10th International Workshop on Interfaces Design for Performance

Santiago de Compostela, Spain, 4-7 September, 2022

Find the locations of interest

Hotel Peregrino EXE
(Registration desk/ Reception Cocktail)

IMATUS (Conference Hall)

Cafetería Matemáticas (Lunches)

R. Don Quijote (Conference Dinner)

Organising committee

Dr Victoria García Rocha
Instituto de Ciencia y Tecnología del Carbono, INCAR
Consejo Superior de Investigaciones Científicas, CSIC, Spain

Prof Eduardo Saiz
Centre for Advanced Structural Ceramics
Imperial College London, UK

Dr. Jaime Franco
CIFP Politécnico de Santiago, U
Xunta de Galicia, Spain

Dr Iuliia Tirichenko
Centre for Advanced Structural Ceramics
Imperial College London, UK

Prof Francisco Guitian
Instituto de Materiales
Universidade de Santiago de Compostela, Spain

Prof Finn Giulilani
Centre for Advanced Structural Ceramics
Imperial College London, UK

Dr. Florian Bouville
Centre for Advanced Structural Ceramics
Imperial College London, UK

CONFERENCE VENUE:

Instituto de Materiales de Galicia– IMATUS
(Avenida do Mestre Mateo, 25, 15706 Santiago de Compostela)

SOCIAL EVENTS:

Sunday 4th, 19:30h - An informal WELCOME RECEPTION will be held at Hotel Exe Peregrino (Av. de Rosalía de Castro, S/N, 15706 Santiago de Compostela)

Wednesday 7th, 20:30h - The WORKSHOP DINNER will be held at Restaurante Don Quijote (Rúa das Galeras, 20, Santiago de Compostela, 15705).

Sunday 4th

7:30 pm-Welcome Reception at Hotel Exe Peregrino

Monday 5th

9:00	**Prof. Carmen Alvarez** **Registration and Welcome** Instituto de Ciencia de Materiales (IMATUS)
9:30	**Prof. Christina Scheu** Max-Planck-Institut für Eisenforschung, Germany Unravelling secrets of interfaces in renewable energy application
10:00	**Dr. Ainara Aguadero** Instituto de Ciencia de Materiales de Madrid, CSIC, Spain Importance of Interfaces in Enabling Fast Charging Solid State Batteries
10:30	**Student poster presentations**
11:00	**Break**
11:45	**Prof. Andreas Mortensen** EPFL, Switzerland Dynamic wetting in pressure infiltration
12:15	**Dr. Esther Garcia-Tuñón** University of Liverpool, UK New insights on complex fluids for 3d printing using large amplitude oscillatory shear (LAOS) tests and Fourier transform rheology
12:45	**Lunch**
14:15	**Dr. Florian Bouville** Imperial College of London, UK Processing-structure-property relationships in nacre-inspired ceramics
14:45	**Prof. Diletta Giuntini** TU/e Netherlands Nano- and microstructuring ceramics for macroscale performance
15:15	**Break**
15:45	**Prof. Raul Bermejo** Montanuniversität Leoben, Austria The role of interfaces on the fracture behavior of textured layered ceramics
16:15	**Prof. Finn Giuliani** Imperial College of London, UK Small scale stable fracture of interfaces and grain boundaries
16:45	**Break**
17:15	**Dr. Katharina Marquardt** Imperial College of London, UK Grain- boundary energy variation and evolution during dislocation-assisted grain- boundary sliding in polycrystaline Mg_2SiO_4 – linking Earth and Materials sciences
17:45	**Prof. Roger French** Case Western Reserve University, USA Transformative Applications of Materials Data Science: Spatiotemporal Studies and Convolutional and Graph Neural Network Learning To Solve Materials Challenges

Tuesday 6th

9:30	**Prof. Suelen Barg** University of Augsburg, Germany Building 3D Architectures and Devices from 2D Materials
10:00	**Prof. Sylvain Meille** INSA Lyon, France Bulk nacre-like ceramics: a simple processing approach and related properties
10:30	**Student poster presentations**
11:00	**Break**
11:45	**Prof. Greg Rohrer** Carnegie Mellon University, USA Examination of the driving force for grain boundary migration in polycrystals
12:15	**Prof. Richard Todd** Oxford University, UK On the role of interfaces in ultra-rapid densification of ceramics
12:45	**Lunch**
14:15	**Dr. Laura Silvestroni** CNR-ISTEC, Italy Functionally Graded Ultra-high Temperature Ceramics: From Thermo-elastic Numerical Analysis To Damage Tolerant Composites
14:45	**Prof. Hortense Le Ferrand** Nanyang University, Singapore Local microstructure designs to tailor the properties of platelet-reinforced composites
15:15	**Break**
15:45	**Prof. Alex Porter** Imperial College of London, UK Imaging Interactions between Airborne Pollution Particles and Human Cells
16:15	**Dr. Laura Maggini** Universität Wien, Austria Manufacturing of Polymer-based “Colourfunctional” Electrochromic Displays
16:45	**Break**
17:15	**Prof. David Kisalius** University of California, Irvine, USA Biological Blueprints Towards Next Generation Advanced Materials
17:45	**Prof. Pablo Zavattieri** Purdue University, USA Harnessing the emergent behavior of architected materials: bioinspiration and beyond

Wednesday 7th

10:00	**Dr. Dominique Chatain** CINaM, CNRS, France Hetero-epitaxial relationships and atomic structure at Ag/Ni interfaces
10:30	**Prof. Gerhard Dehm** Max-Planck-Institut für Eisenforschung, Germany New insights on the atomic grain boundary structure in pure and alloyed Cu and Fe
11:00	**Break**
11:45	**Prof. Joaquin Ramirez Rico** Universidad de Sevilla, Spain Biomass and wood derived materials for structural and energy applications
12:15	**Prof. Vikran Jayaram** Indian Institute of Science, India Rapid mechanical evaluation of materials using small scale bending in conjunction with in-situ strain measurements
12:45	**Lunch**
14:15	**Dr. Oriol Gavalda** University of Nottingham, UK Brittle fracture at the nanoscale
14:45	**Dr. Jon Molina-Aldareguia** IMDEA Materiales, Spain Fracture behavior of metal-ceramic and metal-metal nanolaminates
15:15	**Break**
15:45	**Dr. Barbara Putz** Montanuniversität Leoben, Austria Designing interfaces via atomic and molecular layer deposition
16:15	**Dr. Wolfgang Reinheimer** Forschungszentrum Jülich, Germany Novel high heating rate sintering methods for ceramics: From fundamentals to economic potential
16:45	**Break**
17:15	**Dr. Alan Porporati** CeramTec, Germany Ceramics in Dental Implantology: Past, Present and Future
20:30	**Workshop dinner/Restaurante Don Quijote**

Poster Presentations

Monday 5th

Pluronic®/casein mixed nanomicelles that solubilize resveratrol and preserve its antioxidant activity
Carmen Alvarez-Lorenzo, Universidad de Santiago de Compostela

3D printing of magnetically aligned composites within enhanced properties
Lizhi Guan, Nanyang Technological University, Singapore

Quantifying local fracture toughness in nacre-like ceramics
Victoria Vilchez, Imperial College London, UK

Digital Light Processing of Carbides
Ollie Osborn, Imperial College London, UK

Additive manufacturing of thermoset polymer matrix composites with shape memory capabilities
Yinglun Hong, Imperial College London, UK

A strategy for improved prediction of freeze-cast microstructures
Katie Lewthwaite, University of Manchester, UK

Tuesday 6th

Robocasting of quasicrystalline ZnO structures
Naïma Saadi, University of Liverpool, UK

Direct and indirect routes to design fluorescent pH branched copolymer surfactants
Francesca Miricola, University of Liverpool, UK

Photocatalytic $SrTiO_3$ structures with hierarchical porosity via DIW of 'smart' formulations
Emma Jones, University of Liverpool, UK

Nickel-iron nanoparticles supported on graphene oxide aerogels by freeze-casting
Miriam López, Institute of Carbon Science and Technology, Spain

Influence of iron on the activity of nickel catalysts supported on graphene for water splitting reactions
María González-Ingelmo, Institute of Carbon Science and Technology, Spain

Design and fabrication of a low-cost printer head for extrusion of pastes by direct ink writing
Pablo Rodríguez-Lagar, Institute of Carbon Science and Technology, Spain

Talk Abstracts

Unravelling secrets of interfaces in renewable energy application

Prof. Christina Scheu

Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

As global warming is a threat for human society, measures have to be taken to minimize it. Promising solutions include harvesting of solar energy to produce green hydrogen by light induced water splitting which is used in fuel cells or to generate electricity with solar cells. In this regard, thermoelectric devices can also contribute to the renewable energy sector as they convert waste heat into electricity. In all of these functional materials interfaces play an important role and they can have a positive or detrimental effect on the properties. For example, in Si solar cells, impurities at heterophase interfaces can act as recombination centre reducing the efficiency of the solar module [1]. In thermoelectric materials phonons can be scattered at interfaces reducing the thermal conductivity which is a beneficial effect. On the other hand, charge carriers can be scattered which decrease the electrical conductivity, an unwanted effect as it lowers efficiency in thermoelectric devices [2,3].

A great challenge is to unravel both, the atomic arrangement as well as the chemical composition at the interfaces with highest spatial resolution and sensitivity. In our work, we correlate aberration corrected scanning transmission electron microscopy (STEM) with atom probe tomography (APT) to overcome the limits of both techniques. We apply the methodology at identical location either by directly doing the STEM measurement at the APT needle or by taking lift-outs by a focused ion beam in adjacent regions. This allowed us to detect trace impurities at facetted grain boundaries in Si [1] explaining the lower performance. Furthermore, we unravelled the structure and composition of low angle grain boundaries in AgSbTe [2] and PbTe [3] thermoelectrics material. For the AgSbTe [2] the grain boundary consists of a network of planar faults, while in PbTe they are composed of a dense network of dislocation. In both cases, segregation occurred which positively affected the efficiency. These examples will be discussed in-depth during the presentation.

[1] C. Liebscher, A. Stoffers, M. Alam, L. Lymperakis, O. Cojocaru-Miredin, B. Gault, J. Neugebauer, G. Dehm, C. Scheu, and D. Raabe Phys. Rev. Materials 2, (023804) (2018)
[2] L Abdellaoui, S Zhang, S Zaefferer, R Bueno-Villoro, A Baranovskiy, O Cojocaru-Mirédin, Y Yu, Y Amouyal, D Raabe, GJ Snyder and C Scheu, Acta Materialia, 178 (2019), 135.
[3] L Abdellaoui, Z Chen, Y Yu, T Luo, R Hanus, T Schwarz, R Bueno, O Cojocaru-Mirédin, GJ Snyder, D Raabe, Y Pei, C Scheu and S Zhang, Advanced Functional Materials, 31 (2021), 2101214.
[4] The author would like to acknowledge all colleagues who have contributed to the work.

