E: Thin Films and Surface Engineering：I

Symposium Organizers :

Chuang Dong, Dalian University of Technology, China; Hongbo Guo, Beihang University, China; Hiroshi Masumoto, Tohoku University, Japan; Ho Won Jang, Seoul National University, Korea; Mingxing Zhang, University of Queensland, Australia

Monday PM　　Room：313 (3rd Floor)
August 19, 2019　　Symposium：E

Chairs:
Robert Vassen, Forschungszentrum Jülich GmbH, Germany; Christopher Berndt, Swinburne University, Australia

13:30-14:00 Keynote (1226505)

Engineered Surface Properties of Quasicrystalline Materials

Jean-Marie Dubois, Institut Jean Lamour / Institut Jean Lamour, France

Quasicrystals are crystals like others from a thermodynamics point of view. They grow through a peritectic reaction upon cooling a liquid alloy of the appropriate composition. They may also form surface coatings and thin films when processed with adequate technologies. They order on the long distance, giving rise to sharp spots in diffraction experiments. Yet, the ordering scheme is different from the one in normal crystals because translational symmetry does not operate in conventional 3-dim space, but in higher dimensions. As a result, electron transport and more generally transport properties are by essence very different from what they are in classical metals, alloys and intermetallic compounds.
This characteristic leads to very different surface properties compared to normal crystals. The first and most important property is the surface energy, which is found significantly below the values inherent to the metallic constituents. From this on, other properties that are related to the surface energy like solid-solid adhesion and friction are also found much different from what they are in normal crystals.
The author studied those properties in close collaboration with Pr Esther Belin-Ferré (1939-2018) who measured partial densities of states in a wealth of sintered specimens and surface treated samples and the group of Pr Jackson Guedes de Lima (1948-2018) who dealt with HVOF coatings. The purpose of the conference will be to give a rapid account of the most salient results obtained in this frame and which appeared in the articles listed below. These topics are: friction and surface energy, wetting and surface energy, self-lubricating coatings made of quasicrystals, other applications if time allows.

14:00-14:25 Invited (1235786)

Surface Severe Plastic Deformation for Improved Mechanical Properties and Optimum Reactivity

Thierry Grosdidier, Université de Lorraine, France

As failure is often initiated from the surface, surface treatments involving severe plastic deformation of the outer part of a work piece are being developed. Mechanical surface treatment techniques, deriving from the traditional pre-strain shot peening but involving much longer treatment durations, have been developed for which the shots are set in motion within a confined chamber and have a wide variety of incidence angles when colliding onto the surface. They are found in the literature under different names such as Surface Mechanical Attrition Treatment (SMAT) or Ultrasonic Shot Peening (USP).
While the effect of using cryonenic temperature (CT) has been used to reduce further the grain sizes on Cu or carbon steels, this presentation focusses on the effect of CT in metals susceptible to form martensite: the austenitic stainless steels. It will be shown that the use of cryogenic temperature did not increase the surface hardness significantly but greatly increased the subsurface hardness and, in some cases, changed the martensitic phase transformation sequences. Another new interesting aspect of surface modifications by applying SMAT will be demonstrated by the analysis of Ti-V-Cr alloys used for H-storage applications. While bulk SPD such as high pressure torsion did not allow H-storage reversion, the alloys that were mechanically activated by SMAT and processed a gradient microstructure could activate and store reversibly hydrogen.

14:25-14:50 Invited (1227917)

Morphology, Structure and Mechanical Properties of Titanium Alloy Processed via Surface Severe Plastic Deformation

Yingang Liu, The University of Queensland, Australia

Titanium and titanium alloys are the advanced structural materials and widely used in aerospace engineering. The usage amount of titanium and titanium alloys in aeroengine is up to thirty percent of the components, such as the fans, compressor discs and blades. Therefore, service environment for titanium and titanium alloys is extremely harsh, including high temperature, high pressure, high rotational speed, friction, scour and so on. Fatigue failure of blades and fans in aeroengine has become the biggest difficulty which affects reliability of the aeroengine in practical application. Solving fatigue fracture of blades and fans in aeroengine has been determined to be the key technology of aeroengine.

Surface strengthening and surface modification are the most economical and effective approaches to solve this key problem. Based on severe plastic deformation, manufacturing of gradient nanostructure with the grain size gradually changing from nanometer scale at the topmost surface to micrometre scale in the substrate materials is an effective approach to improve the mechanical performance of the components. Shot peening is a well-developed and widely-used surface mechanical treatment method to introduce compressive residual stress on the surface of metallic component in order to improve the fatigue life. In this research, high energy shot peening (HESP) driven by the computerized numerical control was adopted to fabricate gradient nanostructure in the surface layer of titanium alloy. The surface morphology, microstructure, fine structure, hardness and tensile properties of titanium alloy after HESP were examined in depth by means of 3D confocal microscopy, scanning electron microscope, electron back scattering diffraction, high-resolution transmission electron microscope, hardness tester and electronic universal testing machine. On this basis, the formation and evolution of nanostructure in titanium alloy were analysed. The results showed that gradient nanostructure was created in titanium alloy via HESP and the thickness of nanocrystalline layer was up to 40 μm. Correspondingly, the increased hardness, enhanced strength and plasticity were achieved.

14:50-15:10 (1222405)

VO_2-Based Thermochromic Smart Glazing Coatings

Xun Cao, Hongjie Luo, Ping Jin, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Energy consumption has become an urgent issue not only for the global environment, but also for people's lives. Among total energy consumptions, buildings take nearly 30%. For buildings, energy exchange through windows accounts for over 50% by means of conduction, convection and radiation. To reduce energy consumption, we must develop new structures for glass surfaces to enhance their thermal insulation properties. Vanadium dioxide (VO_2) is the most well-known thermochromic material, which exhibits a notable optical change from transparent to reflecting in the infrared upon a semiconductor-to-metal phase transition. Thermochromic window coatings offer some possibilities to achieve energy efficiency in window. In this presentation, I will sort out the urgent problems and critical obstacles which we are facing on the present VO_2 research for smart window applications. First, the VO_2 films without impurity can be fabricated by different methods including sputtering deposition, sol-gel synthesis, and pulsed laser deposition. Second, it is a big challenge to get a high-quality VO_2 films with good performance of proper phase-change transition temperature, high visible luminance transmittance, high solar modulation ratio, as well as good durability at a relative low growth temperature. Third, the mechanism of the phase-transition behavior in VO_2 materials is also very interesting. Realizing control of properties of VO_2 by defects modulation is an efficient route for understanding the nature of phase-transition and developing novel functional devices for practical applications.

15:10-15:30 (1234207)

Contributed Surface Functionalization of 2D Materials for Flexible Low-Power Electronics

Qiong Peng, Jian Zhou, Zhimei Sun, Beihang University, China

Surface engineering plays an essential role in modulating the performance of 2D monolayer and heterostructure materials for electronic devices. Meanwhile, the mechanistic investigation on surface engineering from the atomic level is of great significance for the predictive design of advanced materials. Yet the understanding of the fundamental relationship between structure and performance is falling far behind the synthesis and empirical researches. Here, on the basis of first-principles calculations, we report that surface functionalization can not only effectively modulate nontrivial topological transitions in group-III monochalcogenides, but also controllably regulate Schottky barriers in metal-semiconductor heterostructures. For the fully O-functionalized GaSe monolayer, GaSeO, a novel quantum spin Hall state is revealed with a large bandgap of 178meV, in which the nontrivial band topology originates from the s-p band inversion in the crystal field. In addition, for 2D metal-semiconductor heterostructures composed of Nb_2CT_2 (T = OH, F, and O) MXenes and MoS_2, the Schottky barriers (SB) at the contact interfaces can be effectively modulated via appropriate functionalization of MXenes. Particularly, a n-type SB-free contact is available in $MoS_2/Nb_2C(OH)_2$ heterostructure and a different p-type Schottky contact is found in MoS_2/Nb_2CO_2 heterostructure, in which the controllable Schottky barriers are derived from the tunable metal work function induced by functionalized termination. Our work provides significantly mechanistic insights into the surface engineering on 2D materials for flexible low-power electronics.

15:30-16:10 Tea Break

16:10-16:40 Keynote (1234217)

Atomic Layer Deposition Techniques: Electrocatalysts and Charge Transporting Layers

Hyunjung Shin, Sungkyunkwan University, Korea

Atomic layer deposition (ALD) is now being recognized as a powerful, general tool for modifying the surfaces of nanomaterials in applications for many renewable energy conversion devices. However, ALD involves slow processes particularly when it is subjected to nanoporous media with high-aspect ratios. A comparative study of the ALD coating onto two distinctive templates having nanopores, i.e., two- and three-dimensionally ordered media (DOM), of similar porosity and pore dimension. Comparison of the ALD coating profiles across the thickness of both templates reveals fundamentally distinct coating mechanism; while a uniform growth zone develops along the pores of the 2-DOM, a gradual decrease in the deposition is observed in those of the 3-DOM as ALD pulse time increases. The present model study helps universally predict the ALD behaviors into nanoporous media even with different types of pore connectivity.

