

**MASSIVE ONLINE OPEN COURSE (MOOC)
ON MATERIALS UNDER EXTREME CONDITIONS
FOR KEY INDUSTRIAL SECTORS**

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**The VIRTUAL Centre for Integration of INNOVATIVE synthesis
and Processing METHODS FOR SUSTAINABLE advanced
Materials operating under extreme Conditions**



CONTENT

1. General overview
2. Synthesis, consolidation and manufacturing
3. Characterization
4. Modelling
5. Applications

ONLINE VIDEO COURSE

The access to the video please request the password by email to Dr Radu Robert PITICESCU [rpiticescu@imnr.ro], coordinator of SUPERMAT, or Dr Alain LARGETEAU [alain.largeteau@u-bordeaux.fr], coordinator of XtrMat2018.

1. GENERAL OVERVIEW

Introduction on the importance of advanced materials operating under extreme conditions to be written based on the SUPERMAT original proposal

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The need for materials working under extreme conditions (e.g. supporting simultaneously one or more external constraints related to high pressures, strains and strain rates, high or low temperatures, high erosion and corrosion environment, strong magnetic or electric fields, photon/radiation fluxes) is a key factor in meeting the increase in global energy challenges associated with minimizing the environmental impact in production, distribution and consumption of resources, which is demanded by future energy technologies. **Development and understanding of materials under extreme environments open new opportunities in every area of technology, including automotive and aerospace, military equipment, energy generation and storage, electronics, biomedical, chemical and photochemical, metallurgy and machining tools, etc.** The atomic and molecular origins of how any given extreme environment affects the physical and chemical degradation processes occurring in the bulk and surfaces of exposed materials is instrumental to design the next generation materials that can outperform current technology or enable new applications. This is the case, for example, of resistant materials for lead corrosion applications in nuclear fission and concentrated solar power systems. **In this regard, modern modelling tools play an instrumental role and are central to the SUPERMAT proposal.** Molecular dynamics computer simulations have significantly contributed to the understanding of damage processes in materials in different environments, over all time- and length- scales, thus opening new opportunities for developing new materials with tailored properties to withstand thermo-mechanical extremes. Numerical modelling for the analysis of multilayered coatings at individual length scales (Continuum, Molecular and Nano-scale, as well as multi-scale) has been reported intensively. Examples include Finite Element Method (FEM), Molecular Dynamics (MD), first-principles calculations and multi-scale modelling. On the manufacturing side, new processing methods enabling to produce bulk materials (e.g. *spark plasma sintering, field assisted sintering, gel casting*) with controlled the surface/interface properties have been extensively studied to obtain different materials solutions required in many fields of application. On the other hand, modern coatings methods (*physical, chemical, electrochemical*) feature advantages such as (i) versatility of materials range to be coated, (ii) properties independent of thermodynamic compositional constraints, (iii) the ability to control defects states and concentrations, (iv) the controllable production of different microstructures and morphologies (including nanosized architectures), (v) the ability to accommodate large residual strains associated with thermal cycles, and (vi) ecological benefits.

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Benefit of extreme pressure in materials sciences

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INTRODUCTION

Initially, high pressure has been applied mainly in Physics to study the geology of earth and Chemistry aspects to develop diamond and quartz for industrial applications. The development of high pressure in different scientific domains are strongly dependent on the knowledge of the associated technologies. At the beginning, high pressure was mainly used in synthesis of minerals from extraction of metals from ores and for crystal growth of α -quartz called as hydrothermal crystal growth. In the case of ceramics, application of very high pressure has been reported to have yielded nanostructured materials. High pressure is currently used actively as a probing tool to study the structure, chemical bonding and physical properties to understand the fundamental behavior of materials under high pressure. High pressure techniques are also employed in developing new and novel materials to unique properties. Other vital applications of high pressure in material science includes fabrication of high strength materials, compensate the stoichiometry of the non-stoichiometric compounds with gas pressure and to investigate the meta-stable materials that will not change its characteristics during ambient pressure states. In the present talk, the benefits of high pressure in various domains of materials science ranging from nanomaterials, bulk crystals, fabrication of ultra-hard materials and high pressure as a characterization tool will be discussed in detail.

STATE OF THE ART

High pressure research over last six decades was employing different workhorse tools of high pressure technology such as diamond anvil cells and large volume synthetic presses such as multi-anvil, toroidal, belt and piston-cylinder various research solutions. The wide range of aforesaid technology was employed to find ultrahard materials and cutting tools, structure-chemical-property relationships and understanding of various properties under dynamic compression. High pressure technology is also used in food technology and packaging methods, where the materials science and biosciences are in unison to obtain very interesting properties than obtained by other conventional techniques such as decontamination and gamma ray irradiation. Replicating the geomimetic properties, high pressure technology is successfully employed in the field of crystal growth popularly termed as “hydrothermal crystal growth”. The aforesaid technique involves employing high pressure and low temperature (orders less than its melting point) to obtain single crystals for technological applications. The materials which have interesting properties in their low temperature phase while lost with high temperatures owing to their phase transitions cannot use conventional high temperature single crystal growth techniques. In the present talk we will also discuss about the single crystals of Quartz obtained by employing high pressure technique. Other example is the obtaining nanostructured ceramics for optical and biological applications.

RESULTS

Recent trends focus on the utilization of piezoelectric material owing to its increasing demands for manufacturing of actuators and high frequency stability applications. These applications include timing and frequency control circuits, radio frequency low pass filters for video and digital cameras etc. α - Quartz type materials are one among the best known for piezoelectric applications. The substitution of germanium (Ge) in the α -quartz structure is a method investigated to improve the piezoelectric properties and the thermal stability of α -quartz. α - Quartz (SiO_2) and Germanium Oxide (GeO_2) are the current frontrunners for piezoelectric applications due to its high electromechanical coupling co-efficient. It is a difficult task to obtain large crystals of SiO_2 by conventional crystal growth techniques. However with hydrothermal crystal growth, where the crystal growth is carried out under subcritical by varying temperature and pressure, helps in obtaining single crystals. The various parameters and their physico-chemical kinetic processes in obtaining crystals of SiO_2 requires detailed investigation. As the solubility of SiO_2 in water is slow, conventionally NaOH is added to accelerate the crystal growth rate. In the present work, we have demonstrated the growth of $\text{Si}_{0.8}\text{Ge}_{0.2}\text{O}_2$ single crystals by hydrothermal at high pressures > 2000 bar.

DISCUSSION

High-quality synthetic SiO_2 α -quartz is industrially produced but has certain limitations such as low electromechanical coupling factor of about 8% and degradation of its piezoelectric properties from 250 to 573 °C due to increased disorder followed by the $\alpha - \beta$ phase transition. Other materials in this family are well known for their improved piezoelectric properties and higher thermal stability. It has already been shown for pure SiO_2 α -quartz that these properties could be improved by substituting some of the silicon atoms in the network by larger atoms such as germanium. Until now, hydrothermal crystal growth is the only technique, which can be used to obtain large $\text{Si}_{1-x}\text{Ge}_x\text{O}_2$ crystals. By optimizing the temperature gradient and growth rate, it is possible to limit OH contamination. The growth rate of SiO_2 is slow; hence, some mineralizers such as NaOH and Na_2CO_3 are used. However, in the case of $\text{Si}_{1-x}\text{Ge}_x\text{O}_2$, the presence of Na^+ ions induces the formation of sodium germanates ($\text{Na}_4\text{Ge}_9\text{O}_{20}$), which precipitate in the bottom of the autoclave leading to a decrease in the germanium content in the grown crystal. With the help of high pressure we have shown the possibility of incorporating Ge in to the matrix and at the same time used water as a solvent for crystal growth.

CONCLUSIONS

In the abstract, we have shown one of the possible usage of high pressure and how it is beneficial on the materials properties. During the talk, many similar examples pertaining to high pressure and their role in the fabrication of cutting tools, nanostructured ceramics and enhancement of properties will be presented and discussed in detail.

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Impacts of the High Pressure on materials at nanoscale

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Abstract

Under high pressure in the GPa or tenths of GPa range, the atomic volume of bulk materials can be reduced in the order of 10% or more. The associated bond length contraction may lead to strong changes in their properties including the electronic structure. With progressive compression, competing atomic organizations may become more favorable and phase transitions between different crystallographic structures take place. Therefore high pressure and high temperature techniques have extensively been used to elaborate new materials since the first synthesis of synthetic diamond in 1954. Since the mid 90-ies, the nanoscience is a booming field. Moving from the macroscale to the nanoscale domain can lead to severe changes in the physical properties of materials. At the nanoscale, the prominence of surface atoms, involving a different contribution to the cohesive energy through their associated surface energy, can totally modify the phases energy landscape with many different consequences (San-Miguel, 2006). Depending on the importance of such modifications, (i) the phase diagram may be just shifted with changes in the transition pressures or (ii) involve new crystallographic changes, (iii) or amorphous structures or (iv) even introduce the (meta)stabilization of new phases. Consequently, the transformation or consolidation of nanomaterials under high pressure offers a promising approach for the engineering of new materials. We will review the present knowledge of the high pressure effects on nanocrystals (Machon et al., 2011), carbon nanotubes (Balima et al., 2016; Torres-Dias et al., 2015) and fullerenes (Poloni et al., 2009). Recent advances and future challenges in the use of extreme thermodynamic conditions to develop new functional nanomaterials will be reviewed together with the specificities of the experimental environment required for these investigations.