Importance of Interfaces in Enabling Fast Charging Solid State Batteries

E. Querel[1], I. Seymour[1], R. Brugge[1], A. Cavallaro[1], N. Nabi[1], F. Pesci[1] and *Dr. A. Aguadero*[1,2]

1. Department of Materials, Imperial College London, SW7 2AZ, London UK
2. Instituto de Ciencia de Materiales de Madrid, CSIC, 28049, Cantoblanco, Spain *
Corresponding author: ainara.aguadero@csic.es; a.aguadero@imperial.ac.uk

Key words: Interfaces; solid state batteries; alkaline metal; solid electrolytes

The need to develop safer batteries with enhanced energy densities is promoting the development of non-flammable solid electrolytes and their integration with alkali metal negative electrodes. A major challenge is the optimization of the dynamic metal/solid electrolyte interfaces that lead to premature cell degradation specially at high current densities. Whereas some of these problems can be solved by the application of high pressures or temperatures during operation, the integration of these systems requires optimization of performance in unpressurised systems at room temperature. Two of the best solid state alkaline-ion conductors are derivatives of $Li_7La_3Zr_2O_{12}$ Garnet-type structures for Li and $Na_3Zr_2Si_2PO_{12}$ NaSICON type structures for Na able to reach values of $15\text{-}10^{-1}$ mS/cm at RT. In this work, we focus on the study of Na/NaSICON and Li/Garnet interfaces paying particular attention to the effect that surface chemistry has on the charge transfer resistance and stability under high current densities. The study brings a combination of surface sensitive techniques including secondary ion mass spectrometry, low energy ion scattering and x-ray photoelectron spectroscopy with electrochemical and computational analysis. We prove that the surface chemistry of solid electrolytes has a dominant role on the design of stable, high-performance metal/solid electrolyte interfaces and that the tuning of the surface chemistry is a powerful tool to improve the performance of these devices at high current densities.

Dynamic wetting in pressure infiltration

G. Schneider, L. Weber, *Prof. A. Mortensen*

Laboratory of Mechanical Metallurgy, Institute of Materials, Ecole Polytechnique Fédérale de Lausanne, EPFL Station 12, 1015 Lausanne, Switzerland

Interesting parallels, first pointed out by J. Gil Sevillano, L. Kubin and coworkers, exists between dislocational plasticity and pressure infiltration: the dependence of plastic strain or infiltrant saturation, respectively, is studied as a function of two main governing parameters, namely stress (the applied pressure in infiltration) and temperature, while both processes are governed by the force-driven motion of lines (dislocations or solid/liquid/vapour triple lines respectively) through a random 3D energy landscape.

An important question that has motivated the build-up of a vast body of knowledge in plasticity is the influence exerted by thermally activated phenomena on the link between stress, temperature and strain rate. We build here on approaches developed in plasticity to explore the physics of pressure infiltration in the presence of thermally activated phenomena that are known, from sessile drop data, to impart a time-dependence to wetting, and hence to infiltration. Specifically, we address the influence of interfacial reaction, by means of experiments with Cu-46 at.pct.Si infiltrating carbon preforms, and the influence of solid phase solution/reprecipitation, with the infiltration of alumina by aluminium well above the melting point of aluminium.

We use an apparatus, designed and built in our laboratory, that measures saturation curves (defined as plots of the infiltrated fraction pore space versus the driving pressure), at high temperature (≈1300°C) and under high pressures (≈150 atmospheres), those being conditions relevant to the processing of metal matrix composite materials. We conduct experiments in which the infiltration pressure is held constant and then abruptly changed; the parallel in plasticity is stress-jump creep testing. We show that, in the presence of thermally activated interfacial phenomena, flow of the metal under fixed applied pressure does not cease completely, but rather tends towards a low and relatively constant velocity. We measure this velocity, to find that at given temperature it is a dual function of pressure and saturation. Drawing on the similarity that exists between those experiments and stress-jump creep tests, we show that one can propose a similar physical description of the coupling between thermal activation, pressure and the rate of infiltration. In particular we show that the rate of steady-state metal ingress driven by thermally activated triple line phenomena depends not only on the infiltration temperature but also on the driving pressure, in a way that in both systems can be described by an activation volume on the order of 100 nm^3.

New insights on complex fluids for 3d printing using large amplitude oscillatory shear (LAOS) tests and Fourier transform rheology

Dr. Esther Garcia-Tuñon[1,2],* Bin Ling[1,2] and David J C Dennis[2]

1. Materials Innovation Factory,

2. School of Engineering, University of Liverpool, The Quadrangle, L69 3GH Liverpool, UK
Corresponding author: egarciat@liverpool.ac.uk

Within the wider umbrella of Additive Manufacturing or 3D printing techniques, direct ink writing (DIW) is an expanding multi-disciplinary research field with a growing number of applications, from 2D materials such as graphene-based materials and MXNEs for energy devices, to self-healing polymers and gels for tissue engineering. DIW requires the careful design of soft solids containing advanced materials. They must be carefully formulated to obtain a shear thinning yield stress fluid. These complex fluids must: 1) flow through narrow nozzles; 2) be able to recover their original structure in very short timescales; and 3) retain the designed shape upon deposition. We have previously proposed 'printability' protocols using continuous shear and oscillatory rheology[1] for graphene oxide (GO) suspensions and gels, and we have also demonstrated how GO can be used as formulation base for different materials.[2]

In this talk I will present the latest findings in our complex fluids research. We have expanded and deepened our protocols and developed new tools to quantify differences between printable formulations (with different additives, active materials and therefore microstructure) using large amplitude oscillatory shear (LAOS). We have applied an existing mathematical framework[3] to a library of conductive formulations using Pluronic F127 and GO combined with different active materials (such as graphite and carbon nanotubes).[4] Using raw data collection (monitoring strain, stress and time) and developing our own MATLAB code, FT rheology has enable us to identify and quantify non-linearities that are unique for each formulation. 3D Lissajous plots help us to show and compare their fingerprints visually and qualitatively. Using these tools, we can objectively and quantitatively identify the 'yielding' region for each formulation, from the onset of non-linearities to bulk flow, which is directly related with their printability. Our analysis provides new insights on yield stress fluids for DIW that can be expanded to many other applications, such as drilling fluids, gels, emulsions, and colloidal formulations.

[1] Corker, A., et al., *3D printing with 2D colloids: designing rheology protocols to predict 'printability'of soft-materials.* Soft Matter, 2019. 15(6): p. 1444-1456.
[2] Garcia-Tunon, E., et al., *Graphene oxide: an all-in-one processing additive for 3D printing.* ACS applied materials & interfaces, 2017. 9(38): p. 32977-32989.
[3] Ewoldt, R.H., A. Hosoi, and G.H. McKinley, *New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear.* Journal of Rheology, 2008. 52(6): p. 1427-1458.
[4] Corker, A., *Formulation and Rheology of Carbon-based Materials for Printing of Conductive Three-dimensional Structures*. Thesis. Department of Mechanical, Materials and Aerospace Engineering. 2022, University of Liverpool.

Processing-structure-property relationships in nacre-inspired ceramics

Dr. Florian Bouville

Centre for Advanced Structural Ceramics, Imperial College London, UK

Composites with intricate microstructures are ubiquitous in the natural world where they fulfil the specific functional demands imposed by the environment. For instance, nacre presents a fracture toughness 40 times higher than its main constituent, a crystalline form of calcium carbonate. This relative increase in toughness value is obtained as a crack propagating within this natural brick-and-mortar structure have to interact with the multiple reinforcing mechanisms present from the nanometre to the millimetre scale. The boost in performance obtained has pushed scientists in the last few decades to use nacre as a blueprint to increase the toughness of synthetic ceramics and composites. More recently, our ability to reproduce accurately the structure of nacre from the nanometre to the millimetre scale has improved with the introduction of Magnetically-Assisted Slip Casting (M.A.S.C.), a technique that combines an aqueous-based slip casting process with magnetically-directed anisotropic particle assembly. Using this approach and pressure-assisted sintering, we are now able to carefully study several structure-property relationships in these composites, from the amount and strength of the added nanobridges, the toughness of the polymeric, metallic, or ceramic mortar used, to finally the large-scale orientation of the bricks. Using these results, we can fine tune the structural properties of nacre-inspired alumina-based composites to reach strengths up to 670 MPa, K_{IC} up to 6 MPa.$m^{1/2}$ with subsequent stable crack propagation and this even at temperature up to 1200°C. Now, pushing these materials further will only be possible with a deeper understanding of the complex fracture behaviour that includes deflection and branching. Our most recent study focuses on exactly that, using a combination of fracture mechanics and FEM to access the stress intensity factors at the tips of multiple cracks and link these with the change in microstructure.

Nano- and microstructuring ceramics for macroscale performance

Cong Yan[1], Alexander Plunkett[2], Büsra Bor[2], Berta Domènech[2], Gerold Schneider[2],

Prof. Diletta Giuntini[1,2]

1. Eindhoven University of Technology, Eindhoven, Netherlands
2. Hamburg University of Technology, Hamburg, Germany

The great potential of engineering materials at the nano- and microscale to foster emergent properties at the macroscale is particularly relevant for ceramics and ceramic-based composites. A remarkable example is found in the field of biomimetics, in which researchers have been drawing lessons from naturally occurring highly mineralized materials to design toughened ceramics via hierarchical structuring. Multiscale material design is also key to preserving nanoscale-characteristic behaviors up to human-scale components. Fabrication of such materials is however a tricky task. Control of the arrangement of nano- and micro- building blocks requires finely tuned self-assembly procedures and careful compositional design, whilst interfaces between components largely control the macroscale material response. This talk will address these aspects with a focus on ceramic-organic nanocomposites with multiple levels of hierarchy, underlining strategies to foster both enhanced mechanical behavior and a unique combination of electromagnetic and thermal properties for energy applications.

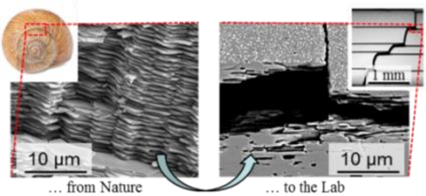
The role of interfaces on the fracture behavior of textured layered ceramics

Prof. Raul Bermejo

Chair of Structural and Functional Ceramics, Department of Materials Science, Montanuniversität Leoben, Austria.

Keywords: Layered ceramics; Residual stresses; Textured microstructure; Crack arrest; Damage tolerance; Fracture mechanics, Contact Damage, Micro-mechanics.

Embedding textured alumina layers has been established as a novel design strategy to enhance the fracture resistance in ceramic laminates designed with "strong interfaces". It has been demonstrated that tuning the location of "protective" layers within a ceramic multilayer architecture can increase its fracture resistance by five times (from 3.5 to 17 MPam$^{1/2}$) relative to constituent bulk ceramic layers, while retaining high strength (~500 MPa) [1]. The use of tailored residual stresses in embedded layers can act as an effective barrier to the propagation of cracks from surface flaws (e.g. under bending, contact or thermal shock loading), providing the material with a minimum design strength, below which no failure occurs. Moreover, by orienting (texturing) the grain structure, similar to the organized microstructure found in natural systems such as nacre, crack propagation can be controlled within the textured ceramic layers [2]. In this work, the role of interfaces on the fracture resistance will be discussed, covering aspects from the macro- to microscopic scale. In this regard, recent findings on the fracture resistance of grain boundaries between textured grains [3] shed light on understanding the fracture process of textured layered ceramics, which should be explored in light of novel processing techniques such as additive manufacturing [4].



[1] R. Bermejo, "Towards seashells under stress: bio-inspired concepts to design tough and reliable ceramic components", *J. Eur. Ceram. Soc.* (2017). https://doi.org/10.1016/j.jeurceramsoc.2017.04.041.
[2] G.L. Messing, S.F. Poterala, Y.F. Chang, T. Frueh, E.R Kupp, B.H. Watson, R.L. Walton, M.J. Brova, A.-K. Hofer, R. Bermejo, R.J. Jr. Meyer, "Texture-engineered ceramics – Property enhancements through crystallographic tailoring", *J. Mater. Res.* (2017). https://doi.org/10.1557/jmr.2017.207.
[3] J. Schlacher, T. Csanádi, M. Vojtko, R. Papšík, R. Bermejo, "Micro-scale fracture toughness of textured alumina ceramics", *J. Eur. Ceram. Soc.* (2022). https://doi.org/10.1016/j.jeurceramsoc.2022.06.028.
[4] A.-K. Hofer, I. Kraleva, R. Bermejo, "Additive manufacturing of highly textured alumina ceramics", *Open Ceramics* (2021). https://doi.org/10.1016/j.oceram.2021.100085.