ALD techniques are now utilizing in forming electrocatalytic as well as charge transporting layers for photo electrochemical and solar cells. Exposing edges of few layers of MoS_2 as efficient electrocatalysts can be formed by ALD in this study. CH3NH3PbI3 with perovskite crystal structure has attracted considerable interest for high power conversion efficiency (PCE, now certified 23.7%). ALD chemistry for TiO_2 and ZnO are well known and the process requires relatively low deposition temperature as low as ~ 100˚C, which is applicable to deposit onto the halide perovskite layer. In this presentation, highly efficient perovskite solar cells having a long-term stability that adapts uniform and dense inorganic charge transport layers grown by ALD are reported. The devices shows excellent water-resistant properties and long-term stability at 85˚C under illumination compared to devices without ETL grown by ALD.

16:40-17:05 Invited (1234406)

ALD Enabled Synthesis of Nanostructured Materials and Its Applications

Se Hun Kwon, Pusan University, Korea

One-dimensional nanostructured materials such as nanodots, nanowires, nanotubes, nanorods, and nanobelts have attracted special attention because they possess unique structural one dimensionality and possible quantum confinement effects in two dimensions. As a result, they are expected to play an important role as building blocks in future nanoscale functional devices. Potential applications for these nanostructured materials have been expanded through the efforts of several researchers. To date, various approaches have been developed for the fabrication of various nanostructured materials such as hydrothermal synthesis, anodization of metal sheets, template-assisted growth, and seeded growth. Of these methods, the template-assisted approach combined with atomic layer deposition (ALD) has been distinguished from the others as a simple and well-controlled method. Because ALD is a vapor-phase non-line-of-sight deposition process, it can provide excellent control over the wall thickness of nanostructures at the sub-angstrom scale and can be used to create highly conformal coatings of dense inorganic film even on nano-sized templates with high aspect ratios.

Herein, highly ordered freestanding nanostructure arrays with atomic layer control of wall thickness were fabricated by a hybrid process of versatile nanoporous template and ALD. The ultrafine thickness tunability of the ALD process made it possible to develop functional nanostructures with various wall thicknesses. In addition, various ALD processed metal and oxides enalbed us to creat various functionality, which is useful for various advanced applications. In this presentation, we will discuss some recent examples and emerging application areas.

17:05-17:30 Invited (1233789)

Wafer-Scale Growth and Assembly of 2D Semiconductors

Kibum Kang, KAIST, Korea

High-performance semiconducting films with precisely engineered thicknesses and compositions are essential for developing next generation electronic devices, which are becoming more integrated, complex, and multifunctional. My talk will introduce the novel processes that enable atomic-scale control of the thickness and spatial composition of semiconducting films on the wafer-scale. These processes include: (i) the wafer-scale generation of monolayer van der Waals semiconductors such as transition metal dichalcogenides (TMDCs) via metal-organic chemical vapor deposition (MOCVD), (ii) the atomic-level engineering of vertical thickness and composition through the layer-by-layer assembly of TMDC monolayers, and (iii) the transfer of atomically engineered films, using their van der Waals nature, onto arbitrary substrates. These capabilities provide a new material platform for both fundamental research and practical applications, including incorporation into existing integrated circuit technology to form hybrid materials (i.e. TMDC/CMOS) and boost electrical and optical functionality.

17:30-17:50 (1221176)

The New Application of Traditional DC Pulsed Magnetron Sputtering Technique on Deposition of Film with Preferred Orientation

Wanyu Ding, Zhixuan Lv, Weichao Chen, Dalian Jiaotong University, China; Jindong Liu, Dalian Jiaotong University, China / Jilin Institute of Chemical Technology, China

The traditional DC pulsed magnetron sputtering technique has been widely used in the field of film deposition. In general, the film deposited by traditional DC pulsed magnetron sputtering technique displays amorphous structure or crystal structure without preferred orientation.

Actually, for some special film, such as TiO_2 film, ITO film, and so on, the different lattice plane could display the different property. So, it is interesting to prepare film with some special preferred orientation, such as anatase TiO_2 film with (001) preferred orientation, bcc bixbyite ITO film with (100) preferred orientation. This presentation introduces the new application of traditional DC pulsed magnetron sputtering technique on deposition of TiO_2 and ITO film film with preferred orientation, as well as the special application of TiO_2 and ITO film with preferred orientation.

Firstly, the traditional DC pulsed magnetron sputtering technique was used to prepare anatase TiO_2 film with (001) preferred orientation. With lower sputtering power density, the deposited TiO_2 film was amorphous structure with nano-size anatase crystal nucleus. After annealing treatment, anatase TiO_2 film displays (001) preferred orientation. In case of anatase TiO_2 films with (001) preferred orientation, during N ion beam bombardment process, the stable structure for implanted N was to bond with two 2-fold O at outer layer of (001) surface and one 5-fold Ti at sublayers of (001) surface, for both substitutional and interstitial doping N. On the contrary, the stable structure for implanted N was to bond with one 2-fold O and two 5-fold Ti at (101) surface for both substitutional and interstitial doping N. With same N ion beam bombardment process, anatase TiO_2 films with (001) preferred orientation could effectively improve the formation of N-Ti bond.

Secondly, the traditional direct current pulsed magnetron sputtering technology was used to prepare ITO film. In case of the sputtering power density higher than critical point, parts kinetic energy of incident particles was transformed as the crystal energy in ITO crystal lattices, which worked for the growth of ITO grains along the certain direction. Besides, the incident In-O and Sn-O group should be considered, which resulted in the growth ratio along normal direction of film surface was much higher than those of parallel to film surface. For this reason, ITO columnar crystalline gains were formed and ITO film displayed (100) preferred orientation. ITO film with (100) preferred orientation displays the satisfactory optical and electrical properties, respectively. In case low energy methyl cation beam bombardment process, ITO film with (100) preferred orientation could effectively restrain the diffusion of methyl cation.

17:50-18:10 (1235908)

Novel Methods for Thin Film Thickness Measurements and Chemical State Analysis

Wenbing Yun, Sylvia Lewis, Benjamin Stripe, Xiaolin Yang, SH Lau, Srivatsan Seshdri, Ruimin Qiao, Sigray Inc., USA

Driven by device scaling and new materials, the non-destructive precise metrology of ultrathin films and elemental dose measurement with high spatial resolution and high throughput is desired capability for semiconductor IC manufacturing and nanotechnology research. Current challenges for such metrology include: non-destructive capabilities for buried layers, thickness measurements on 3D structures, and sufficiently high sensitivities to detect sub-Angstrom equivalent thicknesses.

Here we present three major x-ray characterization systems enabled by patented new innovations in the x-ray source and x-ray optic technology. The first system, the AttoMap micro X-ray fluorescence (microXRF) system, provides down to 0.1A equivalent film thickness measurements for dopants and can achieve accuracy better than 1% within seconds. The second system, the QuantumLeap X-ray absorption spectroscopy (XAS) system, enables chemical information on microns-thick films such as oxidation states and chemical bond lengths.

We will first review the AttoMap's intrinsic advantages for thin film measurements, including nondestructive, non-contact, ultrahigh trace level sensitivity, and high precision, and high spatial resolution for thin films and 3D IC structures. The system achieves spatial resolution at 10~40 micrometers. Examples, including demonstrations of sensitivity for 0.1A equivalent film thickness will be shown, in addition to the system's linearity and accuracy characterization. Because it can be used in ambient pressure, this non-destructive technique can be used as a complementary upstream technique to SIMS or FIB-SEM to identify regions of interest.

Recent results from the QuantumLeap XAS will furthermore be reviewed. The QuantumLeap is the first laboratory, non-synchrotron X-ray absorption spectroscopy system with sub-eV resolution and 100μm spatial resolution. The system achieves fingerprinting measurements of samples down to seconds and has demonstrated advantages for catalyst characterization.

The final is a new design for X-ray photoelectron spectroscopy (XPS) enabled by an ultrahigh brightness, multi-energy X-ray source for depth-dependent characterization of interfaces and of hydrated interfaces.

E: Thin Films and Surface Engineering: II

Symposium Organizers :

Chuang Dong, Dalian University of Technology, China; Hongbo Guo, Beihang University, China; Hiroshi Masumoto, Tohoku University, Japan; Ho Won Jang, Seoul National University, Korea; Mingxing Zhang, University of Queensland, Austrlia

Tuesday AM	Room: 313 (3rd Floor)
August 20, 2019	Symposium：E

Chairs:
Jean-Marie Dubois, Institute Jean Lamour / Institute Jean Lamour, France
Hyunjung Shin, Sungkyunkwan University, Korea

8:30-9:00 Keynote (1262628)

Advanced Ceramic Coatings for High Temperature Use Made by Thermal Spray Techniques

Robert Vassen, Forschungszentrum Jülich GmbH, Germany

Thermal spray technologies offer the possibility to manufacture coatings with a wide range of different microstructures. Such coatings especially for the use at high temperatures are applied on structural components in gas turbines. Several examples will be given in the presentation.