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2. SYNTHESIS, CONSOLIDATION AND MANUFACTURING

Manufacturing and synthesis of materials in extreme conditions in the path of Gérard Demazeau towards exploring pressure potentialities

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Abstract

Temperature and Pressure are the principal parameters in Universe, pressure presents the largest scale in comparison to temperature. The range of pressure is very large, from approximately 10-30 bar (partial pressure in the space of hydrogen) to 1030 bar (pressure in the center of a neutron star). More than 90% of materials in universe is submitted to a pressure higher than 106 bar. Then, 1 bar on the earth is like an exceptional condition. The use of pressure parameter is important for improving knowledge of phenomena in chemistry, physics, biology and in other domains. Consequently this knowledge is very useful for development of industrial processes to fabricate materials for different applications. Development of pressure equipment is quite recent in comparison to temperature because research in high pressure needs interdisciplinary knowledge such as mechanics (to resist pressure), chemistry (to avoid corrosion), physics (to measure pressure and temperature), etc. Materials fabricated by application of pressure are comparatively less developed than those fabricated by application of temperature. The design of high pressure equipment depends mainly on the media used, which could be gas, liquid or solid and also depends on the compressibility of this pressure transmitter. The objectives of such equipment for laboratories is either synthesis of materials or in situ characterization and are mainly employed for synthesis in industrial applications. During the last half century, the research fields of Professor Gerard DEMAZEAU led to initiate new developments for high pressure equipment. These advancements led to the innovative design of HP equipment for development of new domains of investigation actually in materials science such as sintering at low temperature for thermal sensitive composition, to densify biocomposite with cold decontamination simultaneously, to reach very high density for obtaining optical ceramics, to consolidate porous materials, to diminish parameters of synthesis (P, T, t) for industrial transfer, etc. The main concepts governing the combination of pressure and temperature effect on materials synthesis will be described for driving interesting properties.

Best available methods for developing ceramic coatings for high temperature applications

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INTRODUCTION

Functional metal oxides are important classes of materials that display insulative, semiconductive, conductive (electronic, ionic or mixed), magnetic and even superconducting behavior. In general, these materials are complex multicomponent systems, and their properties are achieved via manipulation of the defect chemistry imposed through alloying. High attention is paid to fabricate these materials in the form of thin films or as thick film multilayers so as to harness their capabilities within devices including RF/microwave systems, power electronics, sensors, batteries and fuel cells. Wide range of future opportunities are foreseen related to high-temperature and harsh environment applications. The number of materials that can be used in extreme environments is very limited because they are restricted by some basic requirements: high melting point; chemical inertness; low thermal conductivity; no phase transformation between room temperature and operation temperature; good adherence to the metallic substrate; thermal expansion match with the metallic substrate; low sintering rate of the porous microstructure.

STATE OF THE ART

In general, deposition processes may principally be divided into two types: (i) processes involving droplet transfer such as plasma spraying, arc spraying, wire-explosion spraying, and detonation gun coating; (ii) processes involving an atom-by-atom transfer mode such as the PVD processes of evaporation, cathodic arc deposition and sputtering, chemical vapour deposition (CVD), and electro-deposition.

The main steps in the formation of any deposit are: (1) Synthesis of the material to be deposited by transition from a condensed phase (solid or liquid to the vapour phase or by a reaction between the components of the compound; (2) Transport of the vapours between the source and substrate and (3) Condensation of vapours followed by film nucleation and growth.

RESULTS AND DISCUSSION

The air plasma spraying (APS) process is an adaptable and cost effective technique with high deposition rate (in m/s level) and is most suitable for producing thicker coatings. The process is versatile and has been used to deposit TBCs for many years. APS is characterized by the high temperature of the plasma jet, which allows the melting of high melting point materials to yield an effective thermal spray. The high speed Ar-He or Ar-H₂ hot plasma jet dissolves the ceramic and metallic feedstock powder and accelerates it to high velocity. The impact of the spray onto the prepared surface of the substrate forms a coating by solidifying rapidly. The plasma spray creates “splats”, the flattened particle boundaries that run parallel to the ceramic-metal interfaces. APS coatings are characterized by a highly porous flat and thin (lamellar) microstructure with the presence of mini pores and cracks (Fig.1).

EB-PVD is a popular processing technique for ceramic top coats in TBCs. The microstructure of EB-PVD coatings exhibits improved strain tolerance and thermal shock resistance, which significantly enhances their life time. The crystal nuclei form at favoured sites and grow both laterally and along the thickness to form individual columns, which yield a high inter columnar porosity. Such coatings have a lower in-plane Young's modulus, which increases the relief of stress during thermo-mechanical loading. The resulting understanding of the nature and architecture of the porosity has allowed their impact on the thermal and mechanical properties of the coatings to be established. EB-PVD is often preferred over APS because it offers a higher growth rate and columnar coatings with higher lifetime. EB-PVD Yttria-stabilized zirconia top coats have demonstrated good performance by surviving 1200 thermal cycles with 1 hour duration. EB-PVD made possible to obtain new coating systems such as perovskite BaZrO₃ (Fig.2) or pyrochlore La₂Zr₂O₇ thin films.

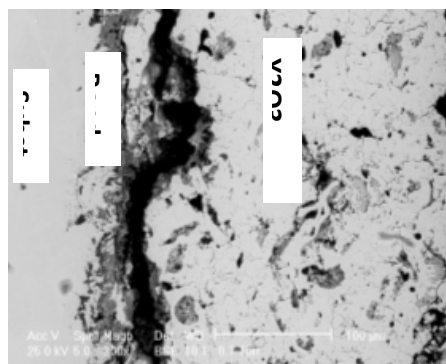


Fig. 1. SEM of YSZ thermal sprayed TBC

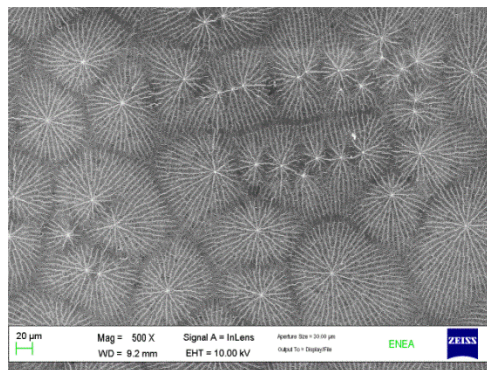


Fig.2 SEM of BaZrO₃ EB-PVD film

CONCLUSIONS

Different oxide materials with various structures are available to obtain coatings with design properties for extreme environments applications. The best available technologies are those allowing to control in a reproducible and convenient way the structure, properties and adhesion of the coatings assuring an economical implementation in the desired applications. For these materials thermal spraying and EB-PVD seems to be the most preferred methods and they will be further selected for different tests on new oxide materials coatings to be implemented for extreme environmental applications. New coating material systems with very high thermal stability may be obtained.

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Materials consolidation by high pressure in solid and liquid medium for extreme conditions

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INTRODUCTION

Researchers are developing new processing and development for variety of applications. These continuous research processing leads to remove the existing hurdles and create new protocols for materials processing and consolidation. Industries cannot undertake a completely new processing technique and hence is dependent on the well-established technologies. National and international labs work on the small scale to develop and improve the new technologies and old technologies respectively. New developments of materials consolidation includes new methods of materials handling, powder processing/preparation, sintering, coating and surface finishing. Vital components of materials consolidation involves shaping of starting material to the desired shape and geometry in order to obtain required, structural, mechanical, chemical and thermal efficiency. The aforesaid depends mainly on the method of choice of sintering process. High pressure technology recently has removed the threshold limit of high pressure and high temperature employed for fabrication technology. These advances in the material consolidation advances have wide spread applications in the field of airplanes, wind turbines, cutting tools, ultra-high temperature ceramics, filters for metal ores and meta-stable compounds. High pressure technology can be divided into 3 divisions based on medium of pressure transmission such as (1) Solid (2) Liquid and (3) Gas. The perspective of the talk will be to elaborate on the various sintering techniques employing solid and liquid medium to generate high pressure and their recent advances for the fabrication of materials to be employed extreme conditions.

STATE OF THE ART

Recent surge of using high pressure technologies for sintering is an important milestone in the development of materials consolidation. Materials with microstructure made from nanograins are preferred owing to their increase in hardness and good fracture strength. The behavior of material consolidation is highly dependent on fabrication methodology, composition, grain boundary and other important processes such as diffusion, creep, crack propagation, oxidation, corrosion and growth of defects at high temperature. In the case of materials such as refractories, the challenge is to obtain dense ceramics without employing any sintering additives. The competition between densification and microstructure coarsening occurs parallel during densification of nanopowders. High pressure sintering techniques reduces the sintering temperature and time to activate solid state diffusion. During the final stages of sintering gives lead to rapid grain growth, which is suppressed /improved by applying high pressure. Successful employment of high pressure technology for diamond and related materials, refractories, high dense transparent ceramics, diffusion bonding and composites lead to improvements in their properties.

RESULTS

Transparent ceramics with nanograins is one of the widely studied topics by the ceramics society. In order to obtain the transparent ceramics, it is important to obtain maximum density and porosity in the orders of 100 ppm/ < 0.01 vol %. Various sintering parameters interplay to obtain the desired result, where the prime factors being sintering temperature (Ts), dwell time (t) and Pressure (Ps) and the point of pressure application (AP). With the help of the aforesaid sintering parameters, it is necessary to optimize the conditions to obtain optimal grain size, density and porosity. Other than the grain boundaries, porosity is one of the main scattering centers of light. In order to obtain the minimal porosity, it is necessary to stay at high sintering temperatures for long time, but at the risk of grain growth, which will impede the transparency of the ceramics. Usually the grain growth is accompanied with the pore growth. It is necessary to have the nanostructured materials to have improved mechanical strength which in turn positively/negatively (depends on inherent material property) influences other functional properties. Rapid sintering techniques such as Spark Plasma Sintering (SPS) helps in obtaining maximum densification in short duration of time at comparatively lesser sintering temperatures in comparison to other classical sintering. Simultaneous application of pressure and the help of Joules heating aids in avoiding Ostwald's ripening. Application of very high pressure has been reported to have yielded nanostructured materials. Most of the current transparent ceramics are limited only to cubic materials, currently extended to non-cubic materials as well though in early stages.