Small scale stable fracture of interfaces and grain boundaries

Prof. Finn Giuliani

Imperial College London, London, United Kingdom

The fracture toughness of ceramics is often dominated by the structure of their grain boundaries. Our capacity to improve the performance of ceramic components depends on our ability to investigate the properties of individual grain boundaries. To measure the fracture energy of individual interfaces we have used a double cantilever geometry to obtain stable crack growth and we calculate the fracture energy under a constant wedging displacement. This approach has been validated on SiC where it gives a good approximation of the surface energy and then extended to SiC bi-crystals along with Ni-Al_2O_3 interfaces where crack blunting and bridging mechanism can be observed and measured. Finally, this has been applied to WC-Co with and without additions of Cr. Here we show how to identify specific boundaries for testing and how the distribution of low angle grain boundaries can be correlated with the measured fracture energies.

Grain-boundary energy variation and evolution during dislocation-assisted grain-boundary sliding in polycrystaline Mg_2SiO_4 – linking Earth and Materials sciences

Dr. Katharina Marquardt[1*], Alexandra Austin[1], Marina Sedlak[1], Louise Rossett[1], Filippe Ferreira[2], Lars Hansen[3], Sanae Koizumi[4]

1. Department of Materials, Imperial College London, London, U.K.
Institute für Geowissenschaften, Universität Heidelberg, Heidelberg, Germany
2. Department of Earth and Environmental Sciences, University of Minnesota, Minneapolis, MN, USA
3. Earthquake Research Institute (ERI) Tokyo, University of Tokyo, Tokyo, Japan

Forsterite, the Mg-endmember of the olivine solid solution, is a refractory material of interest for high-temperature engineering applications and well-studied in relation to its abundance in Earth's upper mantle. The microstructure and physical properties of polycrystalline forsterite are controlled by the anisotropy of grain-boundary energy and its evolution in conjunction with dynamic processes such as deformation and recrystallization.

Here we compile results from recent investigations of (i) variation in grain-boundary energy anisotropy variation studied using AFM and grooving, (ii) grain-boundary population from EBSD measurements, and (iii) the evolution of these distributions during deformation in the dislocation-assisted grain-boundary sliding regime. The change in plane populations, and relative energies as well as grain size, are key factors influencing the interconnectivity of melt, the extractability of melt from the upper mantle, and the attenuation of seismic waves.

In this presentation we will strongly focus on the relative grain boundary energy for forsterite samples with 4 different grain sizes. Here we extracted the grain boundary energy anisotropy from grain boundary grooves formed during annealing. About 100 grain boundaries per sample were analysed by atomic force microscopy (AFM). The groove geometry was evaluated using a simplified form of Young's equation approximating the surface energy as constant and neglecting the torque terms. We discuss our data in the light of grain boundary energy anisotropy in ceramic systems as well as in comparison to the absolute grain boundary energies reported for one natural sample (Duyster and Stöckhert, 2001).

[1] Duyster J. and Stöckhert B. (2001) Grain boundary energies in olivine derived from natural microstructures. *Contrib. to Mineral. Petrol.* **140**, 567–576.

Transformative Applications of Materials Data Science: Spatiotemporal Studies and Convolutional and Graph Neural Network Learning To Solve Materials Challenges

Prof. Roger H. French

SDLE Research Center, Materials Science, Case Western Reserve University, Cleveland OH 44106

Petabyte-scale datasets, including time-series, spectra and images, can be collected using recent advances in computing and communication. Data-driven AI/ML models, such as deep representation learning, trained on these datasets can illuminate critical features and challenge our current understandings in ways that affect society's, industry, and academia's choices. Materials science datasets amassed from laboratory experiments have typically been small and sparse, but our ability to use petabyte datasets from complex materials systems in their real-world applications enables us to shift from observational studies to predictive and inferential science1.

Our work combines multiple disciplines to address aging issues in photovoltaic (PV) modules and power plants, including elucidating the fundamental mechanisms and degradation pathways2,3. This permits epidemiological studies of the performance loss rate (PLR) as a function of PV module types and climate zones4,5. Our automated image processing and deep learning pipeline applied to electroluminescent (EL) images of PV modules enable identification of active degradation mechanisms and predict their associated power losses6. Deep representation learning, using spatiotemporal-graph (st-graph) neural network models, allows us to more accurately predict power of fleets of PV power plants, by leveraging the geospatial and temporal coherence and relationships amongst thousands of these systems as a network7. These results underlay our current efforts using st-graphs and knowledge graph methods to summarize domain-relevant features to address research questions that have been inaccessible to quantitative analysis to this day.

[1] A. Khalilnejad, et al., "Automated Pipeline Framework for Processing of Large-Scale Building Energy Time Series Data," PLOS ONE, vol. 15, no. 12, p. e0240461, Dec. 2020.
[2] H. E. Yang, R. H. French, and L. S. Bruckman, Eds., Durability and Reliability of Polymers and Other Materials in Photovoltaic Modules, 1st Edition. Amsterdam: Elsevier, William Andrew Applied Science Publishers, 2019.
[3] R.H. French, et al., Degradation science: Mesoscopic evolution and temporal analytics of photovoltaic energy materials, Curr. Op.Sol. State & Matls. Sci. 19 (2015) 212–226.
[4] R. H. French, et al., "Assessment of Performance Loss Rate of PV Power Systems," IEA-PVPS, 2021.
[5] J. Liu, et al, "Degradation mechanisms and partial shading of glass-backsheet and double-glass photovoltaic modules in three climate zones determined by remote monitoring of time-series current–voltage and power datastreams," Solar Energy, vol. 224, pp. 1291–1301, Aug. 2021.
[6] A. M. Karimi, et al., "Generalized and Mechanistic PV Module Performance Prediction From Computer Vision and Machine Learning on Electroluminescence Images," IEEE J. Photovoltaics, vol. 10, no. 3, pp. 878–887, May 2020.
[7] A. M. Karimi, et al., "Spatiotemporal Graph Neural Network for Performance Prediction of Photovoltaic Power Systems," in Proceedings of the Association for Advancement of Artificial Intelligence Conference on Artificial Intelligence, Virtual, 2021, vol. 35, p. 8.

Building 3D Architectures and Devices from 2D Materials

Prof. Suelen Barg[1,2,3]

1. Institute of Materials Resource Management (MRM), Augsburg University, Am Technologiezentrum 8, 86159, Augsburg, Germany
2. Department of Materials, School of Natural Sciences, Faculty of Science and Engineering and The Henry Royce Institute, Royce Hub Building,
3. The University of Manchester, Manchester, UK

The incorporation of 2D Materials into different matrixes, substrates, and architectures has the potential to enable an efficient delivery of functional and structural properties in support of the energy transition. Among 2D materials, graphene and MXenes (especially the most studied MXene member, $Ti_3C_2T_x$) are being intensively researched due to their potential for scalable fabrication, high electrical conductivity, and compatibility with existing colloidal processing routes. Further, MXenes present unique processability advantages such as their additive-free dispersibility in water due to their hydrophilic nature and the expendable need for reduction steps.

This talk will present an overview of colloidal processing approaches towards 3D architectures built from 2D Materials, with emphasis on ice- templating and material extrusion additive manufacturing-based approaches. The potential of these processes and materials will be exemplified in specific applications such as in the development of vertically aligned MXene electrodes and multi-material configurations ($Ti_3C_2T_x$-hBN-$Ti_3C_2T_x$) for high-rate performance flexible supercapacitors, as well as in the development of composites for electrothermal heating.

Biomass and wood derived materials for structural and energy applications

Prof. Joaquin Ramírez-Rico

Dpto. Física de la Materia Condensada / Instituto de Ciencia de Materiales Universidad de Sevilla-CSIC, SPAIN

Materials development is driven by microstructural complexity, sometimes inspired by biological systems like bones, shells, and wood. In one approach, one selects the main microstructural features responsible for improved properties and designs processes to obtain materials with such microstructures. In a different approach, it is possible to use natural materials directly as microstructural templates.

Among natural materials, wood is an interesting template due to its hierarchical structure and highly interconnected porosity optimized for fluid transport and mechanical strength. By thermal decomposition of wood or other vegetable templates, a porous carbon scaffold can be obtained that retains the structure of the precursor. This carbon scaffold can be infiltrated with silicon to obtain highly porous SiC ceramics with high mechanical strength or can be functionalized to be used as an electrode in energy storage applications. Interestingly, the microstructure and porosity of the resulting material can be controlled simply by choosing from a wide range of commercially available, sustainable wood materials.

In this presentation we will review the fabrication and properties of biomass templated structural and functional materials with a wide range of applications from hot-gas filtering to long-bone prosthesis, from catalyst supports to supercapacitor and battery electrodes.

Examination of the driving force for grain boundary migration in polycrystals

Prof. Gregory Rohrer

Carnegie Mellon University, USA

Using high-energy diffraction microscopy, we have measured the microstructures of Ni and Fe polycrystals at multiple times during annealing. Thousands of grains and grain boundaries were tracked and their velocities and curvatures were classified by their crystallographic characteristics. Among the findings, two are noteworthy and will be discussed in this talk. First, the velocities vary with all five crystallographic grain boundary parameters. Second, grain boundary velocity is independent of grain boundary mean curvature. Because curvature is thought to be an important component of the driving force, velocity and curvature are expected to be correlated positively. However, the evidence for such a correlation is poor. An alternate mechanism for reducing the total grain boundary energy, based on the anisotropy of the grain boundary energy, will be discussed.

On the role of interfaces in ultra-rapid densification of ceramics

Prof. Richard I. Todd[1*], Zonghao Guo[1], Wei Ji[1,2], Yasuhiro Kubota[1], Jaspreet Singh[1]

1. University of Oxford, Department of Materials, Parks Road, Oxford OX1 3PH.
2. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China.

For most of technological history, sintering has been a slow process, taking place on the timescale of hours or even days. Recently, however, sintering in only a few seconds has been demonstrated using processes such as flash sintering and ultra rapid heating using an external heat source. It is not yet clear how densification occurs so quickly but there is widespread suspicion that the interfaces are involved, at least indirectly, as is always the case during sintering. Direct investigation of the interfacial structure using electron microscopy is challenging not only because of the usual requirements of atomic resolution, compatible diffraction conditions, high contrast segregants, thin specimens etc. but also because of the highly dynamic nature of the sintering and the fine grain and pore sizes involved. Instead, this presentation uses measurements of more accessible microstructural quantities such as grain size, pore size, grain boundary segregation and homogenisation rates along with the kinetics of rapid sintering and its response to an applied stress to investigate possible explanations for ultra-rapid densification, including the traditional competition between coarsening and densification, transient melting of impurities and non-equilibrium grain boundary structures. The results presented are mainly on YSZ and alumina subjected to flash sintering or ultra high-rate sintering.

**Functionally Graded Ultra-high Temperature Ceramics:
From Thermo-elastic Numerical Analysis To Damage Tolerant Composites**

Dr. Laura Silvestroni[1*], Cesare Melandri[1], Diego Pavan[2], Antonio Mattia Grande[2]

1. National Research Council of Italy - Institute for Science and Technology for Ceramics, Italy
2. Dept. of Aerospace Science and Technology, Politecnico di Milano, Italy

Functionally graded ultra-high temperature ceramics containing variable amounts of short carbon fiber were designed to combine and maximize the toughening contributions due to fiber bridging and residual stresses upon layering. Stress fields evaluated by finite element model on $(AB)_nA$ and more complex asymmetric architectures were compared to the experimental fracture toughness pointing to an effective toughness increment in those structures where the notch fell in zones of residual compression. For the best composites, toughness at room temperature achieved 7 $MPa \cdot m^{0.5}$ and further increased to 10 $MPa \cdot m^{0.5}$ when tested at 1500°C within a light ZrB_2-based composite with density below 4 $g/^3$.