First, thermal barrier coatings (TBCs) which are used to protect metallic parts are addressed. Different microstructures are used for this application. The standard are micro-cracked coatings produced by atmospheric plasma spraying (APS). More advanced coatings show a columnar microstructure with high strain tolerance. The manufacture of these coatings by suspension plasma spraying (SPS) and by plasma spray - physical vapor deposition (PS-PVD) will be described, furthermore also characteristics of theses coatings will be given.

More recently, ceramic matrix composites are introduced into gas turbines. Although their temperature capability is higher than these of metallic substrates, they need protective coatings against water vapor recession. These coatings have to be rather dense to avoid the water vapor attack. Also such coatings can be produced by thermal spray techniques. Examples of $Yb_2Si_2O_7$ coatings prepared by APS, PS-PVD, SPS and high velocity oxygen fuel (HVOF) will be described. In addition to the high density also a high crystallinity is of importance for a good performance of the coatings.

9:00-9:25 Invited (1350288)

New TBC Materials and Structures

Xueqiang Cao, Wuhan University of Technology, China

Thermal barrier coatings (TBCs) have very important applications in gas turbines for higher thermal efficiency and protection of components at high temperature. TBCs of rare earth materials such as lanthanum zirconate ($La_2Zr_2O_7$, LZ), lanthanum cerate ($La_2Ce_2O_7$, LC), lanthanum cerium zirconate ($La_2(Zr0.7Ce0.3)_2O_7$, LZ_7C_3) were prepared by electron beam-physical vapor deposition (EB-PVD) and atmospheric plasma spraying (APS). The composition, crystal structure, surface and cross-sectional morphology, cyclic oxidation behavior of these coatings were studied. These coatings have partially deviated from their original compositions due to the different evaporation rates of oxides, and the deviation could be reduced by properly controlling the deposition condition. A double ceramic layer-thermal barrier coatings (DCL-TBCs) of LZ_7C_3 and LC could also be deposited with a single LZ7C3 ingot by properly controlling the deposition energy. The failure of DCL-TBCs is a result of the sintering of LZ_7C_3 coating and the chemical incompatibility of LC and TGO. Since no single material that has been studied so far satisfies all the requirements for high temperature applications, DCL-TBCs is an important development direction of TBCs.

9:25-9:50 Invited (1235535)

The Thermal Stability, Oxidation Behaviour and Elevated Temperature Wear Resistance of High Entropy Alloy Claddings

Daniel Fabijanic, Lordat Pacal, Qi Chao, Deakin University, Australia

High entropy alloys (HEAs) (or compositionally complex alloys) containing 4~5 strategically selected principle (5~35 at.%) alloying elements can form simple solid solutions instead of brittle intermetallic compounds, contrary to conventional phase rule prediction. Bulk samples of these alloys manufactured by diverse techniques (arc and induction melting, selective laser melting, spark plasma sintering etc.) have demonstrated an attractive suite of properties, especially at elevated temperatures. Much less explored is the prospect of HEAs as protective coatings in high temperature environments.

In this work AlxCoCrFeNi (x=0.3, 0.6 and 0.85) high entropy alloy and AlCoCrFeNi2.1 eutectic high entropy alloy (EHEA) claddings were produced by blown-powder coaxial direct laser deposition (DLD, Optomec MR-7) on 253MA austenitic steel, Inconel 600 and peak-aged Inconel 718 substrates. These alloy deposits were selected to produce claddings with a wide range of phase compositions and phase distribution (from coarse dendritic to fine lamellar). A mixture of blended elemental powders was the feedstock material and process parameters (laser power, laser scanning speed, laser spot size, powder feed-rate and hatch distance) optimized for minimal dilution, low defect density and maximum deposition efficiency were utilized from our previous research to produce single layer multi-track deposits of ~250μm thickness. Isothermal annealing at 800, 900 and 1000℃ for up to 500h was applied to assess the thermal stability of the cladding microstructure and to quantify the degree of inter-diffusion between the clad and substrate. The as-deposited and annealed claddings were extensively characterized for phase content (XRD), micro- and macro-chemical homogeneity (SEM-EDS line scans and mapping), and crystallographic texture (SEM-EBSD), and micro-hardness maps and profiles determined. Annealing was performed in air allowing the continuous oxidation behaviour to be studied. Finally high temperature self-mated pin-on-disc sliding wear was conducted in an ambient atmosphere at 500~900℃ and wear mechanisms determined.

In line with the literature, an increase in the Al mole fraction from 0.3 to 0.6 and 0.85 in the AlxCoCrFeNi system resulted in a change in crystal structure from FCC, to FCC+BCC and BCC, with and attendant increase in microhardness. A eutectic (slightly hyper) clad microstructure was produced for the AlCoCrFeNi2.1 alloy having alternating lamellae of Lc1 FCC and B2 BCC of ~2μm thickness. Generally, the thermal stability of the cladding microstructure and the clad-substrate interface was high, however decreased with an increase in Al content, with BCC converting to FCC and significant thermal softening observed upon isothermal treatment at 1000ºC. Conversely, oxidation resistance systematically improved with aluminum content forming a dense and adherent alumina scale. Alumina formation also favoured low friction and wear rate in the self-mated HEAs sliding wear couples tested at high temperature, with the oxide glaze preventing damaging metal-metal contact. HEAs are very promising highly stable cladding materials to protect high temperature alloys against oxidation and wear at temperatures above 800℃.

9:50-10:10 (1257513)

Toughened $Gd_2Zr_2O_7$ for Thermal Barrier Coating Applications

Lei Guo, Zheng Yan, Fuxing Ye, Tianjin University, China

Thermal barrier coatings (TBCs) are commonly used to protect metallic components of turbine engines from oxidation and erosion, leading to increased operating temperature and improved engine efficiency. The widely used TBCs are made of yttria stabilized zirconia (YSZ), however, its sustainable temperature is not higher than 1200℃. With an ever-growing demand for increasing the engine operating temperature, there is thus on-going research to develop alternative TBC materials. $Gd_2Zr_2O_7$ has excellent high-temperature capability and low thermal conductivity, which has been considered as a promising TBC candidate. However, $Gd_2Zr_2O_7$ TBCs have not been used in industry mainly due to the poor toughness.

To improve the toughness of $Gd_2Zr_2O_7$, our group has done much work and obtained some interesting results. Sc_2O_3 doped $Gd_2Zr_2O_7$ was produced, and its ordering degree decreased and the lattice parameter increased with increasing the Sc_2O_3 content, which caused an increase in the toughness. Non-stoichiometry $Gd_{2-x}Zr_{2+x}O_{7+x/2}$ (x = 0, 0.1, 0.3, 0.5, 0.7) ceramics was designed, and excess ZrO2 in the compound benefited the fracture toughness, probably attributed to the increased fracture energy, ferroelastic toughening and compressive stress. RE_2O_3 (RE=Yb, Dy, Er, Y) stabilized ZrO_2 with a ferroelastic phase structure was doped into $Gd_2Zr_2O_7$, which caused an obvious increase in the toughness. Composition - microstructure - mechanical property relationships and toughening mechanisms of $GdPO_4$-doped $Gd_2Zr_2O_7$composites were investigated. $GdPO_4$ existed as a second phase in the matrix, which refined $Gd_2Zr_2O_7$ grains, strengthened grain interfaces, and introduced residual stress in the composites. At low dopant contents < 30mol%, the toughness of composites increased without sacrificing hardness and Young's modulus. The strengthened interfaces, and cracks deflection, bridging and bifurcation in $GdPO_4$ grains resulting from the layer structure and the generated tensile stress contributed to the initial increase in the toughness.

10:10-10:30 (1235956)

The Design of Novel Gradient Y_2O_3 Doped ZrO_2 Coatings and the CMAS Corrosion Resistance

Jian He, Pin Cao, Hui Peng, Hongbo Guo, Beihang University, China

As the turbine inlet temperature increases continually, the calcium-magnesium-alumina-silicate (CMAS) from volcanic ash, air dust, runway debris, etc. ingested by engines can be melted and deposited on thermal barrier coatings (TBCs), which leads to severe degradation of TBCs. Especially for the EB-PVD YSZ TBCs, the columnar structures will accelerate the CMAS attack because the columnar intergranular gaps can act as fast infiltration paths for the molten CMAS. In viewing of this, novel gradient Y_2O_3 doped ZrO_2 coatings were designed and prepared by EB-PVD in this paper. The CMAS corrosion behavior at 1250℃ was investigated and the protection mechanism of the novel coatings against CMAS was clarified. Meanwhile, the thermal shock resistance was evaluated at 1100℃.

The results showed that the Y_2O_3 contents at the top of coatings reached 50wt.% and decreased gradually along the thickness. The resistance to CMAS corrosion of the gradient coatings got much improved, compared with the traditional YSZ coatings, since they could react with CMAS to form dense continuous apatite and melilite phases. The phases can prevent the further infiltration of the molten CMAS by occupying the infiltration paths. In addition, the thermal cycle lifetime of the coatings was not reduced because the columnar structures were remained.