DISCUSSION

Optical materials with high refractive index (> 2) have attracted the interest of researchers. Amongst Zirconia and Yttria stabilized Zirconia have been widely studied in the form of single crystals, thin films and ceramics owing to its high refractive index and high mechanical and thermal properties. In the room temperature, pure Zirconia (PZ) exists in the monoclinic form, 3 Yttria stabilized Zirconia (3YSZ) in a mixture of tetragonal and monoclinic form and 8 Yttria stabilized Zirconia (8YSZ) exists in tetragonal form. In order to obtain the cubic form of Zirconia, it is necessary to heat the material $> 2200^{\circ}\text{C}$. However if the influence of pressure it is possible to tune the tetragonal form which has properties close to cubic Zirconia in terms of transparency.

CONCLUSIONS

At ICMCB, we have studied the influence of pressure on grain size, porosity, and density, mechanical and optical properties. The fabrication methodology to obtain transparent ceramics of PZ, 3YSZ and 8YSZ by spark plasma sintering and the influence of pressure on its various properties will be discussed in detail. Similar examples of the high pressure on the influence of material properties arising from different sintering methodologies will be discussed with apt examples. Discussions on the innovations of solid and liquid pressure medium will help to understand their employment in the materials under extreme conditions.

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Reactive and Non-reactive Spark Plasma Sintering of Ultra High Temperature Ceramics and related applications

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Abstract:

Ultra High Temperature Ceramics (UHTCs) represent an important class of ceramics with a unique combination of physical, thermal and mechanical properties, such as melting temperatures above 3000°C, high hardness, high electrical and thermal conductivity, high refractoriness, chemical inertness, good thermal shock resistance. These characteristics make UHTCs suitable for several room- and high-temperature structural applications, like cutting tools, high temperature crucibles, microelectronics, thermal protection structures for aerospace vehicles. Moreover, UHTCs possess also good spectral selectivity and low emittance at high temperatures, of interest for energy applications. Due to the high melting temperature, sintering of UHTC powders requires high temperature and pressure assisted technique, but, under these processing conditions, residual porosity and coarse microstructure are often obtained. Low heating rates and long processing time are generally necessary, when traditional Hot Pressing (HP) is adopted. Alternatively, dense UHTCs with uniform and fine microstructure can be fabricated, relatively faster and at lower temperature levels by taking advantage of the Spark Plasma Sintering (SPS) technology. Densification could be also improved when starting from powders obtained by Self propagating High-temperature Synthesis (SHS), whose higher sinterability is related to higher defect concentration and fine grain size which favor the formation of stronger bonds at the interfaces among the different ceramic phases formed in-situ. The preparation of bulk monophasic MB₂ and MC (M = Zr, Hf, Ta, Ti) and related composites by means of reactive SPS (RSPS) and SHS followed by SPS (SHS-SPS), is described in this work. UHTC powders have been consolidated by SPS at 1750-1900°C, to produce 95% or denser materials. It was generally found that SHS-SPS approach allowed for the obtainment of denser materials, and more uniform and finer microstructure, under relatively milder conditions with respect to RSPS. Hardness, fracture toughness and oxidation resistance of dense UHTCs are similar to, and in some cases superior than those related to analogous products synthesized by alternative, less rapid, methods. The combination of the SHS and SPS techniques was also recently exploited for the preparation of porous graded materials (PMGs), for solar energy applications, being absorption conditions for the incident radiation improved on porous surfaces. Specifically, PGM products were obtained after consolidation by SPS of ZrB₂ SHS powders by taking advantage of an asymmetric die configuration with changing cross section. Due to the temperature gradient established along the longitudinal direction, porosity changes were generated across the volume.

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Influence of current parameters on phase composition for superhard composites sintered under high pressure

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Abstract

Commercially available polycrystalline diamond compacts (PCD) consisting of a diamond-cobalt layer on a WC-Co substrate are used for drilling and machining applications. The presence of the cobalt phase in a diamond layer has a strong influence on decreasing its thermal resistance. Thermal stability of a PCD material can be defined as the resistance to graphitization in an inert atmosphere and at elevated temperatures. It is possible to increase thermal resistance of PCD materials by reducing the cobalt content or by manufacturing diamond compacts with a non-cobalt bonding phase. Past studies have confirmed that introducing phases of high-temperature resistance ceramic to polycrystalline diamond improves its resistance to oxidation and graphitization in high temperatures. Diamond is an allotropic form of the element carbon, with a cubic structure, which is thermodynamically stable at pressures above 1.6 GPa at room temperature and metastable under atmospheric pressure. By annealing the polycrystalline diamond in contact with air, two processes occur simultaneously: one is the oxidation of coal from the diamond to form CO and CO₂ gases, the second is transition into graphite. For the presently known PCD materials, both these phenomena occur at similar temperatures of about 1000 K. Studies regarding temperature resistance of different diamond composites with the addition of carbides and borides, obtained using HP-HT method (without pulsed current) confirm that the introduction of a high-melting phase positively influences the stability of the diamond composites at high temperatures, and diamond composites exhibit high values of hardness and density at these temperatures. The aim of the research was to analyze the influence of pulsed current under ultra-high pressure HP SPS / FAST (Spark Plasma Sintering / Field Assisted Sintering Technology) on the phase composition of diamond composites containing a boride bonding phase. The FAST method applies current pulses lasting from a few to a few hundred milliseconds, and the current increases up to several thousand amps. The main advantage of sintering with the use of high-current DC pulse, which requires considerably more energy than other methods, is a very short duration of the process (up to several minutes) The surface of particles is activated and ultra-high pressure fulfills the conditions required to obtain diamond composites using FAST method. In this work, an HP SPS device was used to sinter diamond composites with titanium boron bonding phase. The material thus obtained was then compared with a HP-HT sintered sample, to investigate the influence of the heating by means of direct pulsed current on the crystallite size and phase composition of diamond with 10 wt.% of Ti+2B bonding phase. Both HP SPS and HP-HT processes were carried out during 20s at 8.0±0.2 GPa and at the temperature of 1650±50 °C. When comparing HP-HT with HP SPS, the XRD analysis carried out showed that the different types of current used for heating have a significant influence on the kinetics of the sintering process, which is visible in the differences in phase composition and in the level of lattice strain.

High-Energy Ball Milling: a powerful technique for the synthesis of new alloys and nanostructured materials

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Starting from the pioneering work of J. Benjamin and co-workers in late '60s and early '70s, the mechanical processing of powders by ball milling (BM) has rapidly become one of the most intensely studied subjects in materials science [1]. Extensively used to fabricate and activate inorganic and organic materials in granular forms, it revealed a unique capability of inducing the formation of metastable phases, i.e. amorphous alloys and nanostructured compounds [1]. Hence, the enormous interest attracted so far. BM is a relatively simple powder processing method susceptible of industrial exploitation on different scales [1-4]. In a typical experiment, the reactor is filled partially with powder and milling tools in the desired mass or volume ratio. The periodic movement of the reactor, or of one of its parts, allows milling tools to collide with each other. During each collision, a fraction of the powder charge is trapped between the milling tools and subjected to high-strain-rate mechanical loading, which generates non-hydrostatic stresses at the points of contact between powder particles. The intensity of such local stresses can be sufficient to induce severe mechanical deformation processes accompanied by cold-welding and fracturing [1-4].

Physical and chemical transformations can also take place, driven by the repeated mechanical deformation. In general, individually processed metals develop a nanostructure with final grain size in the range between 5 and 20 nm depending on metal and processing conditions [5-8]. For metal mixtures, grain size reduction can be accompanied by mechanical alloying, which involves the formation of crystalline and amorphous alloys by gradual dissolution of the metals into each other [1-4].

The formation of metastable structures is related to the far-from-equilibrium processing conditions experienced by metals [9,10]. Characterizing such conditions in terms of fundamental quantities and throwing light on the mechanisms underlying transformations is a necessary step to foster a definite progress in the field and meet the increasing demand for a successful technological application of BM. To this aim, various open issues have to be suitably dealt with. For instance, is it possible to refer the kinetics of mechanically activated transformations to individual collisions? How do the properties of powder affect the kinetics? What is the effect of a given metal on the mechanochemical behaviour of the other one? The present contribution aims at providing an overview on the state of the art of experimental and theoretical attempts addressing the above mentioned issues.

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Continuous synthesis of nanomaterials using high pressure microfluidics

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Abstract

Over the last few years, a new field of investigation, so called: high pressure/high temperature microfluidics has been quickly developed with the idea to combine the advantages of size reduction and hydrodynamics control provided by microfluidics tools (advanced control of the operating conditions, reproducibility, in situ, in line and on line characterization techniques implementation, fast screening capability, improvement of heat and mass transfer and low reagent consumption during optimization) to the properties of fluids systems operated in non conventional conditions (hydrothermal/solvothermal and supercritical conditions). The recent development of microreactors able to withstand such conditions has opened avenues towards numerous opportunities to study and characterize a large numbers of processes, which are generally limited to the use of blind stainless steel devices. This talk will first highlight the main strategies used to develop high pressure / high temperature compatible microsystems. Then, some applications of HP/HT microreactors will be presented. In particular, we will focus on the work realized at ICMCB concerning the synthesis of inorganic nanostructures at supercritical conditions in micro- and millireactors, which is a versatile approach that takes advantages of the continuous flow synthesis and the fast heat transfers provided by the small devices, while benefiting from the high supersaturations occurring at supercritical conditions, leading to high quality nanocrystals.

Hydrothermal sintering: a low temperature densification process for ceramics and multimaterials. Recent trends and prospects

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The development of new high performance advanced materials faces the challenge of implementing low temperature densification processes to overcome current technological limitations. Therefore, the impressive performances of processes such as Cold Sintering Process (CSP) [1-4], Water-assisted Flash Sintering or FAST/SPS, cool-SPS create a tremendous excitement in the ceramists' community. In this context, the hydro-/solvothetical sintering (HSS), inspired by the natural processes of geological and biological mineralization, has recently emerged as a major opportunity to develop new and/or optimized materials that respond to today's scientific, technological and related socioeconomic issues [5-8]. Both HSS and CSP are based on dissolution-precipitation mechanism induced by a pressure solution creep as a driving force for the densification. However, they differ from each other due to the balance between thermodynamics and kinetics that strongly influences the predominance of the involved elementary steps. In the thermodynamically controlled HSS, the operating temperature range (<450°C) is not suitable for appreciable bulk diffusion but is sufficient to enhance strong reactivity at the interfaces due to hydro-/solvothetical conditions. These specific conditions also represent a powerful lever to tune the nature of the precipitated phase. The objective here is to present opinions and propose future outlook for HSS based on recent advances. The general background and history of HSS will be first highlighted. The experimental apparatus and its specific technological design evolution will be described. All the potentialities of HSS will be presented mainly from the results obtained on silica used as a common theme to study the sintering of amorphous (silica) or metastable (α -quartz) materials, to fabricate 0-3 type functional nanocomposites (manganite-silica). A description of the current understanding of chemical and mechanical-chemical mechanisms necessary for densification will be proposed. Finally, opportunities and challenges to expand the method more generically to other systems will be discussed.