Local microstructure designs to tailor the properties of platelet-reinforced composites

Prof. Hortense Le Ferrand

Nanyang Technological University, Singapore

Platelet-reinforced composites with nacre-like microstructure (horizontally aligned platelets) are best to enhance strength and toughness when an external load is applied perpendicularly to the microstructure. If the material had to sustain loads from multiple directions, how should the microstructure be? If the material has to exhibit other functional properties, can the same microstructure be used? These are sample questions this talk will aim to address. First, I will introduce platelet-reinforced composites and what makes them special. Then, I will present our latest experimental results on the fabrication of platelet-reinforced composites with complex microstructures and their mechanical response. More specifically, magnetically assisted slip casting in complex mould shapes are used to create layered structures with varying microplatelet angles for horizontal, vertical, as well as curved layers in PDMS-Al_2O_3 composites. Our results show that curved layers and 90 ° angle between microplatelets in each layer can double the stiffness and increase the toughness of the composites for horizontal and vertical loading directions. Finally, I will present our recent work on functional properties of microstructured functional materials. Employing similar fabrication method in BN-polymer composites, we observed the impact of the microstructure on the thermal conductivity of the composites, reaching the unusually high value of 12.1 mW/K. By tuning the microstructure, the heat can be directed from a heat source toward specific areas for optimum thermal management. These results show promising opportunities for the realization of computer-optimized microstructural designs for target applications.

Imaging Interactions between Airborne Pollution Particles and Human Cells

Prof. Alexandra Porter[1], Victoria Garcia Giner[1*], Sharon Mumby[2], Gloria Young[1], Fan Chung[2], Ian Adcock[2], Maria Harkiolaki[3]

1. Faculty of Engineering, Department of Materials, Imperial College London, UK
2. Faculty of Medicine, National Heart & Lung Institute, Imperial College London, UK
3. Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire, United Kingdom

Air pollution is becoming one of the most pressing issues because of the increasing levels of pollution around the world. Airborne particulate matter (PM) can trigger cellular oxidative stress and inflammation, which are the basis for respiratory diseases associated with pollution. Understanding the effects of PM pollution on respiratory system cells is key to develop strategies to reduce personal exposure, especially in congested areas. Currently, there is no correlated cell-level information about the effects of PM on primary human epithelial cells metabolism, the structural damage of cellular organelles and the size and chemistry fractions of PM that cause this cellular damage. In a collaboration with the National Heart and Lung Institute, we have been focusing on the impacts of pollution PM collected from a London Underground platform on the health of cell organelles and cellular metabolism. We have shown that the PM collected from the London Underground is composed of trace quantities of redox-active transition metals, including Cu, Cr, Fe and Mo that could damage respiratory cells by generating damaging free radicals. We have exposed human nasal epithelial cells from healthy and asthmatic volunteers to this pollution PM. We have chemically fixed and stained the cells, embedded them in a resin and cut ultrathin sections for transmission electron microscopy and analysed the chemistry of intracellular nanoparticles of pollution using high resolution electron microscopy. In parallel, cryo soft Xray tomography (cryo-SXT) with structured illumination microscopy (cryo-SIM) (B24 Beamline, DLS) was employed to generate whole-cell structural and metabolically relevant information about the cells exposed to PM in their near-native state. Our data indicates significant mitochondrial alterations associated with PM co-localisation inside the cells. I will discuss how optimisation of cryo-focussed ion beam milling scanning electron microscopy (FIB-SEM) techniques could be used subsequently in specific areas for higher resolution imaging and complementary compositional analysis, as well as for lamella preparation for high-resolution cryo-TEM, where oxidation states and composition of damaging PM can be attained. In future, the development of this multidimensional workflow will bring together imaging of whole-cell structure and metabolism with chemical analysis of the PM to identify which chemistries are most damaging to intracellular cell organelles and their mechanisms of toxicity. This novel approach will offer new insights into how to mitigate the health effects of pollution PM.

Manufacturing of Polymer-based "Colourfunctional" Electrochromic Displays

Dr. Laura Maggini

University of Vienna, Institute for Organic Chemistry, Währinger Strasse 38, 1090 Vienna, Austria

Because of their rich, modulable library of vibrant colours and straightforward processing, electrochromic polymers have gained thrust for integration into flexible, low-power-consuming displays. However, the slower switching speeds recorded upon device integration, as well as their limited resilience towards degradation, have so far considerably limited their applicability.

Integration of nanodopants in their formulation has been devised as a powerful strategy to address their short comes. However, formulation alone cannot solve the issues these materials encounter once integrated in an operating device.

Since the electrochromic displays are produced by printing thin layers of these materials with high-performance electrolytes into 'electrochromic stacks', to pursue enhanced performances and full exploitation of the capabilities of these polymers into consumer products, it is crucial to investigate and optimise the way these materials are printed onto the electrodes and their interface with their adjacent layers. Only the truly "colorfunctional" electrochromic displays will be achieved, ready to satisfy the society's soaring demand for Internet of Things devices with sustainable, colourful and interconnected display interfaces.

Biological Blueprints Towards Next Generation Advanced Materials

Prof. David Kisailus

Materials Science and Engineering, University of California

For centuries, engineers have strived to make materials that are stronger, lighter and more efficient. Natural systems have developed well-orchestrated strategies, exemplified in the biological tissues of numerous animal and plant species, to synthesize and construct materials from a limited selection of available starting materials. The resulting structures display multiscale architectures with incredible fidelity and often exhibit properties that are frequently superior to mechanical properties exhibited by engineering materials. These biological systems modulate controlled synthesis and hierarchical assembly by using organic scaffolds and structure-directing agents, combined with ions, clusters and nano-scaled building blocks that are integrated into macroscale structures.

We are investigating organisms that have taken advantage of hundreds of millions of years of evolutionary changes to derive structures, which are not only strong and tough, but also display multifunctional features including damage sensing and self-cooling. We discuss the mechanical properties and functionality stemming from these hierarchical features as well as how they are formed. From the investigation of synthesis-structure-property relationships in these unique organisms, we are now developing and fabricating cost-effective and environmentally friendly advanced nanomaterials for energy conversion and storage, as well as water purification. We utilize organic materials as templates to regulate interfacial interactions that result in controlled particle size, phase and surface area that ultimately dictate performance.

[1]. “Nano-Architected Tough Biological Composites from Assembled Chitinous Scaffolds”, W. Huang, D. Kisailus, et al., *Accounts of Chemical Research*, **55** (10) (2022) 1360-1371. DOI: 10.1021/acs.accounts.2c00110

[2]. “Mesocrystalline Ordering and Phase Transformation of Iron Oxide Biominerals in the Ultrahard Teeth of *Cryptochiton stelleri*,” T. Wang, D. Kisailus, et al., *Small Structures*, (2022) 2100202. DOI: 10.1002/sstr.202100202

[3]. “Toughening Mechanisms of the Elytra of the Diabolical Ironclad Beetle,” J. Rivera, D. Kisailus, et al., *Nature,* **586** (2020) 543-548.

[4]. “A natural impact resistant bi-continuous composite nanoparticle coating,” W. Huang, D. Kisailus, et al., *Nature Materials,* **9** (11) (2020) 1236-1243.

[5]. “Multiscale toughening mechanisms in biological materials and bioinspired designs,” W. Huang, D. Kisailus, et al., *Advanced Materials*, **31** (2019) 1901561.

[6]. “Integrated transcriptomic and proteomic analyses of a molecular mechanism of radular teeth biomineralization in Cryptochiton stelleri,” M. Nemoto, D. Kisailus, et al., *Scientific Reports*, **9** (2019), 856.

[7]. “Electrocatalytic N-Doped Graphitic Nanofiber - Metal/Metal Oxide Nanoparticle Composites,” H. Tang, D. Kisailus, et al., *Small*, **14** (2018), 1703459.

[8]. “Biomimetic Structural Materials: Inspiration from Design and Assembly,” N. Yaraghi, D. Kisailus, Annual Reviews of Physical Chemistry, **69** (2018) 23-57.

[9]. Phase transformations and structural developments in the radular teeth of *Cryptochiton stelleri,*” Q. Wang, D. Kisailus, et al., *Adv. Funct. Mater.,* **23** (2013) 2908–2917.

[10].“The Stomatopod Dactyl Club: A Formidable Damage-Tolerant Biological Hammer,” J. Weaver, D. Kisailus, et al., *Science*, **336** (2012) 1275-1280.

Harnessing the emergent behavior of architected materials: bioinspiration and beyond

Prof. Pablo D. Zavattieri

Lyles School of Civil Engineering, Purdue University, West Lafayette, Indiana 47907, USA

Materials with mesoscale architecture have inner structures with geometrical features that are orders of magnitude lower than that of the intended engineering application. Their topology and geometry can be designed to attain specific properties and even emergent behavior that may be out of reach for conventional materials. On the other hand, most natural materials are complex composites whose mechanical properties are often outstanding, considering the weak constituents from which they are assembled. The secret is through their hierarchical architectures that are synthesized through a bottom-up process. In this talk, I will describe some interesting mechanics problems that we encountered as we studied some extraordinary naturally-occurring materials with mesoscale architecture, and how we can translate these lessons to engineered architectured materials. In the second part of the talk we will talk about another family of architecture materials that exhibit mechanical instabilities associated with reversible deformation which can be exploited to enable solid-state energy dissipation and mimic the shape memory and the pseudo-elastic behavior observed in shape memory alloys.

Hetero-epitaxial relationships and atomic structure at Ag/Ni interfaces

Dr. Dominique Chatain[1], Paul Wynblatt[2], Velimir Radmilovic[3], Ulrich Dahmen[4]

1. Aix-Marseille Univ, CNRS, CINaM, Marseille, France
2. Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh PA 15213, USA
3. Nanotechnology and Functional Materials Center, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia
4. NCEM-Molecular Foundry, LNBL, Berkeley, CA 94720, USA

The orientation relationship (OR) of a film on a single-crystal substrate is essential for a fundamental understanding of the factors that control thin film growth and texture. Among the several parameters which govern the OR, we concentrate on the role of terraces, steps and defects to accommodate structural differences or lattice mismatch across the hetero-interface between the two abutting phases. The different definitions for the heteroepitaxial relationship at an interface depend on whether the interface is considered from a surface science, a phase transformation or a grain boundary perspective. We propose an optimal choice based on the study of Ag on more than 200 Ni(hkl) surfaces.

New insights on the atomic grain boundary structure in pure and alloyed Cu and Fe

Prof. Gerhard Dehm

MPI für Eisenforschung GmbH, Düsseldorf, Germany

Grain boundaries in alloys are an important tool to improve the material's mechanical and functional properties such as strength, intergranular fracture, electrical resistivity and magnetic coercivity. The property change is often not only a consequence of the amount of grain boundaries present, but also of grain boundary segregation leading to changes in the atomic structure and composition and thus the local bonding characteristics. Grain boundaries span a complex multidimensional space starting with the misorientation between two grains, the inclination of the grain boundary plane, possible grain boundary nano-faceting, translations of atoms at the grain boundary, defects such as vacancies, impurities on substitutional or interstitial sites, line defects (disconnections) with a step and/or Burgers vector component, and finally second phase particles. In order to shed light on all these aspects we performed atomic resolved scanning transmission electron microscopy (STEM) studies on well-defined tilt grain boundaries in Cu and Fe combined with atomistic simulations.