10:30-10:50 Tea Break

10:50-11:20 Keynote (1224690)

Thermal Spray Coatings: Relating Processing Conditions to Microstructural Evolution

Christopher Berndt, Andrew Ang, Swinburne University, Australia

Thermal spray coatings (TSCs) and the associated technology represent a USD$14 billion global industry. Pre-1950 TSCs were based on flame spray, wire sprayings and low energy plasma techniques in relatively low risk applications. Advancements over the last 70 years have focused on matching temperature and velocity distributions of the thermal spray process zone to the particle size chemistry, morphology and size distribution. The applications of these coatings has now extended to the harsh and extreme conditions that are experienced under mechanical wear, corrosion and thermal environments.

The overall outcome is that the microstructural building blocks of TSCs have evolved from being ad hoc and unpredictable to heterogeneous structures that can be classified into ordered taxometric classifications. Moreover, the 3-dimensional structure of TSCs arises under dynamic conditions because the ground state of the coatings changes as multiple layers a created. The thermal spray process is constrained by the rules of physics. The rapid solidification processes are founded on the pioneering work of J. Madejski, i.e., where is the flattening ratio of the particle diameter to splat thickness and may be related to the Reynold's number of the thermal spray process. There have been many technical and theoretical advancements to the Madejski proposition over the past 4 decades. Thus, the traditional Madejski approach must be modified to account for real-time conditions.

The scientific outcome is that the flattening ratio (the diameter-to-thickness ratio of a splat) can be found. A thorough understanding this scientific question will enable the manufacture of improved products on the basis of fundamental science that is related to the wetting behaviour and viscosity of the impacting particles. There is a compelling and urgent need to provide a rigorous scientific understanding behind TSCs. The basis for this fundamental framework will be presented by describing how processing conditions influence microstructures for the growing family of thermal spray technologies.

11:20-11:45 Invited (1235974)

Plasma Deposition of Advanced Thin Films and Nanostructured Materials

Avi Bendavid, Fabio Isa, Phil Martin, CSIRO, Australia

It has long been recognized that surface engineering can enhance drastically the performance of a material. We at CSIRO have been developing plasma-based thin film deposition processes over the past three decades. CSIRO employs a range of PVD and CVD facilities for the synthesis of advanced thin film materials and nanomaterials. Our focus is on the application of thin films and nanostructures science for industrial applications and highly advanced instrumentation. One of the deposition techniques that we utilized extensively is the filtered cathodic vacuum arc deposition (FCVAD). It has been used in the deposition of a wide range of materials with unique properties. The benefit of the vacuum arc was recognized early on as a potentially effective source of energetic, ionized material for depositing thin films at high deposition rates with bulk properties and for the synthesis of new advanced materials. This talk will review the work that has been undertaken at CSIRO in developing new advanced thin films, nanostructured materials and applications using different filtered cathodic arc configurations. In this talk, we will describe the deposition of super-high precision coatings on the optics used in the detection of gravitational radiation in the Laser Interferometer Gravitational-Wave Observatory (LIGO) experiment. Through changing the functionality of surfaces, we can enhance optical, biological, chemical, structural and electrical properties and create sensors used in gas, SERS active substrates, nanodiamonds, hybrid electrodes for energy storage and optical devices. In this paper, our various capabilities with examples of applications are presented.

11:45-12:10 Invited (1235905)

Neutron Residual Stress Analysis of Single- and Two-Phase Cold-Sprayed Coatings

Vladimir Luzin, Australian Nuclear Science and Technology Organisation / School of Engineering, The University of Newcastle, Australia; Mingxing Zhang, School of Mechanical and Mining Engineering, The University of Queensland, Australia

Neutron diffraction for residual stress analysis is a powerful technique in application to coatings of different kinds, provided that they are metallic or ceramic. This non-destructive stress measurement technique combines advantages of high spatial resolution up to 0.1mm and high accuracy of just few MPa. Also, in contrast to any mechanical methods, the neutron diffraction is exceptionally beneficial when two-phase are to be investigated because different phases can be studied through different diffraction reflection in the overall diffraction pattern. In case of multiple phases, not only mechanical stress (macro-stress) can be determined, but also phase incompatibility stress (micro-stresses) can be studied, both providing experimental basis for understanding of the macro- and micro-mechanics.

The results of through-thickness residual stress profiling achieved by the neutron diffraction experiments at the Australian OPAL research reactor are reported in the case of selected one-phase and two-phase (metal-ceramic composite) coatings. Although with focus on the cold spray technique, the approach is easily generalized to other spraying techniques, e.g. HVOF or plasma sprays. The link of the experimental results to the mechanisms of macro- and micro-stress formation, which usually combine the thermal and plastic deformation mechanisms, as well as connection of these mechanisms to spraying parameters, will be discussed.

12:10-12:30 (1448648)

Microstructures of $La_2Ce_2O_7$ Coatings Produced by Plasma Spray-Physical Vapor Deposition

Cong Zhao, Wenting He, Liangliang Wei, Hongbo Guo, Beihang University, China

$La_2Ce_2O_7$ (LC) coatings were produced by plasma spray-physical vapor deposition (PS-PVD). To achieve the quasi-columnar microstructure, the process-structure relationships response for net power, spray distance and carrier gas flow were investigated. It was found that the net power and carrier gas flow played more significant roles than the spray distance to acquire high-ratio vapors. The corresponding phase and chemical compositions of coatings were studied by X-ray diffraction (XRD) and energy dispersive spectrometer (EDS), respectively. The results indicate that the lattice parameters of LC phases have positive correlations with average La/Ce ratios of the coatings. This may be related to different ionic radii between La^{3+} and Ce^{4+}. As the ionic radius of La^{3+} is larger, if the lattice parameter of LC phase is high, the La/Ce ratio is supposed to increase. The regional characteristics of the optimized coating were investigated by transmission electron microscope (TEM). The selected area electron diffraction (SAED) patterns confirmed Face Centered Cubic (FCC) structure, which is in accordance with defect fluorite structure. It is widely accepted as the structure of traditional LC phase. However, super-lattice patterns revealed it is not defect fluorite but pyrochlore structure. The "particle-interruption" mechanisms in the quasi-columnar coating were also discussed, mainly divided into two aspects: surface temperature and sub-column growth route.

E: Thin Films and Surface Engineering: III

Symposium Organizers :

Chuang Dong, Dalian University of Technology, China; Hongbo Guo, Beihang University, China; Hiroshi Masumoto, Tohoku University, Japan; Ho Won Jang, Seoul National University, Korea; Mingxing Zhang, University of Queensland, Austrlia

Tuesday PM Room: 313 (3rd Floor)
August 20, 2019 Symposium：E

Chairs:
Soo Young Kim, Chung Ang University, Korea
Xueqiang Cao, Wuhan University of Technology, China

13:30-14:00 Keynote (1287606)

Corrosion, Wettability, and Cytocompatibility of Ta and Ta-N Films Deposited on Ti6Al4V by Cathodic Arc Deposition

Yue Zhao, Sina Jamali, University of Wollongong, Australia; Ayching Hee, University of Adelaide, Australia; Huiliang Cao, SICCAS, China; Avi Bendavid, Phil Martin, CSIRO, Australia

Tantalum and tantalum nitride thin films were produced by filtered cathodic vacuum arc deposition method as a bio-stable surface treatment on Ti_6Al_4V titanium alloy for knee/hip joint implant applications. Effect of nitrogen to argon gas ratio on microstructure of the deposited film was observed by TEM. Corrosion behavior of the films in simulated biological fluid solution was examined by electrochemical impedance spectroscopy. It was found that both the Ta and Ta-N films enhanced corrosion resistance of the Ti_6Al_4V substrate with the best protective characteristics achieved by the Ta-N film deposited at 0.25 N_2/Ar gas ratio. The protective characteristic was attributed to the formation of tantalum oxide and oxynitride compound at the surface, as verified by X-ray photoelectron spectroscopy. Increasing N_2/Ar gas ratio increased susceptibility to localized corrosion. The effect of bias voltage on the substrate was investigated and it was found The Ta/−100V showed a significant improvement in corrosion resistance because of good cohesion to the substrate and a stable passivation layer on the film surface. The in-vitro cytocompatibility of the materials was investigated using rat bone mesenchymal stem cells, and the results show that the Ta films have no adverse effect on mammalian cell adhesion and spreading proliferation.

14:00-14:25 Invited (1340004)

Metallic Glass Coatings with Beneficial Properties for a Wide Range of Applications

Jinn Chu, National Taiwan University of Science and Technology, Taiwan, China

Glass-forming metallic coating have received increasing attention in recent years because these materials could be obtained readily using PVD processes such as magnetron sputter deposition. Metallic glass coatings are thus now available not only in monolayer and multilayer forms but also in nanotube arrays with sizes up to tens of mm. With the advent of these materials exhibiting unique physical and mechanical properties, the thin-film metallic-glass (TFMG) materials are also of great importance for scientific research and engineering application. In this presentation, some important properties are reviewed, with focuses on the high strength, excellent room-temperature ductility and extremely low coefficient of friction. Then, the TFMG-based applications are introduced, including enhancing electrospun polyacrylonitrile (PAN) membrane for oil/water separation. In this work, which has been published in Surface and Coatings Technology, Vol. 344, p. 33-41 (2019), we used magnetron sputtering to coat PAN membrane with Zr-based TFMG ($Zr_{53}Cu_{26}Al_{16}Ni_5$) to enable the separation of oil and water. The proposed coating also provides protection from chemical and thermal degradation as well as irreversible internal fouling. The smooth TFMG coating also provides a strongly hydrophobic surface (water contact angle of 136°). We also investigated the effects of sodium dodecyl sulfate (SDS) surfactant on oil/water separation performance. The resulting combination of the hydrophobic TFMG-coated membrane with the surfactant enabled oil rejection performance ranging from 95% to 100%, depending on the concentration of SDS. This work confirms that membrane-related problems such as fouling, chemical, and thermal stability can be resolved through the application of metallic glass coatings.