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High pressure synthesis of new light materials with outstanding properties

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Abstract

Modern high pressure chemistry represents a vast exciting area of research which will lead to new industrially important materials. Compared to traditional solid-state chemistry, this field is only just high pressure chemistry takes advantage of advances in X-ray diffraction. Actually, research over the last ten years has seen intensive use of in situ synchrotron radiation for direct observation of both stable and metastable synthesis pathways under extreme conditions. This strategy removes the permits much greater precision in establishing the thermodynamic conditions needed for accessing metastable states.

In this talk, I will show that the use of very high pressures and temperatures combined with the in situ probe by X-ray diffraction with synchrotron radiation is the methodological key to control the composition and microstructure (nanostructuration) of new bulk light materials (borides, carbides, Si compounds, etc.) with outstanding properties and I will give many examples from our recent studies.

3. CHARACTERIZATION

Introduction of new material in space - Qualifaction testing needs

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INTRODUCTION

Materials used for space applications are not different to materials (metals, composites ceramics) used in other fields. However materials in space have to survive the harsh environment in space such as atomic oxygens, high energetic particles, ionization radiation, space debris and micro meteorites and high and low temperatures where the conditions change with the individual space missions. Therefore, a number of tests following dedicated standards (ECSS) have to be done, when new materials are planned to be used in space applications.

STATE OF THE ART

For testing on coupon level tests like mechanical characterization, thermal vacuum compatibility (Thermal, Cycling, Outgassing, CTE and CME) follow the typical standards from ESA (ECSS including other standards like ASTM, ISO-DIN, etc.). Already at subcomponent and component level, only guidelines for the testing activities such static load test, dynamic shaker tests or bake out / thermal cycling exist in typical ECSS standards. The individual procedures differ from test article to test article, space application with its working environment (orbit, deep space, special science missions). Therefore, individual tests are required on subcomponent and component level. State of the art e.g. subcomponent mechanical static and dynamic tests is the usage of a number of sensors such as strain gauges, accelerometers or load sensors to measure the response of the structure. Additional sensors such as acoustic emission sensors for the assessment of early damage onset or growths of existing damages possibly arising from exposure to thermal vacuum are rarely used. In general, there is a need for more information of the in-situ behaviour of components under space relevant conditions.

RESULTS

Aerospace & Advanced Composites GmbH works for the European Space Agency (ESA) since more than 25 years as external materials test house. Within this talk, examples of space relevant tests performed at AAC for the introduction of new materials in different space applications such as cryogenic tanks, planetary exploration or mechanisms such as gears will be shown.

CONCLUSIONS

Harsh space environment requires special testing for the qualification of materials used for satellites, spacecrafts, launchers etc. Therefore often special testing facilities have to be developed that allow the assessment of the behavior of the materials under space environment.

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EU FP7 project: No. 263162: “HarmLES—Dry lubricated Harmonic Drives for space applications”

Corrosion tests for metals and alloys

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Corrosion of metals and alloys is one of the most relevant issues in industrial and civil engineering: it is a process of material or metal deterioration or surface damage in an aggressive environment.

A wide range of examples can be identified, from atmospheric corrosion of steel structures to corrosion of dental alloys due to the effect of saliva and food. Corrosion is a chemical or electrochemical process, in which the valence of metals passes from zero to a positive value, through transfer of electrons to the environment.

The process is ruled by electrochemistry principles, and influenced by such parameters as redox potential, electrolyte composition or temperature.

In order to identify the regions of corrosion and passivation, electrochemical tests can be used at laboratory scale, through manipulating and measuring of potential or current applied to a specimen.

Most experiments impose a potential on the working electrode and measure the resulting current.

In potentiodynamic experiments, the applied potential is increased with time while the current is constantly monitored. The current is plotted versus potential, and the resulting plot can be used to obtain information on stability and corrosion kinetics.

In this lecture, a general overview of electrochemical processes involved in corrosion of metals will be done, with particular regard to concepts such as stability, passivation and corrosion kinetics. The main electrochemical tests will be presented, and correlated to the phenomena occurring at the electrode/electrolyte interface.

Some example of corrosion tests applied to several materials will be given, using data obtained in our laboratory under different operative conditions.

X-ray diffraction under pressure using Diamond Anvil Cell (DAC): Example and specificity of soft molecular materials

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Abstract

Initially dealing mainly with variable temperature measurements only, crystallography under nonambient conditions plays a crucial role to understand physical properties of materials. The role of pressure on materials was explored later due to the complexity of the sample environment, thus the high pressure structural investigations start to grow in the late 1950s with the invention of the Diamond Anvil Cell (DAC) in 1958[1], that was modified in 1974 by the small Merrill-Bassett DAC adapted to commercial diffractometers [2] As the application of pressure is known to change interatomic distances, new properties or rare behaviors are expected under pressure. Exploring the crystal structures of materials under pressure is then of the greatest interest to understand the structure – properties relationships, stabilizing new phases or exploring the phase diagram of materials. Since the late 1950s several structural investigations have been performed first essentially on pure elements and then on inorganic materials. The investigated pressure doesn't stop to increase to reach pressure above 400 GPa nowadays. Nevertheless, obtaining high-pressure structural data is, as a general matter in Science, still a challenge especially when combining several thermodynamic variables such as pressure and temperature, or when data are recorded on molecular materials. Crystal structure investigations under pressure performed on molecular systems significantly starts only in the early 2000s and represent only about 0.2% of the CSD database. Addressing the additional difficulties due to molecular compounds necessary includes instrumental and methodology developments in order to access to a reliable characterization, taking account their specificities such as low symmetries, poor crystallinity and relatively low and narrow pressure working range. Surprisingly, though the scientific community still develops new technics to get accurate data at very high pressure for inorganic materials, working with soft molecular material at pressure below 1 GPa is still challenging especially on a laboratory X-ray source. The crystallographic investigations on molecular compounds under pressure are then scarce despite the new, unexplained or very rare behaviors observed in numerous examples. Typically, despite the crucial role of polymorphism on such materials, (P, T) phase-diagrams of molecular compounds are almost unexplored. After some general aspects X-ray diffraction under pressure, the specificity of molecular compounds will be discussed with some illustrations of experimental setup to address them. Selected examples in the domain of molecular Spin CrossOver (SCO) complexes showing negative linear compressibility [3], unexpected pressure induced phase transition[4] and/or very singular behaviors[5] will be detailed. Finally, the pressure induced SCO on a new compound accurately followed by variable pressure and temperature powder X-ray diffraction will be presented.

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4. MODELLING

Multiscale modeling of multifunctional nanocomposites: Identification of parameters influencing the mechanical, electrical and thermal properties

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INTRODUCTION

Multifunctional nanocomposites represent the next generation of engineering materials as they possess attributes beyond the basic strength and stiffness that typically drive the design of structural materials. Multifunctional nanocomposites can be designed to have integrated mechanical, electrical, thermal, magnetic, sensing and possibly other functionalities that work in synergy to provide advantages that reach beyond that of the sum of the individual capabilities. Materials of this kind have tremendous potential to impact future structural performance by reducing size, weight, cost, power consumption and complexity while improving efficiency, safety and versatility.

It is clear that there are a number of important factors to consider in the design and fabrication of multifunctional nanocomposite materials as it is highly possible in some cases the choices made to tailor one property to dislocate another property. At present, the development of multifunctional materials is done through a trial and error process comprising repeated manufacturing trials and tests. Such a process is highly cost- and time-consuming. An alternative path is the development of a simulation-based design tools.

In this lecture, multiscale models developed for identifying material and fabrication parameters influencing the mechanical, electrical and thermal properties of carbon nanotube (CNT)-reinforced polymer nanocomposites will be presented.

STATE OF THE ART

Classical simulation-based design tool comprises two main steps: the understanding of the link between processing-structure-properties-performance by following a deductive approach and the use of the knowledge gained in the first step in an inductive manner to achieve desired properties and performance by determining the appropriate processing and structural parameters. Both steps require a multiscale modeling approach due to the difference in the scales between the different materials.

The reported models developed for the evaluation of the properties of CNT-based nanocomposites can be categorized into molecular dynamic simulations, analytical modeling approaches and continuum mechanics approaches [1-4]. Molecular dynamic simulations are focused on small time and length scale calculations and cannot be used by multiscale models. Analytical approaches are limited to the micro/mesoscale estimation of the elastic properties having no versatility to incorporate important factors that possibly

counterbalance the role of CNTs as reinforcements. On the other hand, continuum mechanics methods, mainly in the form of finite element analysis, have the potential to be used for parametric evaluation of the properties of CNT-based nanocomposites and modeling of transition from the nano-scale to the macro-scale on the presumption that they incorporate the necessary information from the atomic scale.

RESULTS

In the present work, investigation is carried out on the understanding of material parameters and processing factors affecting the mechanical, thermal and electrical properties of CNT/polymer nanocomposites using numerical and analytical models. The material parameters considered are the CNT aspect ratio, the CNT waviness, the thickness and stiffness of the interphase. The processing factors considered are the CNT volume fraction, the formation of agglomerates and the number and arrangement of CNTs in the agglomerates. The investigation is conducted by means of representative unit cells (RUCs) of CNT agglomerates developed using the DIGIMAT software. The RUCs are solved numerically using the finite element method and analytically using the Mori-Tanaka method. At the same time, homogenization of the RUCs is applied through the use of periodic boundary conditions. The results from the parametric study reveal that the considered parameters and factors govern the reinforcement effectiveness and, under specific combinations, could counterbalance the multifunctionality of nanocomposites.