The research on (111) tilt grain boundaries in pure Cu revealed that a specific grain boundary can exist for the same inclination in two different atomic structures and transforms between them diffusionless by pressure or temperature changes [1,2]. The transformation between both states is accomplished by a disconnection type line defect separating both structures. Alloying with Ta and Zr leads to formation of Ta rich precipitates and Zr segregation to the grain boundaries, respectively [3]. The electrical resistivity was found to depend mainly on the excess volume of the grain boundaries [4]. For Fe the complex interaction of Al, B, and C at a (100) tilt grain boundary was studied. While atomistic calculations reveal a preferential grain boundary segregation for Al in Fe for the binary Fe-Al system, the site competition of C, B and Al leads to an Al repulsion from the grain boundary [5]. However, B and C enrich at the grain boundary. C is predicted to occupy interstitial sites. The site occupancy was further studied by integrated differential phase contrast STEM.

[1] T Meiners, et al., *Observations of grain-boundary phase transformations in an elemental metal*, Nature 579(7799) (2020) 375-378.

[2] L Frommeyer, et al., Dual phase patterning during a congruent grain boundary phase transition in elemental copper, Nature Communications 13 (1), 2022; 1-11.

[3] T Meiners, et al., *Tantalum and Zirconium induced structural transitions at complex [111] tilt grain boundaries in Copper*, Acta Materialia 190 (2020), 93-104

[4] H Bishara, et al., *Understanding grain boundary electrical resistivity in Cu: the effect of boundary structure*, ACS nano, 15, 10; 2021, 16607–16615

[5] A Ahmadian, et al., *Aluminum depletion induced by co-segregation of carbon and boron in a bcc-iron grain boundary*, Nature communications 12.1 (2021): 1-11.

[6] Financial support by the European Research Council (ERC) under Grant agreement No. 787446; GB-CORRELATE and contribution of all involved colleagues is acknowledged.

Bulk nacre-like ceramics: a simple processing approach and related properties

Prof. Sylvain Meille

MATEIS laboratory, INSA Lyon, France

Bio-inspired ceramics developed in the last decades offer a unique combination of high strength and fracture toughness at a low density. In the case of full-mineral solutions, such as nacre-like alumina (Bouville et al., 2014), the structural functionality is kept up to relatively high temperatures. The corresponding microstructure is made of aligned alumina platelets with a nanostructured interphase. The platelets orientation can be achieved using freezecasting and magnetic assist slip casting before sintering. However, processing of such materials is rather complex, and the maximal sample size is limited. Crack propagation measurements are therefore done on samples of few millimeters of characteristic size. A new process simplifying the fabrication of nacre-like alumina samples will be presented. This process enables the fabrication of large samples, up to 10 mm in height, with a controlled alignment of platelets (Saad et al, 2020). A characterization of the size effect in crack propagation is done, coupled with in situ SEM crack propagation tests to study the interaction of the crack with the microstructure. Finally, crack propagation testing in different directions than the commonly tested one is carried out, eased by the relatively large samples processed. The characterization of the anisotropy in mechanical properties of nacre-like alumina is necessary for its potential use as a structural ceramic.

[1] F. Bouville, E. Maire, S. Meille, B. Van de Moortèle, AJ Stevenson, S. Deville, Nature Materials 2014, 10.1038/nmat3915
[2] H. Saad, K. Radi, T. Douillard, D. Jauffres, C. Martin, S. Meille, S. Deville, Materialia 2020, 10.1016/j.mtla.2020.100807

Rapid mechanical evaluation of materials using small scale bending in conjunction with in-situ strain measurements

Prof. Vikram Jayaram, Syed Afzal Idrees Jalali, Faizan Hijazi, Priya Goel, Shobhit Pratap Singh and Praveen Kumar

Department of Materials Engineering, Indian Institute of Science, Bangalore 560012 INDIA

Extracting mechanical behaviour from bending goes back a century to the early experiments by Volterra, Nadai and then Timoshenko and co-workers who investigated the phenomenon of load re-distribution that arises in a non-linear (plastic or creeping) material. Today, with the advent of digital image correlation and computational tools, the variation in strain in a cantilever allows multiple combinations of stress-strain-strain rate response to be extracted from a single sample. When one adds the convenience of bending and the ability to test small samples without the need for gripping, cantilever tests offer the possibility of high throughout testing with vast amounts of data generated from a single test of bulk as well as meso or microscale samples. An aspect of non-linear bending, in contrast to uniaxial tension. is that stresses in the sample are unknown and, in general, require prior knowledge of a constitutive law. This talk will illustrate the basic elements of the technique followed by application to practical alloy systems such as Ti-alloys, boiler steels and additively manufactured Al-alloys as follows:

1. the ability to obtain steady state creep data for multiple stresses from a single test,
2. the existence of so-called invariant points at which the stress does not change even during plasticity and which allow a large number of uniaxial relationships to be extracted from the same test.
3. the use of miniaturised test pieces to carry out residual property measurements and life estimation from small coupons extracted from in-service components.
4. the appearance of length scale effects such as creep hardening due to strain gradients in small cantilevers that contrast with creep softening under uniaxial loading of the same sizes.
5. the ready determination of tension-compression asymmetry in polymers (elasticity) and in alloys based on titanium (creep).

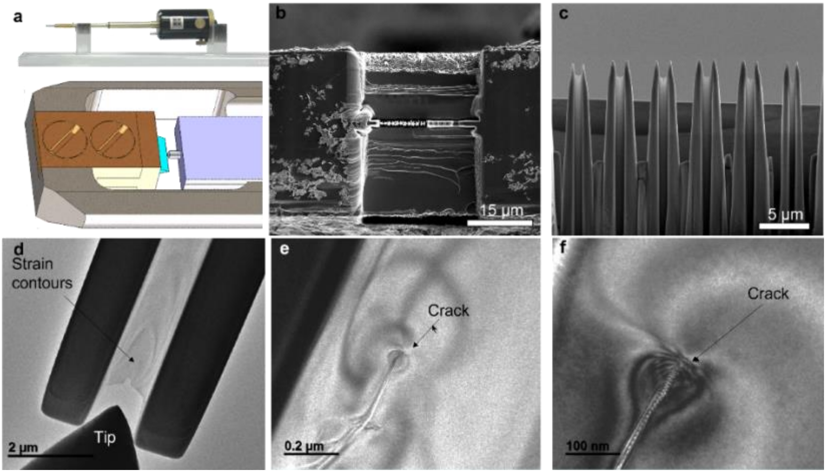
The vast amount of strain data generated across stress and time lends itself to the determination of complex constitutive laws through a process of physics-based machine learning.

Brittle fracture at the nanoscale

Dr. Oriol Gavalda-Diaz[1,2], Eduardo Saiz[1], Finn Giuliani[1]

1. Department of Materials, Imperial College London, London, UK
2. Department of Mechanical, Manufacturing and Materials Engineering, University of Nottingham, UK

Low fracture toughness poses a significant limitation for ceramics in structural applications. In many cases this is due to the low energy dissipated ahead of the crack tip in the absence of a large plastic zone. Several ways to enhance the fracture toughness have been proposed, including modifying the chemistry or microstructure of monolithic ceramics, to promote for example crack deflection or phase transformation ahead of the crack tip. Nevertheless, these events happen at a micro/nanometre scale and are difficult to measure or observe. In this work we use SEM and TEM in-situ setups to understand how these fracture events affect the failure of materials at the bulk scale. In both setups, we manage to achieve stable crack growth which allows us to understand for example how plasticity, phase transformation or crack healing happen in different ceramics and interfaces.



Overview of the TEM in-situ setup. (a) TEM holder (b) SEM top view of the sample after being thinned. (c) SEM front overview of the DCBs (d) TEM view of the indenter and the DCB and (e) and (f) frames obtained during the DCB splitting showing at different magnifications the crack propagating stably.

Fracture behavior of metal-ceramic and metal-metal nanolaminates

Dr. J.M. Molina-Aldareguia

IMDEA Materials Institute, Getafe (Madrid) 28906, Spain

Nanoscale multilayers or nanolaminates are nanostructured materials made up by alternating layers of two or more materials with a layer thickness below ~100 nm. These nanolaminates present very high strengths at ambient temperature. Their unique properties, typically measured by nanoindentation and/or micropillar compression are mainly a result of the high density of interfaces, which change the standard mechanisms of deformation when the layer thicknesses are below ~100 nm. The combination of dissimilar materials together with the small dimensions of the layers are also expected to significantly affect the fracture behavior. However, fracture properties have not been studied in detail so far, mainly due to the lack of appropriate testing techniques to determine fracture toughness at small scales. With the current development of novel nanomechanical testing techniques, it is now possible to test these materials under tension and/or bending, and to determine the fracture behavior of these heterogenous materials Examples will be shown in three different nanoscale multilayer systems, combining metallic and ceramic layers: Cu/Nb and Al/SiC.

Designing interfaces via atomic and molecular layer deposition

Dr. B. Putz[1,2], T.E.J. Edwards[1], I. Utke[1], J. Michler[1]

1. Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, CH 2. Department of Material Physics, Montanuniversität Leoben, 8700 Leoben, AT

Atomic and molecular layer deposition (ALD/MLD) hold enormous potential to design interfaces with tailored mechanical or functional properties, due to the unique way in which materials are built in an atomic layer-by-layer fashion and can reach deepest trenches and pores. When combined with other thin film techniques, such as magnetron sputtering (PVD), without breaking vacuum, the layer-by-layer nature of ALD/MLD can be harvested to design (sub)nanoscale interface and multilayer architectures with extremely good control over the layer thicknesses. For metal-oxide interfaces (Al/Al_2O_3), the minimum ALD layer thickness of one monolayer (nominal thickness 0.14 nm) far exceeds the thickness restrictions of natural oxidation of Al (2-10 nm[1]). High resolution TEM of a single Al_2O_3 ALD cycle (Figure 1, left) shows a distinct but very narrow interface between two adjacent Al sublayers, with atom rows of adjacent Al layers convening without interruption at the single-cycle ALD layer.

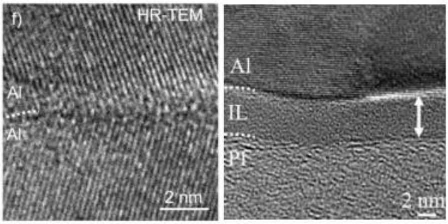


Figure 1
Left: Interface between two PVD Al layers modified by a monolayer of Al_2O_3.[2] Right: Interface between polyimide (PI) and Al, showing a 5 nm amorphous interlayer (IL)[3].

Another interesting area for this combined deposition approach are metal-polymer interfaces, where it is known that thin amorphous interlayers between metal film and polymer substrate favor strong and thermally resistant interfaces[4]. Until now, interlayer formation is governed by the film and substrate chemistry[5] and the deposition method, preventing high interface quality for the majority of material combinations and fabrication routes. Since ultrathin ALD and MLD layers uniquely resemble natural ones in terms of structure and chemistry, interlayer formation can, for the first time, be mimicked artificially to clarify the role of these structures in thin film delamination and reveal underlying mechanisms as a function of thickness and chemistry. Going one step further, trigger mechanisms in artificial interlayers for controlled delamination in conditions beyond those of standard usage, can be investigated for ease-of-recycling opportunities.

[1] Baran, J. D., et al., Phys. Rev. Lett. 112, 1–5 (2014).
[2] Putz, B. et al., Adv. Eng. Mater. (2022).
[3] Putz, B. et al. Surf. Coat. Technol. 332, 368–375 (2017).
[4] Oh, S. H. et al,. Scr. Mater. 65, 456–459 (2011).
[5] Atanasoska, L., et al., J. Vac. Sci. Technol. A 5, 3325–3333 (1987)

Novel high heating rate sintering methods for ceramics: From fundamentals to economic potential

Dr. Wolfgang Rheinheimer

Forschungszentrum Jülich, Germany

For millennia, ceramics have been densified via sintering in a furnace, a time-consuming and energy-intensive process. The need to minimize environmental impact calls for new physical concepts beyond large kilns relying on thermal radiation and insulation.