14:25-14:50 Invited (1234199)

The Oxide Reinforcement Effect of Be on the Oxidation Resistant Be-Containing Mg Alloys

Qiyang Tan, The University of Queensland, Australia

The present experimental work investigated the effect of trace addition of Be on the high temperature oxidation resistance of various Mg alloys, including AZ91, Mg-2Zn, Mg-2Sn, Mg-2Y, AS21, AM60, ZK20 and ZC63. It was found that microalloying with Be significantly improved the oxidation resistance of AZ91, Mg-2Zn, Mg-2Sn, AS21 and ZC63 alloys. But, Be microalloying marginally influenced the oxidation behaviours of the ZK20, AM60 and Mg-2Y alloys. The effectively improved oxidation resistance of the AZ91, Mg-2Zn, Mg-2Sn, AS21 and ZC63 alloys was attributed to the reinforcement effect on the initially formed oxide layer on the alloy surface. It was indirectly confirmed that Be can segregate in the initially formed MgO layer, (i) forming (Mg, Be)O solid solution; and (ii) refining the oxide grains during the oxidation process. The (Mg, Be)O layer with refined grains exhibited higher mechanical properties, including (i) the interfacial adhesion strength between the substrate and the oxide layer; (ii) the hardness; and (iii) the internal bonding strength of the layer. During high-temperature oxidation, the fine-grained (Mg, Be)O layer provided sufficient strength to withstand the internal stress generated by the internal tension stress and the vigorous Mg vaporisation, and therefore prevented oxide layer from cracking and debonding from the substrate. Hence, the oxidation incubation period was effectively increased. For the ZK20 and AM60, experiment exploited that the Zr and Mn solutes in these alloys chemically reacted with Be added, forming thermally stable Be-containing intermetallic compounds and therefore arrested the role of Be in improving their oxidation resistance. For the Y-containing Mg-2Y alloy, as Y can effectively improve the oxidation resistance, the effect of trace addition of Be was covered.

14:50-15:10 (1259900)

Microstructure and Oxidation Resistance of a Pt Modified $\alpha + \gamma + \gamma'$ Coating

Liangliang Wei, Beihang University, China

Platinum modified NiAl coatings, especially single-phase β-NiPtAl coating are widely used as oxidation-resistant coatings or as the bond coats in the thermal barrier coatings (TBCs) system . According to recent research, the single-phase β-NiPtAl coating are not compatible with the new-generation Ni-based single crystal (SC) superalloys contain high amount of refractory elements such as Re, Ru, W and Ta, because numerous topologically closed-packed phases (TCP) and second reaction zone (SRZ) are formed in the SC alloys due to the interdiffusion between the β-NiPtAl coating and SC alloy.
Pt modified $\gamma + \gamma'$ coatings were produced by electroplating of Pt films on a second generation Ni-based single crystal (SC) superalloy, followed by diffusion treatment at high temperature. The effects of processing parameters such as Pt film thickness, diffusion temperature and time on the microstructures of the coatings were investigated. Initial Pt thickness, vacuum diffusion temperature and time have important effects on the microstructures and chemical compositions of the Pt modified $\gamma + \gamma'$ coatings. A new type of Pt modified $\alpha + \gamma + \gamma'$ coating with high contents of Pt and Al was produced by 1h diffusion treatment at 1000℃, which exhibited good oxidation-resistance at 1100℃ but also good compatibility with the SC superalloy.

15:10-15:30 (1234122)

Effect of High Energy Shot Peening on Wear Resistance of TiN Films on TA2 Surface

Conghui Zhang, Xi'an University of Architecture and Technology, China

As a kind of high quality hard film, TiN film can significantly improve the surface hardness and wear resistance of materials, and has been widely used in the fields of dies, cutting tools and so on.In present work,the TiN films were deposited on the surface of pure titanium TA2 without and with high energy shot peening (HESP) by the pulsed magnetron sputtering. The morphology and crystal structure of TiN thin films were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The film-substrate adhesion, hardness and modulus of elasticity of TiN films were measured by scratch tester and nanoindentation tester. The wear resistance of TiN films was measured by micro-tribotester. The results showed that: compared with original pure titanium, TA2 surface treated by HESP could produce a large number of defects and have high chemical activity, which can quickly capture and fix Ti and N plasma during the sputtering process to refine the grain size of TiN film and make the film thicker and denser. With the prolongation of HESP time, the film-substrate adhesion increased from 19.6N of original TA2 to 44.2N of 40min HESP-treated TA2, and the nanohardness of TiN films increased from 14.0GPa of original TA2 to 28.4GPa of 40min HESP-treated TA2. HESP treatment could improve wear resistance and stable friction coefficient of TiN thin films. The specific wear rate of TiN films decreased from 0.061 mm^3/N.m of original TA2 to 0.019mm^3/N·m of 40min HESP-treated TA2.

15:30-15:50 Tea Break

15.50-16:15 Invited (1394072)

Understanding Mechanical Failure of Metal/Ceramic Interfacial Regions Through Microscale Mechanical Testing and Multiscale Simulations

Wenjin Meng, Louisiana State University, USA

We summarize our recent efforts in microscale measurements of the mechanical response of metal/ceramic interfacial regions under shear, compression, and tension loading. Utilizing the nanoscale machining capabilities of focused ion beam (FIB) instruments, microscale pillar specimens containing ceramic-coating/adhesion-interlayer/substrate interfacial regions were fabricated, with the interfacial region at different inclinations with respect to the pillar axis. Quantitative ex-situ and in-situ micro mechanical testing was carried out through axial compression and tension loading on the micro-pillar specimens, and was coupled with morphological/structural characterizations and multiscale simulations, including density functional theory (DFT), molecular dynamics (MD), and crystal plasticity finite element analysis (CPFEA). This combination offers new data and new insights into how metal/ceramic interfacial regions fail under mechanical loading, and suggests approaches for engineering the mechanical performance of metal/ceramic interfaces. Relevance to engineering mechanical integrity of coating/substrate interfaces will be discussed.

16:15-16:40 Invited (1235672)

Quantitative Measurement of Adhesion Strength for Anti-Corrosive Coating Layers on Steel Sheet

Young-Rae Cho, Pusan National University, Korea

Quantitative measurement of adhesion strength for anti-corrosive coating layers such as paint or zinc layer on steel sheet is very important. Also, corrosion is one of the major concerns for the metals degradation in shipbuilding industry. To protect ship steels from these corrosion problems, anti-corrosive paint has been developed. To obtain the intended results, the anti-corrosive paint should be strongly bonded to the steel-sheet substrate. The bonding (adhesion) strength between the paint and the substrate is governed by the degree of contamination on the substrate surface. When the bonding strength is insufficient, the corrosion resistance of the substrate is greatly degraded. The purpose of this study is to investigate the effect of surface contamination or different coating layers on the bonding strength of epoxy-based paint on the carbon steel for ships application. In particular, the effect of the contaminated area on the bonding strength was investigated. In order to understand these phenomena, we used structural steel (SPCC) and anti-corrosive epoxy paint which is mainly used in the shipbuilding or automotive industry. The adhesion strength between SPCC and anti-corrosive paint was measured by using Elcometer 510 made by Elcometer Corp. Dolly is made of aluminum (Al) with a diameter of 20mm. Especially, the theory of adhesion strength for paint or zinc (Zn) layer on the metallic substrate and effect of surface contamination on the adhesion strength will be discussed in details.