CONCLUSIONS

Continuum mechanics-based multiscale models are capable of predicting the properties of multifunctional nanocomposites as functions of critical material and processing factors, provided they incorporate the necessary data from the atomistic scale. Thus, the continuum mechanics-based multiscale models are suitable to be used in simulation-based design tools.

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Application of the nano-calphad method to select stable binary nano-grained alloys

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INTRODUCTION

The goal of this lecture is to show how to select nano-grained alloys being stable both against coarsening and precipitation (and also against corrosion). The selection principle is based on chemical thermodynamics applied to nano-materials, called also “nano-Calphad”. First it is shown that nano-grained solid polycrystals can be stable against coarsening only, if at least two components are present, if they repulse each other and if one of them strongly segregates to the grains boundaries.

STATE OF THE ART

This subject started with the paper of Weismüller in 1993 and is being developed since [1-6]. One of the most recent results of Schuh et al [5-6] is that W-Ti is the “best” stable nano-grained alloy, while the same model excluded the W-Ag nano-alloy as unstable. One could think the work done so far is sufficient. However, there is a common problem in all papers published so far: this is the ill-defined equilibrium between the bulk of the grains and the grain boundary. In this sub-field a new concept was published recently by the author [7-8]. This new concept leads to an improved version to model the stability of nano-grained segregated alloys against both coarsening and precipitation.

THE ESSENCE OF THE IMPROVED THEORY

Nano-grained crystals will be stable against coarsening, if their molar Gibbs energy (taking also into account the role of the grain boundary) will pass through a minimum as function of grain size at fixed average composition of the alloy, and fixed temperature. Further, this alloy will be stable against precipitation, if the Gibbs energy in the above mentioned minimum will be more negative than the same for any other state of the system, including all possible precipitations. In this model for simplicity only binary alloys are considered using the simplest solution model of regular solutions and equal molar volumes of the two components (more complex treatments are possible, but they will only modify the current results). The final equation for the molar Gibbs energy of the nano-alloy is written as (when component B is segregated to GBs):

$$G_m = R \cdot T \cdot [x \cdot \ln x + (1-x) \cdot \ln(1-x)] + \Omega \cdot x \cdot (1-x) + k / (r + 3 \cdot r_a) \cdot V_m / (\omega_B^0) \cdot [\omega_B^0 \cdot \sigma_B^0 \cdot (1 + (3 \cdot r_a) / r) - R \cdot T \cdot \ln x - \Omega \cdot (1-x)^2] \quad (1)$$

where G_m (J/mole) is the molar Gibbs energy of the nano-alloy (relative to the mixture of pure macro-A and pure macro-B as reference states having zero molar Gibbs energy by definition), $R = 8.3145$ J/molK is the universal gas constant, T (K) is the absolute temperature, x is the average mole fraction of component B within the grain (in equilibrium with the GB, at which the mole fraction of component B at GB is taken as about 1 – see Eq.4 middle), Ω (J/mol) is the interaction energy in the bulk of the alloy, $k = 3.36$ is the shape constant of the grains, r (m) is the average grain radius, V_m (m³/mol) is the molar volume of the alloy, ω_B^0 (m²/mole) is the molar GB area of pure component B, σ_B^0 (J/m²) is the GB energy of pure component B, r_a (m) the atomic radius), with:

$$r_a = ((3 \cdot f_b \cdot V_m) / (4 \cdot \pi \cdot N_{Av}))^{1/3} \quad \omega_B^0 = \pi \cdot r_a^2 \cdot N_{Av} / f_{gb} \quad (2)$$

where f_{gb} and f_b and the packing fractions within the grain boundary and the bulk of the grains, $N_{Av} = 6.02 \cdot 10^{23}$ 1/mol is the Avogadro number. Calculations should be performed only at $r > r_{min}$:

$$r_{min} \cong r^*/x_B - 3 \cdot r_a \quad (3)$$

where r_{min} (m) is the minimum grain size at which the nano-grained alloy can be stabilized, r^* (m) is a characteristic size parameter, x_B is the average mole fraction of component B in the alloy, with:

$$r^* = 4/3 \cdot k \cdot f_{gb}/f_b \cdot r_a \quad x = (x_B - y)/(1 - y) \quad y = r^*/(r + 3 \cdot r_a) \quad (4)$$

where y (dimensionless) is the ratio of atoms in the GBs compared to the whole alloy. Based on the above equations, at fixed A-B components (A is mostly in bulk, B is mostly at grain boundaries), fixed temperature T and fixed average composition x_B , the nano-grained alloy will be stable against coarsening and/or precipitation in the given range of two parameters: $\omega_B \cdot \sigma_B$ and Ω . Based on these two parameters stability maps for nano-grained alloys are constructed. For characteristic properties of A = W alloys the condition of stability of the nano-grained tungsten-based alloys is found as:

$$\Omega_{cr} \cong 6,370 + 24.1 \cdot T + (1.08 + 2.73 \cdot [10]^{-4} \cdot T) \cdot \omega_B \cdot \sigma_B \quad (5)$$

where T is in K, Ω_{cr} , and $\omega_B \cdot \sigma_B$ are in J/mol. Comparing the properties of all W-based binary alloys with Eq.(5), the following conclusions are made:

- systems W-Cu, W-Ag, W-Au and W-Mn are safely in the region of stable nano-alloys below 2,000 K,
- system W-Y is in the region of nano-alloy stability below about 1400 K,
- systems W-Cr, W-Sc and W-Ti are surely in the region of non-stable nano-alloys. However, systems W-Cr and W-Sc are at least stable against coarsening (not against precipitation) at least at low temperatures, while system W-Ti is not stable even against coarsening even at relatively low temperature.

In summary, one of the best candidates from the current analysis is a W-Ag alloy with about average 15 at% Ag, being also stable against corrosion above 140°C. Interestingly, this system was found unstable by other authors [6], who found W-Ti stable; the theoretical problems in other papers will be shortly discussed.

CONCLUSIONS

- a simple system of equations (1-4) are derived to select stable nano-grained alloys; a particular solution for W-based alloys is written by Eq.(5). As follows from Eq.(5), severe repulsion between the components in the alloy (such as in W-Ag) is needed for its stabilization, so it will be very difficult to produce them;
- as it is very difficult to make experimentally the difference between thermodynamically stable alloys (such as W-Ag) and kinetically stable alloys (such as W-Ti), it is not easy to confirm the validity of models;
- one of the possible outcome is that for practical applications an optimum alloy is needed, which maybe not thermodynamically stable, but kinetically stable enough for practical purposes, such as W-Ti.

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Multiscale modelling as a successful tool for exploring forefront materials under extreme conditions

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The use of computational codes at different scales has emerged as a powerful approach for understanding internal mechanisms of damage evolution at micro and nano levels, and even aging or degradation simulations are becoming now possible. Multiscale procedure allows the connection among different scales using specific models and techniques (using both software and experimental studies) in order to predict the order of magnitude of several design parameters and the behaviour of new proposed materials during working conditions. Numerical methods like Density Functional Theory, Molecular Dynamics, Monte Carlo, Dislocation Dynamics or Finite Elements Methods are being extensively used for these goals.

The multiscale modeling (MM) approach is an innovative methodology which takes into account the atomic description of the phenomena of a material as well as its macroscopic physical properties. MM considers the characteristic problems of material science, being cheaper than traditional trial and error methods and avoiding the need to build prototypes.

Moreover, modelling of materials under extreme conditions, may enormously benefit from the development of computational databases, allowing a quick connection and sourcing of data for an effective interlinking between scales. We present our advances in two different data bases interesting for nuclear science dealing with radiation damage

As an example of application we will discuss the illustrative case represented by interfaces like Cu/Nb multilayer material, since they could be structured to act as efficient sinks for irradiation-induced vacancy-interstitial pairs, leading to their recombination and in so doing, restoring part of the material to its undamaged state. This kind of immiscible alloys interfaces, may be efficient in the process of trapping and avoiding diffusion of He atoms. Molecular dynamics simulations allowed us to get a deeper insight into structural, dynamics and energetic factors that govern the self-healing ability of the hetero-interface Cu/Nb, and discussing about the helium aggregation and bubbling formation over the interface attraction zones.

Multiscale Modelling of Multi-layered Coatings

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Abstract

The vast majority of engineering components, especially that used in extreme conditions, can degrade or fail catastrophically in service through surface related phenomena such as wear, corrosion and fatigue. Advanced surface engineering technologies are needed to improve resistance to wear, erosion, indentation, corrosion, oxidation, to control interface conditions such as friction and heat transfer, and to reduce adhesion, improve the fatigue life, etc. Advanced surface coatings, especially multi-layered coatings, are still effective and efficient technologies to meet engineering needs and challenges. Nevertheless, these developments could be accelerated if more effective and efficient modelling techniques could be provided.

Although there were various modelling techniques having been developed to assist the analysis of the coating processes and performances of the coated surfaces, there was a need for further developing these techniques that can support design and manufacture of advanced surface systems more accurately and more efficiently. The EU FP7 M3-2S project was to address the urgent scientific, technological and market need for consistently reliable, high performance multilayered surface systems, by developing generic, robust multiscale materials modelling techniques. These covered the range from nano, through micro to macro-scales, for the design, optimisation and performance prediction of multilayered surface systems, for a wide range of engineering applications.

The proposed talk will introduce the background and drivers of the research and technological developments in modelling of multi-layered surface systems, and then focus on the techniques of the modelling at different length-scales as well as their integrations, these including: Molecular dynamics simulations of the physical vapour deposition of the multilayered surface coatings; Atomistic FirstPrinciples Calculations for the analysis of mechanical property constants and interfacial adhesion to support the coating designs and the modelling at higher length-scales; and parametric continuum finite element (FE) modelling, embedded with improved cohesive-zone modelling, serving as the first step in the submodel calculations. Examples of the applications of these modelling techniques will be presented, followed by an outlook on the further work to be undertaken in this field.