This presentation visits three novel sintering methods with high heating rates, i.e. flash sintering, ultra-fast high-temperature sintering (UHS) and photonic sintering. All three processes base on the same physical effect: very high heating rates preserve high driving forces and allow sintering in very short times and comparably low temperatures. It is shown that high-quality microstructures can be obtained even for relatively thick samples, multiphase materials and layered composites, and that physical properties become available that are not accessible by conventional sintering. Beyond microstructures and properties, the process offers outstanding energy efficiency and scalability as needed for in various applications.

Ceramics in Dental Implantology: Past, Present and Future

Dr. Alessandro Alan Porporati[1,2]

1. CeramTec GmbH, Plochingen, Germany
2. University of Trieste, Department of Engineering and Architecture, Trieste, Italy

High aesthetic demand and the increasing percentage of the population that presents phenomena of hypersensitivity to some metals have driven the growing acceptance of zirconia as an effective alternative material to metals in oral implantology.
Moreover, zirconia surface treatments allow comparable bone-to-implant contact to titanium implants without impacting the implant structural integrity. The reduction in the number and presence of pathogenic bacteria on the ceramic surfaces in comparison with the metallic has been shown to lead to oral hygiene advantages for the ceramic implants. This is combined with the high aesthetic result achievable thanks to the translucency and light transmission of the entire restoration.

One-piece reconstructions have been initially employed, two-piece implant systems are being progressively introduced into the market, and the current trend is towards all-ceramic modular implants with screw-retained abutments.

The path has been long; alumina implants were initially exploited and despite manufacturing improvements made over the years, they soon showed their limitation, represented by their sensitivity to stress and stress concentrations. Despite the problems associated with the use of alumina implants, the interest piqued in dentistry by these all-ceramic devices has encouraged the study of alternative ceramic materials.

The main event that changed the course of history was the discovery of zirconia phase transformation at room temperature. It demonstrated, by exploiting the phase transition from tetragonal to monoclinic of zirconia, how it was possible to obtain a tough ceramic material, a property that up till then only metals possessed.

What is the next step? Zirconia meets the requirements of current ceramic dental implant designs. A material with improved biomechanical characteristics and advanced surface texturing for even more ambitious implant geometries may be desirable to expand the ceramic implant portfolio. Advanced manufacturing technologies such as direct ceramic foaming or a new generation of advanced ceramics designed to further enhance the mechanical properties could enable even broader use of ceramics in dentistry and medicine in general.

The presentation provides an overview of the application of ceramic materials in dentistry, with a focus on zirconia material.

Poster Abstracts

Pluronic®/casein mixed nanomicelles that solubilize resveratrol and preserve its antioxidant activity

Maria Vivero-Lopez, Angel Concheiro, *Carmen Alvarez-Lorenzo*

Departamento de Farmacología, Farmacia y Tecnología Farmacéutica, I+D Farma (GI-1645), Facultad de Farmacia, Instituto de Materiales (iMATUS) and Health Research Institute of Santiago de Compostela (IDIS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Introduction: Uncontrolled increase of reactive oxygen species (ROS) is a main cause of age-related diseases, including cardiovascular diseases and cancer. ROS cause cell injures through oxidative damage of DNA, oxidative modification of proteins and lipid peroxidation of membranes. The imbalance between antioxidants and pro-oxidants is exacerbated in elderly people and triggers the generation of proinflammatory cytokines and proteolytic enzymes. Resveratrol is a potent anti-inflammatory agent that has been shown to prolong lifespan in many species, but its low bioavailability after oral administration notably limits the therapeutic outcomes (1). Poor aqueous solubility and limited stability are two main concerns that could be overcome by encapsulation in polymeric micelles. In addition to synthetic block copolymers, natural amphiphilic proteins such as casein are attracting increasing attention for drug formulation (2). The aim of this work was to prepare Pluronic® F127/casein (P/C) mixed micelles that can enhance the apparent solubility of resveratrol and preserve its antioxidant properties.

Methods: Pluronic® F127 and P/C mixed micelles were prepared in phosphate buffer pH 7.0 by adding casein solution (final concentration 0.1%) to Pluronic® solutions (3.15 to 18.9 %). The dispersions were characterized in detail regarding pH, size and Z-potential before and after loading of resveratrol, solubility of resveratrol, and antioxidant activity (DPPH). In situ gelling behaviour was evaluated using a Rheolyst AR-1000N (TA Instruments, UK) rheometer fitted with a cone (60 mm, 2.1°) as a function of temperature (10-45 °C).

Results: Casein micelles had strongly negative surface and mixed micelles showed less negative Z-pot values as the concentration in Pluronic® increased. Casein micelles did not solubilize resveratrol, but mixed micelles increased resveratrol apparent solubility from 0.17 mg/mL in buffer to nearly 9 mg/mL. Resveratrol-encapsulated micelles were stable during storage for 30 days at 4 °C and upon dilution. The DPPH scavenging effect registered for resveratrol-loaded micelles was higher as the content in Pluronic® F127 increased, especially in the mixed micelles, which was in good agreement with the higher content in resveratrol.

Conclusion: P/C mixed micelles evidenced an excellent capability to encapsulate resveratrol enhancing the apparent solubility more than 50 times and preserving the antioxidant capacity. The micelles showed remarkable physical stability against dilution and during prolonged storage. Compared to single Pluronic® F127 micelles, mixed micelles had similar sizes, but the presence of casein endowed the micelles with more negative Z-potential and slightly increased resveratrol solubility and its antioxidant activity, while also exhibiting sol-to-gel transitions in an adequate temperature range for administration through different routes.

Acknowledgements: The work was supported by MCIN/AEI/10.13039/501100011033 [PID 2020-113881RB-I00], Spain, Xunta de Galicia [ED431C 2020/17], and FEDER. M. Vivero-Lopez acknowledges Xunta de Galicia (Consellería de Cultura, Educación e Ordenación Universitaria) for a predoctoral research fellowship [ED481A-2019/120].

[1] A. Amri, J.C. Chaumeil, S. Sfar, C. Charrueau. J Control Release 2012, 158:182-193.
[2] A.O. Elzoghby, W.S. Abo El-Fotoh, N.A. Elgindy. J Control Release 2011, 153:206-216.

3D printing of magnetically aligned composites within enhanced properties

Lizhi Guan[1], Jingbo Fan[2], Xin Ying Chan[1], Hortense Le Ferrand[1,2]

1. School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore
2. School of Materials Science and Engineering, Nanyang Technological University of Singapore, 50 Nanyang Avenue, Singapore 639798, Singapore

Complex hierarchical materials in nature with remarkable performances of such as mechanics, self-morphing, self-healing, superhydrophobic and so on, have inspired researchers designing and fabricating aligned structures for a wide range of applications.[1-3] Conventional techniques like freeze-casting, self-assembly, wet-spinning, vacuum filtration, shear force, electric and magnetic field have been demonstrated to achieve the excellent functional and reinforced structures.[4] Still, they are limited to microstructure control. 3D printing techniques enable to achieve a large diversity of dimensions, multimaterial and multifunctional 3D structures.[5] Particularly, recent 3D printing combined with external force e.g., shear force, magnetic and electrical field have been employed to control microscale and hierarchies at the macroscale for the applications of reinforced structure, supercapacitors as well as soft robotics.[6-8] However, current techniques are limited by low efficient printing, low loading of fillers and single direction alignment control. Herein we developed a method where 3D direct ink writing integrated with magnetic field. The extruded ink was deposited on the substrate of gypsum that can be dried very quickly and maintain the shape fidelity. Meanwhile, the applied magnetic field is capable of tuning the alignment of magnetic platelet modified by iron oxide nanoparticle in the extruded ink.[9] The obtained complex composites possessed anisotropic properties on flexible strength and multifunctional properties of magnetic response, electrical as well as thermal conductivity. This innovation opens up an opportunity to fabricate remarkable complex composites with high printing efficient, tunable loading of fillers, control of alignment distribution.

[1] Studart, A. R., *Advanced Materials* (2012) **24** (37), 5024
[2] Zhao, N., *et al.*, *Advanced Materials* (2014) **26** (41), 6994
[3] Behera, R. P., and Le Ferrand, H., *Matter* (2021) **4** (9), 2831
[4] He, H., *et al.*, *Journal of Materials Chemistry A* (2022)
[5] Saadi, M. A. S. R., *et al.*, *Advanced Materials* (2022), 2108855
[6] Martin, J. J., *et al.*, *Nature Communications* (2015) **6** (1), 8641
[7] Tetik, H., *et al.*, *Advanced Materials* (2022) **34** (2), 2104980
[8] Kim, Y., *et al.*, *Nature* (2018) **558** (7709), 274
[9] Le Ferrand, H., *Journal of the European Ceramic Society* (2021) **41** (1), 24

Quantifying local fracture toughness in nacre-like ceramics

Victoria Vilchez, Florian Bouville

Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, SW7 2AZ, London UK

Unlike synthetic ceramics which are brittle and prone to catastrophic failure, biological materials combine both stiffness and toughness. Nacre, for example, is composed of 95 vol% calcium carbonate yet exhibits a fracture energy 3 orders of magnitude higher than $CaCO_3$. This toughness amplification stems from nacre's brick-and-mortar architecture which provides multiple toughening mechanisms at different length scales. Consequently, nacre has become a blueprint for manufacturing tougher synthetic ceramics. We are now able to accurately reproduce at similar length-scale the architecture of nacre with processes like magnetically assisted slip casting (MASC). MASC enables the controlled alignment of anisotropic platelets decorated with superparamagnetic nanoparticles under low intensity magnetic field during slip casting. Using this process and others, nacre-like ceramics (NLCs) of various compositions have been developed. However, if the reinforcing mechanisms acting in biological nacre have been intensely studied, they are still not well understood in NLCs, in which the complexity of the highly deflected crack paths makes it difficult to evaluate fracture using the standard tools of fracture mechanics. We developed a formulation based on mixedmode stress intensity factors to describe fracture at the crack tip, taking into account the angle of deflection and the presence of multiple cracks. This formulation was applied to experimental data obtained from in situ mechanical testing on NLCs of various compositions and its accuracy confirmed by finite element analysis. This new description of NLCs' fracture gives us a better understanding of the local mechanisms controlling crack propagation, a necessary condition to push their mechanical properties further in the future.

Digital Light Processing of Carbides

Ollie Osborn, Eduardo Saiz

Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, SW7 2AZ, London UK

There is increasing industrial interest in complex parts of silicon carbide and boron carbide. Additive manufacturing (AM) offers a promising alternative to traditional forming processes which, require expensive moulds and struggle with complex geometries. AM has had success with ceramic oxides however, carbides remain challenging because of their high melting points and unfavourable optical properties. Among the available AM methods digital light processing (DLP), where 3D parts are sliced into layers which are sequentially cured by selectively illuminating each layer's pattern, offers superior resolution and surface finish.

Carbide's high refractive indices as well as absorption in the near UV spectrum limits the photocurable resin's cure depth. To overcome this, larger particle sizes are required which, creates a compromise between curing and sintering (liquid phase). As a result, most of the previous research focuses only the forming process or requires additional infiltration steps. In this work presented, high solid loading (40 vol%), photocurable resins containing silicon carbide and sintering aids (alumina and yttria) have been formulated and optimised. The cure depths of the resins are sufficient to print using a 50 mm layer thickness with a relatively low light intensity (1.8 mW/cm^3). This presents the opportunity for low cost, tabletop DLP of silicon carbide.

Works supported by under MAPP: EPSRC Future Manufacturing Hub in Manufacture using Advanced Powder Processes (EP/P006566/1) in collaboration with MTC and Photocentric.