16:40-17:00 (1220538)

Research on A New Rust Stabilization Treatment of Weathering Steel and Its Corrosion Resistance Behavior

Lijun Gao, Jianwei Yang, Jianping Cao, Shengrong Wang, Shougang Group, China

The using of weathering steel without coating had become a new trend. But this using of weathering steel would cause rust scattering and environmental pollution. The formation of stable rust layer would be very long and some areas with high salt content, the dense rust layer would be difficult to form. To solve the problem that rust liquid appeared sagging and flying apart during the initial stage of the using of bare weathering steel. A new rust stabilization surface treatment agent was prepared. The effect of rust stabilization treatment on the rust structure and anticorrosion of weathering steel in the stimulated marine atmosphere were investigated through periodic immersed corrosion test, rust microscopic analysis and electrochemical measurement. The new rust stabilization surface treatment agent was mainly composed of a water-soluble acrylic resin and water is used as a solvent. Additional components added included a promoter, a pigment and a dispersant. Among them, the aqueous solution replaces the organic solvent component added to most of the conventional treatment agents, thereby achieving the purpose of greatly reducing the air pollution and achieving environmental protection effects. The results showed that rust layer of weathering steel after treatment was divided into continuous inner layers and outer layers. After 168h of accelerated corrosion, compared to bare steel, the corrosion rate of treatment weathering steel was reduced to 3.31 ($g·m^{2}·h^{-1}$) from 5.71 ($g·m^{2}·h^{-1}$). The corrosion rate was reduced by 42%. The rust layer resistance of treatment steel increased up to 167.7$\Omega·cm^2$ from 96$\Omega·cm^2$. The rust layer resistance increased by 75%. As the corrosion processing, Cr element aggregated on the junction of inner rust layer and substrate as α-(Fe1-xCrx) OOH. The new stabilization agent could obviously improve rust structure, refine the crystal grain and hinder the permeation of Cl^-, which was helpful for the generation of compact, continuous, stable layers on surface of weathering steel.

17:00-17:20 (1255883)

Grain Shape Effects on the Fracture Toughness of Yttria Partially Stabilized Hafnia Ceramics

Chun Li, Yue Ma, Hongbo Guo, Beihang University

The fracture toughness of ceramics served as top coat in thermal barrier coating system is of great importance. Numerous studies have attempted to improve the fracture toughness of some potential TBC materials which have excellent thermal properties by introducing second phase. In this work, 8 mol.% Y_2O_3 partially stabilized HfO_2 ceramics (Hf0.92Y0.08O1.96, YSH8) with C phase/ M phase/ C phase sandwich structure was utilized to enhance the fracture toughness. YSH8 specimens with different grain shape were obtained by sintering for 2~16h at 1500℃. X ray diffraction (XRD) and scanning electron microscope (SEM) were used to study the microstructure of YSH8, and indentation method was utilized to measure the fracture toughness. Results shows that YSH8 samples sintered for different time have identical phase composition, and all the specimens had a C phase/ M phase/ C phase sandwich structure except for the different length to width ratio of M phase. YSH8 sintered for 4h maintained the highest fracture toughness of ~2.4MPa·$m^{0.5}$, mainly because of the relatively high length to width ratio of the M phase inside the sandwich structure. Finite element simulation of the stress state in the sandwich structure was further investigated to study the effect of grain shape on the fracture toughness. The statistics of the sandwich structures in YSH8 samples were counted and two crack propagation resistance factors further explained the relationship of grain shape of YSH8 ceramics and the fracture toughness. This study put forward a simple way to improve the fracture toughness by conventional sintering method, and an effective approach to roughly predict the crack propagation resistance by FEM method.

17:20-17:40 (1257464)

Effect of Interfaces Discontinuity on Effective Thermal Conductivity of APS Lamellar Thermal Barrier Coating

Shiyi Qiu, Yue Ma, School of Materials Science and Engineering, Beihang University, China; Chenwu Wu, Institute of Mechanics, Chinese Academy of Sciences, China

The thermal barrier coating obtained by atmospheric plasma spraying has a distinct lamellar microstructure and good thermal insulation properties. The 'splat' boundaries in APS TBCs run parallel to the metal/ceramic interface, which are highly effective in reducing the thermal conductivity of APS TBCs. In this paper, the concept of discontinuity in 'splat' boundaries is introduced. Using the finite element simulation method, the microstructure model with random distribution of discontinuous boundaries is established, to investigate the effect of interlayer discontinuity on thermal conductivity. The results show that with the increase of interface discontinuity, the thermal conductivity of the coating decreases, and with the increase of the longitudinal distribution density of interlayer discontinuous boundaries, the thermal conductivity of the coating decreases. The discontinuous boundaries overlap distribution model is an optimization model, which has the lowest effective thermal conductivity because the heat transfer path is the longest. In the discontinuous boundaries overlap distribution model, the discontinuous boundaries distribution is more dispersed, and the thermal conductivity of the coating is larger, but the increasing trend tends to be gentle. These results provide a theoretical reference for the microstructure design of thermal barrier coatings.

17:40-18:00 (1235667)

Heat-Resistant Cux[Ni3Al] Films with R' phase Precipitation Strengthening

Tae Hyung Lee, Howon Jang, Seoul National University, Korea; Donghwa Lee, Postech, Korea

Recently, to replace the expansive noble metals in electrocatalyst, transition metals with low cost and comparable performances are chosen as substitutes. Among transition metals, iron, which is one of the most abundant metal in the earth crust, is relatively out of the attention as an electrocatalyst. Due to its earth abundance and well-organized production system, iron has the one-tenth price of nickel, and even one-fiftieth price for cobalt. Considering that the ultimate goal of the water electrocatalysis system is an integrated system with a photovoltaic cell which demands the scale-up processing, the cost competitiveness can be maximized for the commercialization.

To enjoy the strong cost competitiveness of the iron, the poor catalytic property of the iron based electrocatalysts, particularly its low current density should be enhanced. According to several studies, it is known that certain phase, iron oxyhydroxide, can have much higher current density than existing iron-based electrocatalysts. Especially, iron oxihydroxide (FeOOH) belongs to thermodynamically stable form among iron oxides and presented to have enhanced catalytic property by experiments. Though, there are not enough theoretical investigations on its catalytic activity.

Herein, we investigate the water oxidation mechanism on the Iron oxyhydroxide(FeOOH) electrocatalysts using first-principles calculations based on Density Functional Theory. With calculations of relative surface stabilities and adsorbate coverages, the most stable low-index surfaces of FeOOH will be determined. Next, with the determined FeOOH surfaces, we will compare the theoretical overpotentials achieved by calculating each oxygen evolution reaction steps. For each step, the magnetic state will be checked for the explanation of oxygen evolution reaction process. Furthermore, impacts of the various dopants such as Mn, Ni, Co will be also investigated. With the calculation using hybrid functional, the electronic structure of the iron oxyhydroxide, with and without dopants, will be obtained and it will give the explanation of different OER catalytic activity shown by iron oxyhydroxide with different dopants.

For the strict verification of the calculation data, experiment results of the bare and doped FeOOH will be also presented. All the alpha FeOOH samples are synthesized with electrodeposition method and their electrocatalytic properties will be evaluated. With the comparison of calculation and experiment data, it is expected to figure out how the dopants affect bulk properties, reaction at the surface of the FeOOH and eventually influence the electrocatalytic properties.

E: Thin Films and Surface Engineering: Ⅳ

Symposium Organizers :

Chuang Dong, Dalian University of Technology, China; Hongbo Guo, Beihang University, China; Hiroshi Masumoto, Tohoku University, Japan; Ho Won Jang, Seoul National University, Korea; Mingxing Zhang, University of Queensland, Austrlia

Wednesday AM August 21, 2019 — Room: 313 (3rd Floor) Symposium：E

Chairs:
Yue Zhao, University of Wollongong, Australia
Young-Rae Cho, Pusan National University, Korea

8:30-8:55 Invited (1233785)

Application of Transition Metal Sulfides Synthesized by $(NH_4)_2MeS_4$ Precursors (Me: Metal)

Soo Young Kim, Chung Ang University, Korea

Recently, transition metal dichalcogenides (TMDs) including MoS_2 and WS_2 have attracted increasing attention because of their great potential as semiconductors of electronic devices such as field-effect transistors, organic photovoltaics, memory, logic, and energy storage devices.
First, TMDs were used in order to enhance the stability in air comparing to poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS). TMD layers with a polycrystalline structure were synthesized by a chemical deposition method using uniformly spin-coated $(NH_4)MoS_4$ and $(NH_4)WS_4$ precursor solutions. Organic light emitting diodes (OLEDs) and organic photovoltaic cells based on TMD showed two to six times longer stability in air compared with PEDOT: PSS based devices. Second, TMD layers were applied as the hole transport layer as well as the template for highly polarized OLEDs. The MoS_2 nanosheets were patterned by rubbing/ion-beam treatment. The use of patterned MoS_2 nanosheets not only tuned the polarization of the OLEDs but also dramatically improved the device performance as compared with that of devices using untreated MoS2. Third, TMD nanosheets are used as efficient catalysts for hydrogen evolution reaction, which can potentially replace the expensive platinum catalyst. Finally, tungsten trioxide (WO_3) films synthesized by using TMD precursors, $(NH_4)_2WS_4$, was applied to electrochromic (EC) devices. It is shown that Au-doped WO_3 films are great candidates for the development of smart windows with high EC performance. This presentation will show us many applications of TMD materials.