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Coherent thermodynamic model for solid, liquid and gas phases of elements and simple compounds in wide ranges of pressure and temperature

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Abstract

In contrast to well established thermodynamic models for solids [1,2] the thermodynamic modeling of fluids (liquids and gases) appears to be restricted mostly to just a few materials and to rather small ranges in pressure and temperature. Since most of these approaches start from the ideal gas with virial expansions to fit the experimental data these representations need either up to 180 fitted parameters in the model functions [3,] or different sets of parameters for different ranges in pressure and temperature [4] and these expansions diverge usually in some of the regions not covered by the fitted data. The comparison with the thermodynamic models for solids avoids these divergences in the present approach by the use of a ground state or “cold” energy function for the quenched metastable amorphous or glassy state relating it to the ground state energy of the crystalline solid. With this energy of the ground state the remaining thermal energy can be modeled by non-diverging series expansions. The basic ideas of this approach will be outlined with calculations for argon up to 100 GPa and 3000 K based on the data for the critical point of the fluid and the data for the solid along the melting curve. Since solid argon shows no structural phase transitions up to the highest pressures studied so far a rather simple “cold” energy curve can be used for the fluid in this case. For substances like water with its many phases of ice along the melting curve and its well-known high-density and low-density metastable amorphous forms [5] an appropriate modification of the “cold” energy curve will be discussed as an example for the modifications needed for instants also for all the elements with structural phase transitions under pressure [6].

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5. APPLICATIONS

Materials for extreme conditions: High temperature corrosion and steel design

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Alumina forming alloys have been proposed as a candidate material for use in energy applications, such as different combustion processes, thermal solar power (CSP's) and Gen IV nuclear power, i.e. lead-cooled fast reactors (LFR), due to their good oxidation properties. The excellent oxidation and corrosion resistance is a result of the formation of an alumina (Al_2O_3) layer on the alloy surface instead of chromia (Cr_2O_3) as in the case of standard high temperature steels.

The scientific background to the difference between alumina- and chromia forming alloys will be discussed as well as the development process of new ductile alumina forming construction steels, i.e. ferritic (FeCrAl) steels and austenitic (AFA) steels.

An important factor, when dealing with high temperature alloys, is the reactive element (RE) addition. At high temperatures, small additions of e.g. Y, Zr, Ce, Ti and Hf improves the alloys oxidation properties by balancing the outward diffusion of metal ions and the inward diffusion of oxygen, which leads to a balanced oxide growth and thus a reduction of mechanical stresses and/or porosity in the oxide layer. There is an intricate balance between alloying elements, steel impurities and RE-additions in order to design an excellent high temperature alloy.

New alumina forming steels for new energy technologies

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Abstract

Alumina forming alloys have been proposed as a candidate material for use in energy applications, such as different combustion processes, thermal solar power (CSP's), Gen IV nuclear power, i.e. lead-cooled fast reactors (LFR) and also for fusion reactors due to their good oxidation properties. The excellent oxidation and corrosion resistance is a result of the formation of an alumina (Al_2O_3) layer on the alloy surface instead of chromia (Cr_2O_3) as in the case of standard high temperature steels. The scientific background to the difference between alumina- and chromia forming alloys will be discussed as well as the development process of new ductile alumina forming construction steels, i.e. ferritic (FeCrAl) steels and austenitic (AFA) steels. An important factor, when dealing with high temperature alloys, is the reactive element (RE) addition. At high temperatures, small additions of e.g. Y, La, Ce, Zr, Ti and Hf improves the alloys oxidation properties by changing the outward diffusion of metal ions and the inward diffusion of oxygen ions, which potentially leads to a balanced oxide growth and thus a reduction of mechanical stresses and/or porosity in the oxide layer. There is an intricate balance between alloying elements, steel impurities and RE-additions in order to design an excellent high temperature alloy for a specific environment. Experimental alloys, based on the composition Fe-10Cr-4Al-RE, have been exposed to stagnant liquid lead at different oxygen activities up to 800°C.

Our work has shown, for the first time, that a certain category of steels can operate in liquid lead at very high temperatures with little or no corrosion, and yet with good structure stability. With this new material development, new energy technologies may be able to utilize liquid lead at very high temperatures as heat transfer fluid and achieving increased thermal efficiencies.

Materials for energy conversion stabilized under high-pressure conditions

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Abstract

High pressure is an effective tool in the preparation of new materials with low stability or metastable character. As a brief overview, the high hydrostatic pressure (HP) favors the formation of short and strongly covalent chemical bonds. Additionally, pressure helps to increase the coordination numbers and it favors the denser phases, in perovskite-like or skutterudite-type materials. Finally, the reaction kinetics is enhanced under pressure. For many years we have carried out synthesis under HP addressing the stabilization of very different solid state materials, with distinct functionalities, from the families of rare-earth nickel perovskites RNiO_3 , where we described a charge disproportionation effect, to complex perovskites related to $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$, with colossal magnetoresistance, or metal hydrides with perovskite structure like NaMgH_3 , interesting for hydrogen storage. All of them have been stabilized in “moderate-pressure” conditions, up to 3.5 GPa, in a piston-cylinder press.

After a review of the most paradigmatic systems like RNiO_3 perovskites, which directly connect with the legacy of Prof. Demazeau, I will address recent results on thermoelectric materials (TMs) with skutterudite structure. It is worth recalling that about two thirds of energy (at a global level) is dissipated as heat with no profit. TMs are able to directly transform a thermal gradient into electric energy. The design of novel TMs faces a great challenge since three antagonistic properties must be optimized: they require a high Seebeck voltage (S , thermoelectric power), low electrical resistivity (ρ) and low thermal conductivity (κ). The CoSb_3 -based skutterudite compounds are highlighted as thermoelectric materials with high conversion efficiency. CoSb_3 displays high carrier mobility, high electrical conductivity and a notably good Seebeck coefficient. Nevertheless, its high thermal conductivity ($\kappa \approx 8\text{-}10 \text{ W m}^{-1} \text{ K}^{-1}$ at RT) hinders the optimization of the thermoelectric figure of merit. Fortunately, there are different approaches to reduce the thermal conductivity of CoSb_3 by minimizing the impairment of the electron-transport properties. Nanostructuring and doping are common strategies used to modify the electrical and thermal transport properties. Recently, we have found a novel approach to dramatically reduce κ . In Ln-filled skutterudites (Ln: lanthanide ions like La, Ce, Yb...) synthesized under high-pressure (3.5 GPa in a piston-cylinder press), we discovered that these conditions favor fluctuations in the filling fraction, leading to a “glass-like” ultralow thermal conductivity. The effect of strain-field scattering of high-energy phonons is observed, revealing that an uneven distribution of filling atoms is efficient to further reduce the lattice thermal conductivity of filled crystals. We have observed the segregation into Ln-rich and Ln-poor coexisting skutterudite phases by synchrotron x-ray diffraction. This compositional nanostructuring leads to an improvement of the thermoelectric properties and a reduction of the thermal conductivity to record values lower than $3 \text{ W m}^{-1} \text{ K}^{-1}$ at RT.

Perovskite Materials Discovery using High Pressure - A legacy of Gérard Demazeau

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Abstract

High pressure methods are important for synthesising new materials, and exploring changes of structure and property in dense matter. High pressure materials science will be introduced briefly, and applications for solid state chemistry will be illustrated with reference to new ABO₃ perovskite materials. High pressure often stabilises cations in unusual oxidation or coordination environments, such as in the perovskites TiNiO₃ and LaPdO₃ prepared by Gerard Demazeau and co-workers. Examples we have studied with unusual A cations are PbRuO₃ [1] and Mn-based perovskites such as MnVO₃ [2], while new LnRu_{0.9}O₃ perovskites have the unusual Ru³⁺ state at B sites [3]. New SrCrO_{3-x} [4,5] and CaCrO_{3-x} [6,7] superstructure phases have been synthesised through 'hard-soft' chemistry, where the x = 0 high pressure perovskites prepared under 'hard' high pressure conditions are modified topotactically by soft low temperature reduction. The most reduced CaCrO_{3-x} material, Ca₂Cr₂O₅, is a new brownmillerite phase. New magnetoresistive double perovskite materials such as CaCu₃Fe₂Re₂O₁₂ and Mn₂FeReO₆ have also been stabilised at high pressure [8,9], and a new double double perovskite type MnRMnSbO₆ with order of A and B site cations has recently been discovered [10,11].

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Thin films architectures for high temperature applications

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Abstract

Development and understanding of nanostructured coating materials that can withstand simultaneously one or more external constraints related to high/low temperatures, stress/strain, corrosive/oxidizing atmosphere or electromagnetic fields/fluxes open new opportunities in many area of technology such as automotive, aerospace, energy generation and storage, electronics, biomedical, chemical and photochemical, metallurgy and machining tools, etc. The main approach to meet these complex requirements must consider integrating material systems enabling the optimal adaption of an active surface to the environmental conditions imposed by external constraints [1]. Different coatings methods have been applied for surface properties modification. The actual state-of-the-art is based on surface modification using any type of materials: polymers, metals, ceramics, composites or hybrids [2]. The main features of modern coating technologies (physical, chemical, electrochemical or combined) must consider ability to control defect states, concentrations, microstructures and morphologies at nanosizes, accommodate to the large strains associated with thermal cycles and ecological benefits. Development and innovation in nanostructured coatings is expected to bring also a major improvement in reducing or replacing critical raw materials [3]. Thermal characterization of nanostructured coatings is an important predictive tool for: - Assessment of already existing technologies / materials to check the reproducibility and durability of the systems. Thermal analysis became one of the simplest and rapid to be used standard method for assessing the quality and reproducibility of the coatings; - A simple and accessible tools to study and predict the process parameters, using different thermodynamic and kinetic models, required to preserve the nanostructures during thermal treatment of different novel multi-material coating systems and study the complex correlations between material properties vs. synthesis and processing parameters in real environments. These approaches are fundamental in developing novel nanostructured coating material systems and innovative coating technologies.