Additive manufacturing of thermoset polymer matrix composites with shape memory capabilities

Yinglun Hong1 , Itxaso Azcune2 , Alaitz Rekondo2 and Eduardo Saiz1

1. Centre for Advanced Structural Ceramics, Department of Materials, Imperial College London, London SW72AZ, UK
2. CIDETEC, Basque Research and Technology Alliance (BRTA), Paseo Miramón, 196, 20014 Donostia-San Sebastián, Spain

In comparison to thermoplastic polymers, thermosets possess better chemical resistance, thermal stability and mechanical properties. In particular, shape memory programmable thermosets could be used in wide range of engineering applications such as actuators or aerofoils. However, production of thermoset components with complex structures using conventional mould-casting methods is challenging.

Using additive manufacturing it is possible to fabricate complex parts on-demand. Direct ink writing (DIW) is a straightforward manufacturing technique that builds a part using the continuous extrusion of a paste in layer-by-layer fashion. The feed-stock pastes for DIW are required to exhibit a suitable viscoelastic behaviour which allow them to be extruded smoothly while retaining the printed shape. Since thermoset polymers are not intrinsically 3-D printable, rheological modifiers (e.g. nanoclay (1), fumed silica (2), carbon nanotubes (3)) are usually introduced to achieve that. However, large quantities of additives are often needed what may compromise performance. In this work, printable thermoset pastes for DIW based on a shape memory epoxy vitrimer (4) have been developed by incorporating low amounts (<6wt%) of reduced graphene oxide (rGO). This system is flexible, and anisotropic fillers, for example BN platelets, can be introduced to enhance its thermal and mechanical performance. Composites fabricated using this system have been found to retain the shape memory programmability of the pristine epoxy vitrimer while exhibiting higher thermal conductivity and fracture resistance.

This work has been financially supported by the Office of Naval Research (ONR) under award number N62909-18-1-2056.

[1] Hmeidat NS, Kemp JW, Compton BG. Composites Science and Technology. 2018;160:9-20. [2] Chandrasekaran S, Duoss EB, Worsley MA, Lewicki JP. Journal of Materials Chemistry A. 2018;6(3):853-8.
[3] Lewicki JP, Rodriguez JN, Zhu C, Worsley MA, Wu AS, Kanarska Y, et al.. Scientific reports. 2017;7(1):1-14. 4. Azcune I, Huegun A, de Luzuriaga AR, Saiz E, Rekondo A. European Polymer Journal. 2021;148:110362

A strategy for improved prediction of freeze-cast microstructures

Katie Lewthwaite[1], Suelen Barg[2]

1. University of Manchester, UK
2. Institute of Materials Resource Management, University of Augsburg

Materials with anisotropic microstructures fabricated via freeze-casting have potential use in applications from tissue engineering to energy storage.[1] However, commercial implementation of the process is rare due to a number of factors.[2] One notable issue is reproducibility, since the exact microstructure of freeze-cast materials can vary batch to batch. This is largely due to variations in ice nucleation behaviour which in turn impacts ice growth. To date, publications on freeze-casting are often at the 'proof of concept' stage, and so repeatability is largely yet to be addressed.

In this work, we aim to address the problem in two stages. Firstly, we have proposed a strategy for reducing the variation in ice nucleation and growth behaviour through substrate alteration. We have shown that ice nucleation occurs within a smaller temperature range when the altered substrate is used compared to a pristine, aluminium substrate. The structural features (such as pore spacing and orientation) across a large number of samples are being measured in order to assess the amount of structural variation resulting from each substrate type. For this, we are using graphene oxide as an example material. In the second stage of the work, we aim to use the large data sets collected to develop a method for predicting structural features based on measurements taken during freezing, including the nucleation temperature and freeze front velocity profile. The goal here is to demonstrate how repeatability could be assessed without the need for expensive structural characterisation techniques. This could be useful as a research tool, or quality control measure.

[1] Deville, S. *Freezing Colloids: Observations, Principles, Control, and Use*. (Springer Nature, 2017).
[2] Deville, S. The lure of ice-templating: Recent trends and opportunities for porous materials. *Scr. Mater.* **147**, 119–124 (2018).

Robocasting of quasicrystalline ZnO structures

Naïma Saadi[1], Andy Gleadall[2], Hem-Raj Sharma[3], Ronan McGrath[3] and Esther García-Tuñón[1]

1. School of Engineering and Materials Innovation Factory, University of Liverpool, Liverpool, L69 3GH, UK,
2. Wolfson School of Mechanical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK,
3. Surface Science Research Centre and Department of Physics, University of Liverpool, Liverpool, L69 3BX, UK

Extrusion-based 3D printing presents itself as an innovative method of manufacture that can be utilised to create complex structures from advanced materials. These materials can possess desirable bulk characteristics such as light or acoustic bandgap properties, or multi-material architectures [1]. Whilst 3D printed complex structures discovered in research are almost always confined to lab-based experiments and studies, the scope exists beyond this realm to expand its applications. This works aims to demonstrate the benefits that additive manufacturing (AM) of functional materials can offer in metamaterials, a rapidly growing field.

Metamaterials exploit physical characteristics to achieve physical behaviours not found in nature. Their geometry is the driving factor with unique behaviours coming from the purposeful structure design rather than the constituent materials themselves. Complex hierarchical structures such as quasiperiodic architected materials have been used to manipulate electromagnetic (EM) waves. Quasicrystals display long range order but lack translational symmetry. In this poster we will show how AM can be used to manufacture novel quasiperiodic materials for use in wave propagation.

The square Fibonacci tiling [2] is a model of a simple quasicrystal (QC). It is composed of two 'tiles' or segments, short (S) and long (L), the ratio of which is the 'golden mean' $\tau = (1 + \sqrt{5}) / 2 \approx 1.618$. In 2D these 'short' and 'long' spacings form three tiles: a small square (1×1); a large square ($\tau \times \tau$); and a rectangle ($1 \times \tau$), (Figure. 1). Using a gcode designer [3] and robocasting techniques [4] we propose a way to construct and print a 3D quasicrystal. In this poster we will present our design and coding approaches, the results of the processing and characterisation of ZnO formulations for robocasting, as well as examples of printed quasicrystalline structures. We will also discuss future work to evaluate the EM wave properties of such structures, starting with fundamental studies to determine whether the bandgaps obtained in theoretical calculations are present in the conceptualised structures. The ultimate goal of this work is to better understand how the physical properties of these macro-scale QC structures relate to the atomic-scale QC structures that are currently achieved through common surface science techniques.

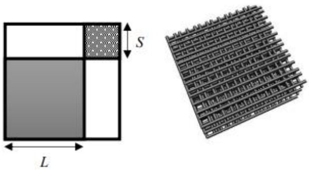


Figure 1 The three allowed tiles (left). A 3D model of the Fibonacci square quasicrystal (right).

[1] Peng E, Zhang D, Ding J. Ceramic Robocasting: Recent Achievements, Potential, and Future Developments. Advanced Materials. 2018;30(47):1802404.
[2] Lifshitz R. The square Fibonacci tiling. Journal of Alloys and Compounds. 2002;342(1-2):186-190.
[3] Gleadall A. FullControl GCode Designer: Open-source software for unconstrained design in additive manufacturing. Additive Manufacturing. 2021;46:102109.
[4] Feilden E, Blanca E, Giuliani F, Saiz E, Vandeperre L. Robocasting of structural ceramic parts with hydrogel inks. Journal of the European Ceramic Society. 2016;36(10):2525-2533.

Direct and indirect routes to design fluorescent pH branched copolymer surfactants

Francesca Miricola[1], Emma Jones[1,2], Marco Marcello[3], Andy Gray[4], Cesar Mendoza[4] and Esther García-Tuñón[1]

1. School of Engineering & Materials Innovation Factory,
2. Leverhulme Research Centre,
3. Centre for Cell Imaging, University of Liverpool, L69 3GH Liverpool,
4. Unilever R&D. Plc.Quarry Road east, Bebington, Wirral CH63 3JW

Personal care liquids are multifunctional materials designed to achieve certain performance attributes, in terms of structure, flow behaviour and transition phase phenomena under different conditions. Most personal care fluids are non-Newtonian water-based emulsions that behave as viscoelastic soft solids, each of them exhibiting a unique 'fingerprint' under shear deformations due to their microstructure. The industrial challenge is to implement relatively simple and scalable characterisation protocols to achieve a better understanding of such complex fluids. These protocols should be able to provide insights on microstructure, local and bulk rheology. We pave the way to tackle this challenge studying the entwined relationships between bulk rheology and microstructure. To achieve this goal, we have first developed a model system based on oil in water emulsions using pH responsive Branched Copolymer Surfactants (BCSs) 1,2 modified with fluorescent tags. Designing fluorescent tag systems for BCSs allow us to observe the microstructure under static conditions in different environments, 2 and to track microstructural changes under different dynamic conditions. Tagged BCSs enable us to combine advanced imaging techniques with flow experiments in micro-channels, 3 and to develop rheo-microscopy protocols. Dynamic studies in micro-channels will provide new insights on: 1) flow behaviours at very small Reynolds (Re) number values; and 2) phase transition phenomena in diffusion controlled laminar flows under 'in situ' triggering assembly and de-assembly (by tuning the pH); and 3) to understand how these (1 and 2) affect the microstructure. Our model formulation system provides a library of gelled fluorescent emulsions for these new studies. In this poster, we will present two new approaches to introduce fluorescent tags into BCS stabilised o/w emulsions: through covalent tagging (or direct), and through hydrophobic interactions (or indirect). Two commercially available fluorophores have been used: fluorescein-o-methacrylate and Nile Red. We will show the synthesis results for these two tags and approaches, their performance stabilising o/w emulsions and their response to different chemical environments.

[1] Woodward, Robert & Chen, Lin & Adams, Dave & Weaver, Jonathan. (2010). Fabrication of large volume, macroscopically defined and responsive engineered emulsions using a homogeneous pH-trigger. Journal of Materials Chemistry - J MATER CHEM. 20.
[2] Garcia-Tunon, E., Barg, S., Bell, R., Weaver, J.V.M., Walter, C., Goyos, L. and Saiz, E. (2013), Designing Smart Particles for the Assembly of Complex Macroscopic Structures. Angew. Chem. Int. Ed., 52: 7805-7808.
[3] Bauer WAC, Kotar J, Cicuta P, Woodward RT, Weaver JVM, Huck WTS. Microfluidic production of monodisperse functional o/w droplets and study of their reversible pH dependent aggregation behaviour. Soft Matter. 2011; 7(9)

Photocatalytic $SrTiO_3$ structures with hierarchical porosity via DIW of 'smart' formulations

Emma Jones[1,2,3], Haofan Yang[1,2], Andrew I. Cooper[1,2] and Esther García-Tuñón [2,3]

1. Leverhulme Research Centre for Functional Materials Design,
2. Materials Innovation Factory
3. School of Engineering, University of Liverpool, L7 3NY

Though undoubtedly an attractive green alternative to highly polluting fossil fuels, it is not yet possible to reliably implement H_2 as a clean fuel source due to a lack of robust methods by which to generate it efficiently. Photocatalytic water splitting, where solar irradiation of a photoactive material induces the generation of H_2 and O_2 from water with no by-products, presents an opportunity to divest entirely from fossil fuels. However, in order to realise the potential of this technology, it is necessary to improve the efficiency of the photocatalytic water splitting reaction that is based on charge separation across manufactured semiconductor heterojunctions, where any defects can lead to charge recombination and loss of activity. Controlling interfaces between materials is a task that many traditional subtractive manufacturing processes struggle to do well. Direct ink writing (DIW) is an additive manufacturing (AM) technique in which structures are built up by the layer-by-layer extrusion of a yield stress and shear thinning soft solid to create self-supporting 3D structures. By tuning the chemistry and microstructure of these formulations, it is possible to fabricate structures in a hierarchical fashion.[1,2]

In this poster we will present, to the best of our knowledge, the first example of the fabrication of highly porous and photocatalytically active $SrTiO_3$ (STO) structures *via* DIW. Printable STO pastes have been formulated using both Pluronic F127 (PF127) and branched copolymer surfactant (BCS), in the latter case employing BCS as the only additive in the formulation of a printable STO suspoemulsion with low binder content (~ 1 wt% of the total volume).[3,4] A series of PF127 and BCS-STO monoliths and grids have been printed, postprocessed and thoroughly characterised to quantify structural properties and functional performance. We will present the results of this characterisation, including density using the Archimedes method, electron microscopy, x-ray diffraction and photocatalytic activity *via* both methylene blue (MB) degradation and H_2 evolution testing.[5,6]

Archimedes density testing showed that the use of BCS leads to a 14% increase in porosity compared to PF127. SEM imaging corroborates this, showing clearly visible pores and surface roughening in structures originating from BCS-STO formulations when compared to PF127-STO formulations. This aligns with an improvement in both MB degradation (21% and 16 % MB degraded in 4 hr respectively) and, crucially, H_2 evolution rate (HER) in BCS-STO printed grids compared to PF127-STO printed grids. Our data demonstrates the potential of manufacturing a hierarchical structure with multiscale porosity from a commercially available raw material that is capable of photocatalytic H_2 evolution. Importantly, the H_2 evolution rate is improved in BCS-STO printed grids when compared to the raw micropowder (19.1 and 17.8 μmol h^{-1} g^{-1} respectively).