8:55-9:20 Invited (1221926)

Tunneling Magneto-Dielectric (TMD) Effect: Recent Advances and Future Perspectives

Yang Cao, Hiroshi Masumoto, Tohoku University, Japan

Single-phase material with multifunctional properties, such as combining both electronic and magnetic properties, holds potential for both fundamental science and device application [Nature 442, 759 (2006).]. In the case of granular ME composites, a BaTiO3/Ni ME compacted composite by virtue of elastic interactions between piezoelectric (Ba_2) and magnetostrictive (Ni) phases, wherein the strain arising from the magnetostrictive phase passes on the piezoelectric phase and generates an electric field. Similar ME effect was also observed in annealed $BaTiO_3$/Co thin films [Appl. Phys. Lett. 92, 062908 (2008).].
Different from the aforementioned strain-mediated MD effect, we recently discovered a kind of MD effect in FeCo-MgF granular nanocomposites, wherein superparamagnetic FeCo granules with sizes of 2~5nm are homogeneously distributed in MgF insulating matrix [Nat. Commun. 5, 4417 (2014).]. This dielectric enhancement is caused by the charge tunneling through the MgF barrier in each granule pair, whereby the tunneling rate depends on the relative orientation of the magnetic moments between two magnetic granules, i.e., the spin-dependent tunneling. By analogy with tunnel-type magnetoresistance (TMR) in granular films, we termed the tunnel-type MD (TMD) effect. These granular films have the practical advantage of thermal stability and do not require any additional treatment, such as binding, compaction, or annealing.
In this presentation, we reviewed the recent advances of this TMD effect and give future perspectives. We first clarified how the granular content determined the frequency dependence of the TMD response and the inter-granular distance play a crucial role in regulating the frequency response of the TMD effect [Appl. Phys. Lett., 111, 122901 (2017).]. From this perspective, the frequency response of the TMD effect was artificially controlled by in-situ insertion of several insulator layers [Appl. Phys. Lett., 113, 022906 (2018).]; this verified the important role of granular distribution played in the regulation of TMD response. Second, to improve the low-field TMD response, we fabricated a two-dimensional (2D) granular heterostructures, wherein a mechanism based on a balanced control of ferromagnetic and super-paramagnetic components has been proposed [Appl. Phys. Lett., 110, 072902 (2017).]. Our recent results have shown that the variation of CoFe granules has induced the high TMD responses ($\Delta\varepsilon'/\varepsilon'_0$) from 2.3% to 4.3%, the enhanced effect was briefly discussed based on the variation in the spin polarization (PT) of magnetic Co-Fe alloy granules.
Theoretical prediction gives its maximum TMD limit of over 20% as if using the high spin-polarized materials

with PT =1, e.g. half-metallic compound. The discovery of room temperature TMD effect would offer a new avenue to achieve the magnetoelectric response, as well as potential applications in magnetoelectric devices.

9:20-9:40 (1221182)

Preparation and Characterization of TiO_2 Nanoparticles by Two Various Precipitations

Shimin Liu, Zhinuo Wang, Yu Guo, Dongdong Liang, Weiwei Jiang, Chaoqian Liu, Hualin Wang, Nan Wang, Wanyu Ding, Dalian Jiaotong University, China

TiO_2 has become the most studied photocatalyst which has been widely used in wastewater treatment, photocatalytic degradation of organic pollutants, photolysis of water and other fields due to its high efficiency, low cost, stable physical and chemical properties. It is well known that the polymorphs of TiO_2 can be divided into anatase, rutile and brookite. Generally, TiO_2 is prepared either from minerals or from a solution of salts or alkoxides by such as the sulfate, chloride and one of the various processes including hydrothermal, coprecipitation, and sol-gel Understanding the nature of crystallization in nanoscale TiO_2 is important for its use in photocatalysis applications. This paper presents the preparation of TiO_2 nanoparticles by precipitation method using titanium tetrachloride and titanium oxalate as raw materials, respectively. The effects of calcination temperature on the structure, crystal size, morphology, energy gap and photocatalytic properties of TiO_2 nanoparticles were investigated. The obtained samples were characterized by thermogravimetry-differential scanning calorimetry, X-ray diffractometry, transmission electron microscopy, and ultraviolet visible spectrophotometer. The results show that with the increase of temperature, the crystal structure of TiO_2 nanoparticles gradually changed. The crystallization temperature of TiO_2 nanoparticles was 250˚c when titanium chloride was used, while it was 450˚c when titanium oxalate was used. TiO_2 powders began to form rutile phase at 450˚c when titanium chloride was chosen. Nevertheless, TiO_2 powders began to form rutile phase at 850° C when titanium oxalate was selected. With the increase of calcination temperature, the particle sizes of the two prepared TiO_2 nanoparticles increased. The grain size of TiO_2 powders obtained using the titanium oxalate was significantly larger than that using the titanium tetrachloride as raw materials heat treated at the same temperature. Lastly, the degradation of methyl orange by TiO_2 powders using the titanium chloride as raw material is as high as 90%, but the maximum degradation was only 39% when titanium oxalate was used.

9:40-10:00 (1232657)

Electrical-Resistivity Properties of Al-Co-Cr-Fe-Ni High-Entropy Alloy Thin Films

Chenyu Wang, Xiaona Li, Linxia Bi, Qing Wang, Chuang Dong, Dalian University of Technology, China; Peter Liaw, The University of Tennessee, USA

High-entropy alloys (HEAs) possess some basic electrical-resistivity characteristics [such as high resistivity values and low temperature coefficients of resistivity (TCRs)] of concentrated disordered solid-solutions due to their properties of highly chemical-disorder. However, the resistivity properties of HEAs still need more comprehensive and in-depth investigation, and the application potential of HEAs as thin-film resistive materials is also worth assessing. In the present work, the AlxCoCrFeNi (x=0.7,1) HEA films were prepared by magnetron sputtering. The resistivity properties of the HEA films from room temperature to 1078K were thoroughly analyzed and compared to the bulk AlxCoCrFeNi HEAs with similar compositions. Results showing: The AlxCoCrFeNi HEA films are consisted of face-centered-cubic (fcc) and body-centered-cubic (bcc) phases, which are more disordered than the bulk HEAs mainly with the B2 (ordered bcc) phase. Differences between the phase structures of the film and bulk AlxCoCrFeNi HEAs is the main reason for their different changing behavior of resistivity with temperature. The large decline of resistivity appeared at around 565K of the HEA films is attributed to their ordering transitions of the bcc to B2 phases, while this phenomenon does not exist in the bulk HEAs. On the premise of considering the s-d scattering effects (additional scattering occurred in transition metal alloys when electrons from the s band transfer to the d band), the parts of the resistivity curves before phase transitions of the HEAs are described. Important characteristics of the resistivity properties of AlxCoCrFeNi HEAs were also investigated, the high resistivity is mainly attributable to the severe lattice distortion (caused by the chemical disorder) and the s-d scattering effects, and the generalized diffraction model can be used to explain the near-zero TCRs. After comparing with the conventional thin-film resistive materials, the multiple-components advantage of HEAs shows contributions to the wider resistivity range of AlxCoCrFeNi films as well as their near-zero TCRs.

10:00-10:20 (1232669)

Theoretical Investigation of the Catalytic Activity of Goethite (α-FeOOH) for the Electrochemical Water Oxidation

Zhumin Li, Xiaona Li, Nanjun Li, Chuang Dong, Dalian University of Technology, China

In many applications (mold's internal), copper and copper alloys not only pursue good conductivity and thermal conductivity, but also require its surface to have high hardness, good thermal conductivity and high temperature corrosion resistance. The surface strengthening method can be used to improve the surface properties while keeping good thermal and electrical conductivity of copper substrate. According to the strengthening theory of Ni-based alloys, the r'-Ni3A1 phase still has the advantage of long range order under high temperature, and good creep performance. Therefore, this article aims to prepare (r'+r) phase precipitation strengthening films on pure Cu surface to improve the mechanical and heat resistance properties of material surface. To obtain r'-Ni3A1 phase, a series of Cu-Ni-Al ternary films were prepared by magnetron sputtering with Ni/Al ratio close to 3. After the initial microstructure and performance characterization, the experimental results showed that r'-Ni3A1 phase existed in the sputtered Cu-Ni-Al films and embedded in the matrix r with nano-state. By this stage, the film has a high hardness, and gradually increases with increasing of the Ni and Al content. The reasons are as follows: first, the solid solution of alloying elements into Cu lattice leads to the strengthening effect of solid solution; The other is the precipitation enhancement caused by the precipitation phase of r'-Ni3A1; The third is the fine grain strengthening effect caused by the uniform nanometer columnar crystal. After annealing 723K for 20h, the hardness of pure Cu film decreased significantly, while Cu-Ni-Al films still maintain a high level, indicating good stability of the films. It also suggests that precipitation strengthening deriving from r'-Ni3A1 phase can partially offset the weakening of the fine grain strengthening due to grain consolidation and solid solution strengthening causing by alloying elements during the annealing process.