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Intermetallics – new materials for extreme conditions

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Abstract

Many of currently used technical materials cannot be imagined without the use of critical raw materials. They require tungsten and cobalt (tool materials, heat resistant alloys), niobium (steel). Therefore there is a need to find substitutes to help the European economy. A promising solution can be the application of intermetallics. Intermetallics are materials offering wide variety of interesting properties, such as high hardness and wear resistance or high chemical resistance. In this paper, the overview of possible substitute materials among intermetallics is presented. Intermetallics based on aluminides and silicides are shown as high-temperature alloys and corrosion resistant materials, composites composed of ceramics in intermetallic matrix as possible tool materials. The historical consequences of the development of these materials, as well as the current and future trends in their research, innovations and application are presented.

Current advances and emerging needs in aeronautical materials: could nanocrystalline alloys offer the desired breakthrough?

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INTRODUCTION

The increase of international competition in aeronautics and the need for modern aircrafts to cope with demanding environmental goals require for the achievement of challenging technological solutions and the development of breakthrough technologies and concepts. The high level goals resulting for the aeronautical community are summarized in the “Flight path 2050”, released by the European Commission in the year 2011 [1]. From the technological viewpoint Europe should maintain leading edge design, manufacturing and system integration capabilities and programs covering the whole innovation process from basic research to full-scale demonstrators. From the environmental viewpoint the main goals are a 75% reduction in CO₂ emissions per passenger kilometre, a 90% reduction in NO_x emissions and a 65% noise reduction as compared to the capabilities of a typical new aircraft in 2000. The progress on advancing existing materials and the ability to develop novel materials offering less weight, increased mechanical properties, more functionalities, more flexibility on applying manufacturing concepts, recyclability, etc., are the key for responding to the emerging needs of increasing efficiency, increasing safety, reducing costs and decrease the environmental foot print. In this lecture current advances and emerging needs in aeronautical materials will be presented and discussed.

STATE OF THE ART

Just two years ago one might summarize the use of aircraft structural materials in a simplified manner as following: not moving main structural parts of an aircraft (the fuselage, the not moving parts of the wings) are made from a number of aluminum alloys. Moveable parts (e.g. flaps, ailerons, etc) as well as the horizontal and vertical stabilizer are made from thermosetting composites. Pylons are made mainly from Titanium and landing gears are made of steel. Yet, since almost two years these figures have been dramatically changed with the composite materials making already 52% of the weight of the widebody Airbus A350 from 22% of the weight of the Airbus A380 aircraft having its first flight about 10 years ago [2]. This (r)evolutionary development will be in the following presented and discussed.

DISCUSSION

First, an overview of the historical evolution of aeronautical materials will be provided along with the technological significance of the advancements achieved through the years for the development of aircraft structures. The progress on the development of aircraft Aluminum alloys will be presented and the strengths and limitations of this significant class of materials will be discussed [3]. Composites have been proved to be excellent aircraft structural materials due to their desirable properties. To them belong their high specific tensile properties, improved resistance to corrosion, possibilities for manufacturing integral structures, etc, [e.g. 4]. Special emphasis will be given on the impact of composite materials to progress from differential

to integral aircraft structures. Furthermore, challenges and problems related to joining of composite structures by bolted joints and adhesives will be discussed. On the other side the wide use of composites is related to the urgent need to face issues like fatigue problems of parts subjected to compression, environmental attack (e.g. humidity, UV aging), lack of electrical conductivity, lack of experience in repair, problems with recycling of thermosettings, etc.

The development of novel aeronautical materials such as multifunctional materials, self-healing materials and nanocrystalline alloys represent a promising way to face a number of the above problems. Yet, as the level of technological readiness of these materials remains still low its advancement is currently subject of intensive research efforts, worldwide. Presented will be the achievements made with these materials as well as the challenges, which still need to be faced.

In this context, special focus will be given to the development of nanocrystalline alloys. Although they are still at an early stage of development with regard to aeronautics applications they offer a huge potential which attracts considerable attention. Their advancement would allow combining the benefits of using metals (e.g. considerable experience in their use, ability for damage tolerance design, experience with repair, recyclability, etc) with specific strength and Modulus of Elasticity values comparable to those of composites. Recent efforts to develop nanocrystalline alloys referring to typical aeronautical materials (Aluminum, Titanium, Magnesium and Nickel alloys) will be presented and discussed [e.g. 5,6].

CONCLUSIONS

An overview of the advancements achieved with aeronautical materials and their significance for improving aircraft structures will be provided. Current needs and challenges resulting from the effort to fully exploit the potential of modern aircraft materials will be discussed. The state of the art on the progress made to develop nanocrystalline alloys offering the potential for their use as aircraft structural alloys will be presented.

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Space engineering – process of satellite hardware development

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INTRODUCTION

Spacecrafts are the one of the highest level complex human product. This is why space engineering is a specific field of engineering. The presentation gives an introduction into this word and show why so long and expensive the satellite development phase.

SPACE MISSION

Participating in a space mission one would meet with the most rigorous standards (ECSS) and the best defined hierarchy for collaboration. The space project runs through sections and milestones – the total timeline used to be 20 years. The main segments are the followings:

A (conception), what to build, when to launch, mission aim, lifetime

B (definition), converting the preliminary plan into a baseline technical solution - define requirements (SRR) - determine schedule - specifications to initiate system - design and development (SSR)

C/D (design, production) - create subsystems - Invitation To Tender (ITT) - design equipment – select materials, processes - procurement - manufacturing - tests –integration

E (mission) - launch - cruise - experiments/services - data acquisition - data analysis

F (disposition)

The full process from the original idea to the launch is controlled by higher level customers and experts.

Thousands of pages documentation as accompanying items ensures the high quality and reliability.

Several reviews minimize the technical risks.

Detailed and tailored requirements specification provide the needs and finally the Verification Control Document shows the compliances and deviations.

Different work logic for subcontractor and supplier.

RESULTS

Thanking for the sophisticated collaborative work space missions are mostly successful despite the very high risks. Nevertheless, it can happen by certain missions less or most serious faults. Experts of space missions are frequently conservatives supported by their previous reliable data base of previous successful and faulty missions. Qualification procedures of new materials and procedures are always long and expensive actions.

CONCLUSIONS

Space engineering offers collaboration regarding applicability for new type materials.

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The BraSiC® process has been developed for brazing at high temperature SiC based materials in order to manufacture large and/or complex industrial components. This technology has already been used for the realisation of the telescopes HERSCHEL and GAIA. The BraSiC® filler alloys are well adapted to SiC based materials since they are non-reactive with SiC, show a good wetting of this material and, in general, the interface SiC / BraSiC® alloy is mechanically strong. In order to manufacture complex or larger components for space applications, the BraSiC® process has recently been optimised to perform multi-staged brazing. The principle of this multi-staged brazing consists in brazing SiC elements in several stages, each stage being associated with a filler alloy and a brazing temperature that allow the joining of some parts of the components without melting of the brazed joints already formed in the previous stages.

Material developments for space applications

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INTRODUCTION

The aim of this presentation is to help scientists to develop new materials for space application. In order to reach this goal we characterize the space environment and summarize experimental data on low temperature long duration space effects on metals. High temperature refractory metal application in space sector is also demonstrated. This is the very specific topic of combustion chambers and nozzles of space launchers and spacecrafts on various orbits.

STATE OF THE ART

The big family of practical artificial materials has been mostly developed on empirical way resulting in more than 500 thousand species. As a product of increasing eager innovation activity worldwide about 5000 new material is produced yearly. The new material survives if its new property is accepted by the market. The trend from simple (with one-two-three components) materials changed up to more and more complex super materials (with more than 200 components). The most typical way of material development is to complete the composition with further additives. Other direction can be structure modification made by technology progress. The theoretical description or model of these new materials is almost impossible. To find further alternative methods is a far intention. The thermodynamic approach seems to be a new possibility.

DISCUSSION

New material is always a risk, since its properties are unknown. The risk can be decreased by property tests. As space missions are typically high risk actions introducing a new material is very expensive and long time operation. High temperature test needs special devices which are out of the frame of our project.

CONCLUSIONS

Before definition phase of any new material the application field must be fundamentally analysed.

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Towards Frictionless Engineering Surface

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INTRODUCTION and STATE OF THE ART

Friction is the force resisting the relative motion of solid surfaces sliding against each other. Friction is directly related to dissipated energy, which is mostly transformed into heat causing local surface structural changes, such as oxidation, and changing mechanical properties. Moreover, high friction is typically related to extensive wear – most materials thus cannot be used in dry sliding conditions. There are only two ways to reduce friction of bulk materials – surface treatment and/or use of (semi)liquid lubricants. If the latter cannot be used, we have to rely on solid lubrication provided by surface adaptation. It is obvious that we cannot find the optimum material for reducing friction without detailed knowledge of sliding phenomena. However, what do we know about friction? Traditional models capture general features related to sliding phenomena: the Prandtl-Tomlinson model predicts stick-slip in a perfect crystal and has been extended to describe the effect of thermal fluctuations (so-called thermolubricity [1]), velocity and temperature on friction. The Frenkel-Kontorova model accurately handles incommensurate surfaces with defects (e.g. dislocations) and is successfully used to understand friction of adsorbed monolayers [2]. Regarding computational methods, molecular dynamics (MD) simulations [3] are perhaps the most effective tool; however, the material combinations are strongly limited due to lack of appropriate potentials. Recently, ab initio methods have been applied to unravel friction at atomic scale [5]. We are witnessing a vibrant period of increasing interest in friction phenomena; old empirical laws are questioned and repurposed [5]. Despite practical and fundamental importance, many key aspects of the dynamics of friction are not yet well understood [3]. Why is there such gap between simulations and experimental tribology? First, interaction with the atmosphere, frictional heating, high contact pressures and, particularly, wear are extremely complex phenomena to accurately describe using computational models. Second, the sliding conditions implemented in silico are typically far from that in real world (system sizes, reachable timescales, sliding speed, load, or temperature). Finally, nanoscale tribology is itself an extremely challenging scientific field. It is clear that now (and in decades to come) we cannot prepare optimum tribological materials purely by computational methods using just the periodic table. Nevertheless, for specific material combinations and contact conditions, multiscale simulations promise a step-change in the design of ultra-low friction solid lubricants. Two material classes emerge as solid lubricants at the macroscale – carbon-based and transition metal dichalcogenides (TMD). Interestingly, these two classes have many common structural and tribological features. They both exist in various allotropes – bulk crystal with low shear strength, fullerene and fullerene-like particles, nanotubes, and 2D sheets. Defect-free low dimensional materials exhibit structural superlubricity [6] and may provide new methods of lubrication. The applicability of low-dimensional materials in mainstream engineering applications is very limited for a variety of reasons, but their use is mainly restricted by surface roughness and wear, which requires

replenishment of the solid lubricant. Here we will briefly describe our efforts to use TMD as solid lubricants and eliminate their drawbacks such as low oxidation and low structural integrity.