We will also discuss future work in this area, and the potential that careful formulation design, a fundamental understanding of complex fluids and AM techniques have to offer in catalyst design and manufacture.

[1] E. García-Tuñón, G. C. Machado, M. Schneider, S. Barg, R. v. Bell and E. Saiz, *J Eur Ceram Soc*, 2017, 37, 199–211.
[2] A. Corker, H. C. H. Ng, R. J. Poole and E. García-Tuñón, *Soft Matter*, 2019, 15, 1444–1456.
[3] E. Feilden, E. García-Tuñón, F. Giuliani, E. Saiz and L. Vandeperre, J Eur Ceram Soc, 2016, 36, 2525–2533.
[4] E. García-Tuñón, S. Barg, R. v. Bell, J. V. M. Weaver, C. Walter, L. Goyos and E. Saiz, Angewandte Chemie - International Edition, 2013, 52, 7805–7808.
[5] M. J. Martín de Vidales, A. Nieto-Márquez, D. Morcuende, E. Atanes, F. Blaya, E. Soriano and F. Fernández-Martínez, Catalysis Today, 2019, 328, 157–163.
[6] E. García-López, G. Marcì, B. Megna, F. Parisi, L. Armelao, A. Trovarelli, M. Boaro and L. Palmisano, Journal of Catalysis, 2015, 321, 13–22.

Nickel-iron nanoparticles supported on graphene oxide aerogels by freeze-casting

López, M., González-Ingelmo, M., Blanco, C., Álvarez, P., Granda, M., Santamaría, R., Rocha, V.G

Institute of Carbon Science and Technology-INCAR, CSIC, 33011-Oviedo, Spain.

Keywords: graphene oxide aerogels, nickel-iron nanoparticles, freeze-casting, lyophilization.

Graphene oxide aerogels are supports for catalysts due to its high electrical conductivity, low density, high superficial area and good chemical and mechanical stability. Besides, if graphene oxide is doped with a metal precursor of nickel-iron nanoparticles, its electrochemical activity could be upgraded, enabling a suitable material for water splitting.

These aerogels can be produced by freeze-casting of a mixture of graphene oxide and nickeliron precursor in water suspension. Freeze casting consists on pouring the aqueous colloidal suspension into a mould that has insulating walls and its subsequent freezing at controlled rate from the copper bottom of the mould. The freezing rate and the solids content influence the size and structure of the aerogel pores, since the ice channels that grow in the sample are lately sublimated by lyophilization (Figure 1).

The synthesis of the nickel-iron nanoparticles was carried out from a lactate precursor, allowing a water-based processing route for the whole synthesis, which in turn, helps to obtain a homogeneous dispersion of this precursor in the graphene oxide colloidal suspension. In addition, exfoliation of large particle size of natural graphite has given rise to large flakes of graphene oxide. Thanks to the combination of large flake size of graphene oxide with catalysts precursors, the freezecasting process of the mixed suspensions generated partially reduced graphene aerogels (650 ºC, 4 mg/cm^3) with a pore size of 20-30 µm and nickel-iron particles 15-40 nm in diameter.

By means of this method, agglomeration of graphene flakes is avoided by the freezing channels present in the aerogel, thus obtaining a large specific surface area and ultradispersing the catalyst along the graphene flakes. All these properties are very favorable in water splitting, making these aerogels very promising to be used as catalyst for this process.

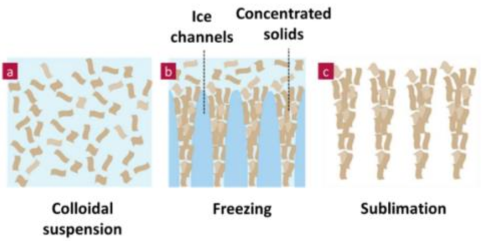


Figure 1. Freeze-casting process of graphene oxide colloidal suspension and nickel-iron particles to obtain a porous structure of concentrated solids.

Influence of iron on the activity of nickel catalysts supported on graphene for water splitting reactions

González-Ingelmo, M., López, M., Blanco, C., Santamaría, R., Álvarez, P., Granda, M., Rocha, V.G.

Instituto de Ciencia y Tecnología del Carbono-INCAR, CSIC, 33011-Oviedo, España.

Keywords: water splitting, oxygen evolution reaction, nickel catalyst, iron impurities, KOH purification

Water splitting is a key reaction for the clean production of hydrogen as sustainable fuel that consist of two half reactions, namely, oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), being OER the bottleneck of this process. The sate-of-the-art electrocatalysts for this reaction are based on noble metals (Ru or Ir complexes). However, high cost and scarcity of precious electrocatalysts seriously prohibit the large-scale application. Thus, it is essential to explore low-cost, earth-abundant, environmentally friendly, efficient and stable materials (e.g., Ni, Co, Fe, Cu and Mo). In particular, Ni-based composites are potential substitutes of noble metals for its abundance and electrochemical efficiency. In this sense, several studies have focused on investigating the activation mechanism of this metal in the OER. These previous studies showed that iron impurities present in the commercial KOH (reagent grade, 90%, flakes, Sigma Aldrich) used as electrolyte significantly alter the nickel catalysts activity [2,3]. Under these premises, water-based nickel lactate as precursor is combined with an aqueous suspension of graphene oxide to freeze cast hierarchical porous structures that are then thermally reduced. In this work, the electrochemical behaviour of these materials is studied for the OER reaction in basic medium containing iron impurities or purified [1] (figure 1a), observing as a result differences that indicate an important role of iron in catalysis. To complete this work, (Ni/Fe)-based graphene casted catalysts (different ratios of metal) are also prepared to study the activity of materials with iron in their composition. An improvement in activity was found by increasing the iron concentration when samples were tested in purified electrolyte (figure 1b). However, the activity of rGO-(Ni/Fe) materials is superior if experiments were carried out using electrolyte with Fe impurities. This shows that the Fe present in the electrolyte also influences the activity of samples that have Fe in their composition. To study the electrocatalytic behaviour of all the synthetized electrocatalysts, electrodes were prepared as follows: 40 µL of 2000 ppm catalyst inks using 0.02wt% Nafion on a 50:50 vol% IPA/H_2O as solvent were drop-casted onto a graphite disc current collector to form a thin film (0.1 $mgcm^{-2}$).

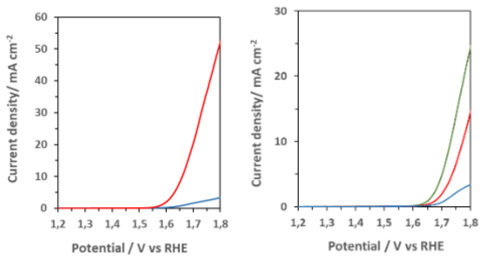


Figure 1. (left) linear sweep voltammetry comparison of rGO-Ni in KOH with Fe impurities (red) and purified (blue); (right) OER activity comparison of rGO-Ni (blue), rGO-(98Ni/2Fe) (red) and rGO-(90Ni/10Fe) (green) in KOH purified.

Design and fabrication of a low-cost printer head for extrusion of pastes by direct ink writing

Rodríguez-Lagar, P., Blanco, C., Santamaría, R., Granda, M., Álvarez, P., Rocha V.G.

Instituto de Ciencia y Tecnología del Carbono-INCAR, CSIC, 33011-Oviedo, España.
*E-mail: pablo.lagar@incar.csic.es

Key words*:* additive manufacturing, direct ink writing, electrodes.

New additive manufacturing techniques have set an entire paradigm for designers, engineers and scientists seeking ways to create objects with complex geometries at an affordable cost. The 3D printing industry has experienced a significant growth since its inception in the 1980s. Nowadays, there are seven types of additive manufacturing (AM) technologies, which together enable the production of objects for a wide range of applications.

Among the AM technologies based on material extrusion, the direct ink writing (DIW) technique stands out for its simplicity and versatility in terms of the wide palette of compatible materials. This technique consists of the extrusion of a pseudoplastic fluid filament designed with a specific rheology that ensures smooth flow during printing and stiffness of the printed object.

The aim of this study was to design and build a low-cost, lightweight printer head (Figure 1) which can be coupled with a commercial low cost Fused Deposition Modelling (FDM) printer, thus enabling DIW printing modes. To size the structure of the extruder system, a static stress simulation was carried out using finite element analysis. The structural parts that make the structure up were printed in PLA by an FDM printer. The operating principle of the device is as follows: the torque of a stepper motor is multiplied by a reduction gearbox (yellow part, Fig 1) and a trapezoidal threaded spindle transforms the rotation onto a linear movement.

The paste extruder system developed allows the printing of pre-loaded material in a 3 mL syringe using different nozzles (0.25-1 mm) being able to apply an extrusion force of more than 200 N. The new printer head has an affordable cost of 150 € and counts with automatic Z-axis levelling.

The developed device enables printing at room temperature with high solid content pastes from granular materials. In this work the pseudoplastic behaviour of the paste needed for DIW printing was achieved using a solution of 25 wt.% Pluronic F-127 as carrier of 85 wt.% Nickel powder (Alfa Aesar, 5-15 µm, 99.8% purity). Ni electrodes with a mesh-like geometry were successfully printed, which in turn increases the surface area, with low internal porosity of the pieces. The printed geometries could be suitable for electrodes in water splitting reactions after a post-processing consisting in thermal-annealing at 900 ℃, 1 h, in inert atmosphere.

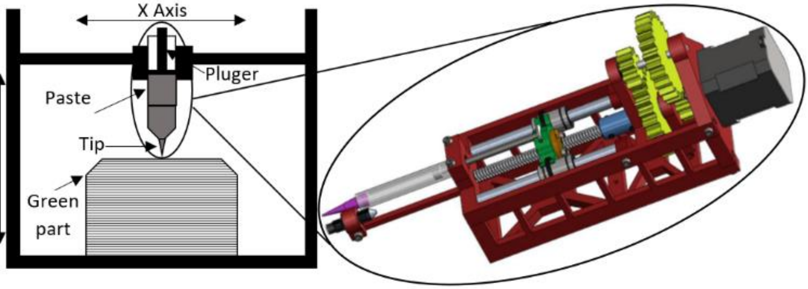


Figure 1. Schematic diagram of the DIW process (left) and CAD model of the printer head with syringe and nozzle (right).