. Scientific Report, **6**:18829, 2016.
7. *Diffusion-based and creep continuum damage modelling of crack formation during high temperature oxidation of ZrN ceramics*. M. Pettinà, R.W. Harrison, L. J. Vandeperre, F. R. Biglari, P. Brown, W. E. Lee, K. Nikbin. Journal of the European Ceramic Society, **36**(9), p: 2341-2349, 2016.
8. *Tungsten carbide is more oxidation resistant than tungsten when processed to full density*. S. A. Humphry-Baker, W. E. Lee. Scripta Materiala, **116**, p: 67-70, 2016.

9. *Attempts to synthesise quaternary MAX phases $(Zr,M)_2AlC$ and $Zr_2(Al,A)C$ as a way to approach Zr_2AlC.* D. Horlait, S. Grasso, A. Chroneos, W. E. Lee. Materials Research Letters, **4**, p: 137-144, 2016.
10. *Light and Strong SiC Networks*. C. Ferraro, E. Garcia-Tunon, V.G. Rocha , S. Barg , M.D. Fariñas, T.E.G. Alvarez-Arenas , G.Sernicola , F.Giuliani , and E. Saiz. Advanced Functional Materials, **26**, p: 1636-1645, 2016.
11. *Sintering behaviour, solid solution formation and characterisation of TaC, HfC and TaC–HfC fabricated by spark plasma sintering*. O. Cedillos-Barraza, S.Grasso, N. Al Nasiri, D. D. Jayaseelan, M. J. Reece, W. E. Lee. Journal of the European Ceramic Society, **36** (7), p: 1539-1548, 2016.
12. *Using coupled micropillar compression and micro-Laue diffraction to investigate deformation mechanisms in a complex metallic alloy $Al1_3Co_4$*. A.Bhowmik, I.P. Dolbnya, T. B.Britton, N. G. Jones, G. Sernicola, C. Walter, P. Gille, D. Dye, W.J. Clegg and F. Giuliani. Applied Physics. Letters, **108**, p: 111902, 2016.
13. *Synthesis, characterization and use of synthesized fine zirconium diboride as an additive for densification of commercial zirconium diboride powder*. N. Patra, N. Al Nasiri, D. D. Jayaseelan, W.E. Lee. Ceramics International, **42**, (8), p: 9565-9570, 2016.
14. *Using graphene oxide as a sacrificial support of polyoxotitanium clusters to replicate its two-dimensionality on pure titania photocatalysts*. S.Eslava, A. Reynal, V.G. Rocha, S. Barg and E. Saiz. Journal of Materials. Chemistry. A, **4**, p: 7200-7206, 2016.
15. *Robocasting of structural ceramic parts with hydrogel inks*. E.Feilden, E. Garcia-Tunon, F. Giuliani, E.Saiz, L.J.Vandeperre. Journal of the European Ceramic Society, **36**, p: 2525-2533, 2016.
16. *Grain bridging locations of monolithic silicon carbide by means of focused ion beam milling technique*. N. Al Nasiri, E. Saiz, F. Giuliani and L.J. Vandeperre. Materials Letters, **173**, p: 214-218, 2016.
17. *Autonomous self-healing structural composites with bio-inspired design*.E. D'Elia, S. Eslava, M.Miranda, T.K. Georgiou, E. Saiz. *Scientific Reports* **6**:25059, 2016.
18. *Synthesis and Characterization of an Alumina Forming Nanolaminated Boride: MoAlB.* S. Kota, E. Zapata-Solvas, A. Ly, J. Lu, O. Elkassabany, A. Huon, W. E. Lee, L. Hultman, S. J. May, M. W. Barsoum. Scientific Reports, **6**:26475, 2016.
19. *Control of drying shrinkage in magnesium silicate hydrate (m-s-h) gel mortars*. T. Zhang, X. Liang, C. Li, M. Lorin, Y. Li, L.J. Vandeperre, C. R. Cheeseman. Cement and Concrete Research, **88**, p: 36–42, 2016.
20. *The effect of prior cold work on the chloride stress corrosion cracking of 304L austenitic stainless steel under atmospheric conditions*.G.G. Scatigno, M.P. Ryan, F. Giuliani, M.R. Wenman. Materials Science and Engineering:A, **668**, p:20-29, 2016.
21. *Ultra-stiff large-area carpets of carbon nanotubes*. S. S. Meysami, P. Dallas, J. Britton, J.G. Lozano, A.T. Murdock, C. Ferraro, E. Saiz, N. Rijnveld, P. Holdway, K. Porfyrakis and N. Grobert. Nanoscale, **8**, p: 11993-12001, 2016.