RESULTS and DISCUSSION

We designed and tested various nanostructured solid lubricant coatings, such as TMD doped with carbon or nitrogen [7]. In all cases, ultra-low friction was due to the formation of a thin tribolayer consisting exclusively of TMD. It is thus clear that the structural transformation is an intrinsic property of the material. Since the frictional properties were apparently controlled by formation of a thin (2-20 nm) TMD tribolayer, we extended my studies to nanotribology using AFM and, particularly, to atomistic simulations of friction. We started with ab initio methods to explore how electrostatic interactions, negligible in comparison with van der Waals and Pauli contributions at zero load, progressively affect the sliding motion at increasing loads for two MoS₂ bilayer configurations. Later, we compared potential barriers to sliding for graphene, MoS₂, MoSe₂ and MoTe₂ [8], and investigate the effect of phonons on friction [9]. For larger scale effects, molecular dynamics is employed. We have just published comprehensive benchmarking results of the existing empirical interaction potentials (also called force fields, FF) for MoS₂ using experimental data and potential energy surface information obtained from the aforementioned ab initio studies [10]. This has enabled us to start to simulate the formation of a crystalline layer from amorphous TMD as a consequence of sliding by employing a state-of-the-art FF, and preliminary results show a promising match with experimentally observed structural changes. Simulations help a lot to understand the nature of frictional energy loss and identify some key mechanisms at the sliding interface; however, a mechanical engineer needs experimental validation and, in particular, an actual value of the friction coefficient. Atomic force microscope (AFM) can provide quantitative data for friction [11] and the contact area is small enough to be captured, at least in a simplified form, by molecular dynamics. Nanotribological measurements by AFM can thus act as functional bridge between simulations and macroscale sliding.

CONCLUSIONS

We show our recent results on solid lubricant coatings with self-adaptive nanostructure. Our ultimate ambition is to prepare thin films, which will produce an ultra-low friction interface based on optimised low-dimensional structures in situ, i.e. during sliding. We try to establish links between fundamental properties of selected 2D materials obtained by ab initio methods (electronic structure, covalency, etc.), molecular dynamics and the intrinsic friction. These results, together with nanoscale experiments, form a base of design of novel sputtered solid lubricant coatings.

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Micro-Manufacturing: Products, Research, Applications and Trends

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INTRODUCTION

Increased demands on micro-products and miniaturised systems/devices have been a main driver to the rapid growth of the interest in research in micro- and nano-manufacturing. This lecture intends to give an overview on the recent developments in micro-manufacturing research, drivers behind the developments, as well as potential influences to the business. The issue associated with the development of materials for micro-manufacturing will also be addressed.

STATE OF THE ART

A comprehensive assessment of micro-manufacturing research was conducted by a WTEC Panel on “International Assessment of Research and Development in Micromanufacturing” (Ehmann, et al. 2005), more than 10 years ago, which showed the status of worldwide, micro-manufacturing research at that time. Substantial momentum driving the research and applications of micro-manufacturing was generated by the European Commission through the funding of several large-scale ‘flagship’ projects in micro-manufacturing in Europe, since its Sixth Framework Programme (EC, 2009; EU cordis website; MINAM, 2012; Qin, 2010). The research and outcomes from these projects have been widely reported from various sources. The research effort has been continuing since EU FP6, together with exploitation of the results from these funded projects, which has seen significant applications and further exploitation taking place in recent years. At the same time, there have been some shifts on the focus of the research and applications recently, such as more industry-driven initiatives, increased interactions with materials and nano-technology research, etc. (MINAM, 2012; Qin, 2015; EU cordis website; International Commercial Micromanufacturing Magazine; Pestarino, 2015).

RESULTS

Recent survey found that the development of micro- and nano-products has been influenced strongly by the advances in micro/nano-manufacturing research, being reflected by:

(i). More emerging products have been developed, driven by needs from specific sectors such as energy, transport, healthcare and consumer electronics, which are closely linked to important societal challenges. There have been targeted developments of micro- and nano-manufacturing technology for particular sectors and markets, e.g. that for energy sourcing, conversion, storage, transport and utilization which involve, largely, thin-film technologies, ceramic technologies, nano-materials and integration into surfaces and bulk-parts.

(ii). Increased introduction/utilisation of nano-materials and nano-technology into micro- and miniaturized products and devices which offers unique performance and extended life such as that used in new medical devices, implantable components, and micro-electronics products.

(iii). Disruptive development of micro-manufacturing technologies, which helped/is helping the development of new products, such as those helped greatly by the development of laser material-processing, micro-machining and forming, advanced coating and joining, micro injection-moulding, and roll-to-roll manufacturing, etc. It is expected that new development of micro- and nano-manufacturing technologies (continuous and disruptive) will further enable and accelerate technical and commercial breakthroughs in many application areas.

(iv). Shorter development time, compared to what happened 20 years ago. Currently, from concept, through research and development, to the diffusion of the product into the market, the time has been shortened considerably.

DISCUSSION

There has been significant progress in micro/nano-manufacturing research, and further development will need to be driven by industry further, which in turn, would help the industry's development, especially by adding values to products and by enhancing manufacturing competitiveness through deploying micro-/nano-manufacturing technologies, being exemplified by:

Improving surface quality through ultra-precision manufacturing (e.g., nano-machining and FIB machining);

Adding surface functionalities of the component/system surfaces through surface texturing (e.g., micro-machining, laser ablation, micro-EDM, micro-ECM) and coating (e.g. multi-layered nano-coating);

Creating new functional structures of the components/systems through micro/nano-forming/replication/sintering and additive manufacturing (e.g. hollow-sectioned, channelled, functionally graded structures);

Converting low-value materials into high-value products such as nano-materials/nano-composite products (e.g. micro/nano-forming, casting and sintering for high-quality components);

Creating value by high-quality assembly from low-value components/materials (e.g. micro-injection moulding assembly, high-precision mechanical, micro-joining and self-assembly).

CONCLUSIONS

The continuing trend of miniaturisation of products, devices and equipment has been a major driver to the development of micro- and nano-manufacturing technology. Compared to the development of 10 years ago, which saw micro-manufacturing research focused significantly on fundamental issues concerning the scaling down of conventional processes and equipment, recent development has been largely applications-driven. RTD effort has been shifted significantly to the transforming of laboratory processes into items of production equipment; and the development has been targeting onto sector-specific applications. In addition to the effort in developing multi-materials processing capabilities, low-cost equipment and pilot production lines, other aspects such as advanced tools and analysis software, high-quality materials and nano-materials, automation, inline inspection, quality assurance, and standardisation, are also being addressed. Considering

that micro-manufacturing bridges between potential, high-impact nano-science and nanotechnology and real-world, low-cost products, it will achieve further significant development over the next 10 years.

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High Pressure Materials and Rechargeable Batteries: are they separate worlds?

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Abstract

The so called “extreme conditions” of synthesis that is high pressure / high temperature (HP/HT) routes are widely used within many fields of Solid State Chemistry to produce novel materials. The main effects of high pressure are a) increasing the density, leading to more compact structures; b) increasing the coordination number for cations, c) decreasing bond lengths, d) increasing metal-metal interactions, etc., and by these means new materials, many of them metastable, have been produced or modified [1] On the other hand, in the field of rechargeable batteries, (sodium or lithium ions) new materials are constantly investigated in order to evaluate their performances as electrodes, electrolytes or interconnectors. At a first glance it seems that these two fields of research are not compatible since open structures allowing lithium or sodium mobility, are a “must” for battery materials together with the presence of transition metals in different oxidation states and sufficiently high mixed electronic-ionic conductivity in the case of electrodes. Therefore, high pressure materials have been traditionally ruled out as host materials for alkaline insertion/extraction reactions. Nevertheless, if the high pressure materials, in spite of their higher density, do still have some open spaces and some paths are available in their structures for allowing ionic diffusion, they should be tested as potential candidates and, if electronic conductivity is enhanced, they may perform even better than the ambient pressure analogue materials. This is the case of β -V₂O₅, the HP form of vanadium pentoxide, where the Van der Waals, interlayer space characteristic of the ambient pressure form remains and the enhanced electronic conductivity reduces the polarization of the cell and improves the power capability [2]. Vanadium oxyfluoride, featuring a distorted ReO₃ structure is another very interesting example which has been firstly prepared in our group under HP/HT conditions although careful ball milling under argon also leads to it [3]. Interestingly enough, the post-spinel form of NaMn₂O₄ has been produced under high pressure conditions and successfully tested as a highly stable electrode for sodium batteries [4] and the lithium analogue has been synthesized by ionic exchange on this material, that is combining a “soft chemistry” procedure with an “extreme conditions” one [5]. Last, but not least, moderate pressures can also be used in hydrothermal or microwave-assisted synthesis yielding interesting materials, some of them nanosized. All these aspects will be reviewed and discussed in the present communication.

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