22. *DFT Predictions of Crystal Structure, Electronic Structure, Compressibility, and Elastic Properties of Hf–Al–C Carbides*.Y. Bai, A. Duff, D. D. Jayaseelan, R.Wang, X. He, W. E. Lee. Journal of the American Ceramic Society, **99** (10), p: 3449-3547, 2016.
23. *Oxidation behaviour of SiC/SiC ceramic matrix composites in air*. N. Al-Nasiri, N. Patra, N. Ni, D. D. Jayaseelan,W. E. Lee. Journal of the European Ceramic Society, **36**(14), p: 3293-3302, 2016.
24. *Complex ceramic architectures by directed assembly of 'responsive' particles*. E.García-Tunon, G.C. Machado ,M.Schneider, S. Barg, R.V. Bell, E. Saiz, Journal of the European Ceramic Society, **37**, p:199-211, 2017.
25. *Porcelain production by direct sintering*. W. Lerdprom, R.K. Chinnam, D.D. Jayaseelan, W.E. Lee. Journal of the European Ceramic Society, **36**(16),p: 4319-4325, 2016.
26. *High Heat Flux Laser Testing of HfB_2 Cylinders*. L. Larrimbe, M. Pettina, K. Nikbin, E. L Jones, A.P. Katz, C.J. Hawkins, J. DeCerbo, P. Brown, L.J. Vandeperre. Journal of the American Ceramic Society, p :1-9, 2016.
27. *Experimental and DFT investigation of $(Cr,Ti)_3AlC_2$ MAX phases stability*. P. A. Burr, D. Horlait, W. E. Lee. Materials Research Letters,p: 1-14, 2016.
28. *Role of sodium hexametaphosphate in MgO/SiO_2 cement pastes.* Y. Jia, B.Wang, Z. Wu, J. Han, T. Zhang, L. J. Vandeperre, C.R. Cheeseman. Cement and Concrete Research, **89**, p: 63–71, 2016.
29. *Temperature dependence of electrical conductivity of a green porcelain mixture*. W.Lerdprom, C.Li, D.D.Jayaseelan, S.J.Skinner, W.E. Lee. Journal of the European Ceramic Society, **37** (1), 343-349, 2017.

In Press

1. Investigating the highest melting temperature materials: A laser melting study of the TaC-HfC system O. Cedillos-Baraza, D. Manara,K. Boboridis, T. Watkins, S. Grasso, D.D. Jayaseelan, R. Konings, MJ. Reece, W.E. Lee. Scientific Reports (accepted Oct 2016).
2. Zirconium Carbide Oxidation: Maltese Cross Formation and Interface Characterisation. C.Gasparinni, R. Podor, D. Horlait, W.E.Lee. Oxidation of Metals (just accepted).

OUTREACH

Newsletters

The CASC's newsletters, together with the annual report, provides news and contact information for visitors to the Centre and for dissemination at meetings and international visits.

Two newsletter were circulated in 2016 (May and December), covering additional CASC research, visitors to the Centre, PhD thesis defences, the sixth CASC Industry Day, the Sir Richard Brook Prize and the seventh summer school, as well as prizes for different CASC members. (http://www.imperial.ac.uk/media/imperial-college/research-centres-and-groups/centre-for-advanced-structural-ceramics/Newsletter-9-for-CASC-2016.pdf and http://www.imperial.ac.uk/media/imperial-college/research-centres-and-groups/centre-for-advanced-structural-ceramics/Newsletter-10-for-CASC-2016.pdf).

Website

The website (http://www.imperial.ac.uk/structural-ceramics/) contains details of CASC staff, visitors, equipment and activities.

Meeting organised by CASC, as well as future UK and international ceramic-related meetings are also advertised on this website.

Previous annual reports and other publicity material are available for downloading.

The website is continually being updated with new information about CASC staff and their research activities and presentations.

Sir 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 Advanced Materials.

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.

The 2015 prize was won by Dr. Sneha Rhode form Imperial College London.The title of her thesis is *"Atomic structure of dislocation cores in III nitride films"* and was supervised by Dr. Shelly Moram.
The award in general covers a certificate, plaque and £1000 cheque.

CASC Industry Day

The sixth CASC Industry Day was held on the 22nd of January 2016 at Imperial College with attendees from industry and university (Morgan Advanced Materials, John Crane, CoorsTek, Kerneos and Queen Mary University).
The industry day was followed with the Steering Group meeting in the afternoon.
The aim is to continue CASC activities and strengthen our relationship to industry.

CASC Industry Day 22 January 2016
Programme

58 Prince's Gate | South Kensington Campus | London SW7 2PG
Imperial College London
10:00 am – 2:00 pm
Imperial College London

10:00 – 10:15	**Coffee**
10:15 – 10:30	**CASC – Industrial Consortium** **Introduction** - ***Professor Eduardo Saiz***
10:30 – 12:50	**Research in progress & Technical capabilities** ***Laura Larrimbe, ICL*** - High heat flux testing of HfB_2 cylinders ***Finn Giuliani, ICL*** - Developments in silicon doped boron carbide ***Carl Zetterström, Kerneos, France*** - Engineering permeable microstructures in refractory castables to facilitate drying ***Doni Daniel, ICL*** - High Emissivity Coating to Improve Thermal Efficiency of Steam Cracking Furnaces ***Na Ni, ICL*** - Degradation of LSCF Solid Oxide Fuel Cell Cathodes at the Nanometre Scale ***Gil Machado, ICL*** - Assembly of calcium phosphate scaffolds using responsive particles for additive manufacturing. ***Ezra Feilden-Irving, ICL*** - 3D Printing of Ceramic Composites
1:00 – 2:00	**Lunch**

CASC Summer School on Ceramics

The 7th edition of the Ceramic Summer School was held on 14, 15 and 16th of September 2016 at Imperial College London.

It brought together a range of attendees and speakers from Industry and academia. Highlights included talks on processing from: Dr Adam Stevenson (St-Gobain), Dr Victoria Garcia Rocha (Cardiff University) and Dr. Martin Schwentenwein (Lithoz GmbH) while Dr Florian Bouville (ETH Zurich) gave an excellent talk on mechanical properties.

The exact date and programme of the next edition will be published early in 2017 after input from our industrial consortium.

CASC Seminars

The following seminars were arranged in CASC during 2016.

- Title: Graphene-Based Materials for Energy Storage
  Speaker: Dr. Cristina Botas, CIC energiGUNE.
  Date: 20th of May, 2016.

- Title: Bio-Inspired Refractory
  Speaker: Dr Pedro Ivo Batistel Galiote Pelissari, ETH Zurich.
  Date: 27th of May, 2016.