10:20-10:40 (1235612)

Comprehensive Study on Morphology Control of TiO_2 Nanorods on Foreign Substrates by Hydrothermal Method

Jongseong Park, HoWon Jang, Seoul National University, China

The hydrothermal method is a facile route for the synthesis of TiO_2 nanostructured materials, but it requires accurate process optimizations and adjustments to circumvent the undesirable morphology products. In this study, systematically controlled experimental studies are carried out under thermodynamic and kinetic considerations to understand the formation of the well–aligned TiO_2 nanorods during the hydrothermal reaction. In this regard, TiO_2 nanorods are synthesized on various types of substrates, including single crystal TiO_2 and sapphire, fluorine doped tin oxide, and silicon. Variable growth parameters are classified and investigated for their effects on the morphological evolution of TiO_2 nanorods. The preferred morphology of TiO_2 nanorods with {110} facet is confirmed based on the crystallographic results for TiO_2 nanorods acquired by extensive transmission electron microscopy studies during the entire growth processes. The presence of the seeds on the substrates is found to be mandatory for the formation, growth and strong adhesion of the TiO_2 on the applied foreign substrates. The results elucidate that the growth kinetic of the process is significantly governed by the amount of the applied HCl concentration, which is highly influential on the morphology of the synthesized TiO_2 nanorods. Accordingly, the growth mechanism for the preferential growth maintaining the rod shape is derived.

E. Thin Films and Surface Engineering

Symposium Organizers :

Chuang Dong, Dalian University of Technology, China; Hongbo Guo, Beihang University, China; Hiroshi Masumoto, Tohoku University, Japan; Ho Won Jang, Seoul National University, Korea; Mingxing Zhang, University of Queensland, Austrlia

August 19-21, 2019
Room: Exhibition Area (3rd Floor)

E-1: Preferred Orientation and Electrical and Optical Properties of NiO Films Deposited by Reactive Pulsed DC Magnetron Sputtering with Different Sputtering Powers(1225360)
Nan Wang, Dalian Jiaotong University, China

Up to now, NiO films with preferred orientation have been prepared by spray pyrolysis, pulsed laser deposition, sol-gel spin coating, chemical vapor deposition, RF magnetron sputtering, DC reactive magnetron sputtering, and so on. Among these methods, magnetron sputtering is more widely used because it is more suitable for industrial large-scale production. Generally, NiO films are deposited by RF magnetron sputtering from NiO ceramic target, but by DC reactive magnetron sputtering from Ni metal target. Evidently, high quality metal target can be more easily fabricated than high quality ceramic target, and the film preparation process based on DC magnetron sputtering can be more easily controlled than that based on RF magnetron sputtering. Therefore, DC reactive magnetron sputtering is promising in the preparation process of NiO films. In previous studies, the NiO films deposited by RF magnetron sputtering usually presented (1 1 1) or (2 0 0) preferred orientation, but those deposited by DC reactive magnetron sputtering generally showed (2 0 0) or (2 2 0) preferred orientation. Such difference of the NiO films in preferred orientation should be determined by the different magnetron sputtering modes and the different sputtering parameters. However, the study on the NiO films deposited by pulsed DC reactive magnetron sputtering is still lacking, and then the preferred orientation of the NiO film deposited by the sputtering method also is not known. In this paper, the NiO films were deposited at room temperature by reactive pulsed DC magnetron sputtering from a Ni target, and the effects of the sputtering power on the preferred orientation and the electrical and optical properties of the deposited films were discussed systematically. The films deposited at the lower sputtering powers presented (2 0 0) orientation, but those deposited at the higher sputtering powers showed (1 1 1) orientation. With increasing the sputtering power, the carrier concentration of the films increased, but the carrier mobility decreased, and then the resistivity decreased.

E-2: Properties of Cu2ZnSnS4 Films Prepared by Single-Target Magnetron Sputtering at Different Sputtering Pressures(1225389)
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Single-target magnetron sputtering method is boomingly developed in preparing CZTS films and numerous correlative studies were reported. For magnetron sputtering method, it is well accepted that the deposition parameters (such as substrate temperature, sputtering power, sputtering pressure, etc.) can seriously affect the growth behavior of the films. There are a lot of literatures reporting the effects of substrate temperature and sputtering power on the properties of CZTS films deposited by the single-target magnetron sputtering. There are only several groups studying the effects of sputtering pressure. Our group recently studied the effects of sputtering pressure on the preferred orientation of the CZTS films deposited at room temperature, and indicated the preferred orientation was gradually converted from (2 2 0) to (1 1 2) with increasing sputtering pressure. However, it is still very limited in the study of sputtering pressure affecting the physical properties of the CZTS film deposited by a single quaternary ceramic target at higher substrate temperature without sulfurization process. In the present work, the effects of the sputtering pressure were investigated on the phase, preferred orientation, composition, morphology, and electrical and optical properties of the CZTS films deposited by single-target magnetron sputtering method at 400℃. The effects of the sputtering pressure on the composition, phase, preferred orientation, surface morphology, and electrical and optical properties of the CZTS films were studied. The results indicated that the content of Zn was remarkably affected by the sputtering pressure. All the deposited films exhibited the single kesterite phase and the well-preferred orientation of (112), and the spatial distribution of the preferred orientation was not almost affected by sputtering pressure. With increasing the sputtering pressure, the granule boundaries became more and more clear, but compactness of the films became poor. Moreover, the electrical properties of the films were seriously affected by the elemental content and the morphology. All the optical bandgaps were almost constant.

E-3 Surface Roughness and Work Function of ITO Films by Ion Bombardment Treatment(1225393)
Hualin Wang, Dalian Jiaotong University, China

Transparent conducting oxides is still a hot topic in material science field, such as tin-doped indium oxide (ITO), aluminum doped zinc oxide and antimony doped tin oxide. ITO is a highly degenerate n-type semiconductor, which has excellent electrical conductivity and highly transparence to the visible light. Due to these unique properties, ITO films have been utilized in devices such as flat panel displays, solar cells, lamps, and so on, especially as the anodes in organic light emitting diodes (OLEDs). As the anode in OLEDs, there is a large demand for ITO films with excellent optical and electrical properties, smooth surface and high work function. Due to the as-deposited ITO films can not meet the requirements. Therefore, the relationship between the properties of ITO and various surface treatments has been widely studied. The most commonly used ITO treatments are polishing, oxygen plasma treatment, ultraviolet (UV) ozone treatment and so on.

In this paper, ITO films were prepared by direct current pulse magnetron sputtering from a ceramic In_2O_3: SnO_2 (90wt.%:10wt.%) target. Due to the high demand for ITO films as the anode in OLEDs, the deposition parameters were optimized. And post-processings by ion bombardment were performed with a linear ion source (AE, PinnacleTM Plus+ 5kW). The thickness, optical and electrical properties, surface morphology and surface work function of ITO films were investigated systematically by the step profiler, spectrophotometer, Hall effect measurement system, atomic force microscopy and kelvin probe force microscopy.

The as-deposited ITO films were bombarded with Ar ion or O ion at different times and ion energies. It was found that O ion bombardment had a significant effect on the work function of ITO, while Ar ion bombardment had a significant effect on the roughness of ITO surface. Bombarding with higher energy of Ar ion at a short time (<2min), could promote the flowing of atoms on the surface of ITO films, and the roughness of ITO films reduced. Due to the selectivity of the sputtering of Ar ion, the roughness of ITO films increased with a longer bombardment time. The work function of ITO films increased from 4.50eV to 4.96eV with the increasing of bombardment time from 0 min to 2min. When the bombardment time was more than 2min, the work function of ITO films didn't increase again. But the sheet resistance of ITO films kept on increasing with the increasing of bombardment time.

In summary, Ion bombardment is a considerable post-processing method to improve the surface flatness and work function of ITO films using for OLED.

E-4: Calcium-Magnesium-Alumina-Silicate (CMAS) Resistance Property of $LaTi_2Al_9O_{19}$ for Thermal Barrier Coating Applications(1257851)

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The higher operating temperatures in gas turbine engines made possible by thermal barrier coatings (TBCs) are engendering a new problem: environmentally ingested airborne silicate particles (sand, ash) melt on the hot TBC surfaces and form calcium-magnesium-alumina-silicate (CMAS) glass deposits. The molten CMAS glass degrades the TBCs, leading to their premature failure. In our study, a kind of newly developed TBC ceramic, $LaTi_2Al_9O_{19}$ (LTA), is found to have high resistance to the penetration of molten CMAS at 1250℃. The formation of a continuous, dense crystalline layer, mainly composed of anorthite ($CaAl_2Si_2O_8$), between the sample surfaces and LTA contributed to this desirable attribute. The accumulation of Al and Ti in the molten CMAS triggered the crystallization of the melt, leading to the formation of many $CaAl_2Si_2O_8$ anorthite crystals above the LTA layer, which could reduce the mobility of the molten CMAS by reducing the amount of Si entering the LTA or YSZ matrix. In this context, we study the resistance of LTA bulk and APS-LTA/YSZ coating to CMAS, and the mechanisms by which the CMAS attacks LTA samples are discussed. The results indicate that Ti is an effective element for altering CMAS composition, and LTA can be an attractive way of mitigating CMAS attack.

E-5: Surface Modification of Mg Alloy by Mechanochemical Cavitation(1220042)

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Among metals with practical uses, Mg is the lightest, with a specific gravity one-quarter that of Fe and two-thirds that of Al. Moreover, it has a high specific strength and specific rigidity, and excellent properties in terms of electromagnetic wave shielding ability and recyclability. However, Mg has the lowest standard electrode potential among practical metals and is chemically very active, so it is easily corroded. Therefore, to increase the corrosion resistance, it is necessary to improve the surface of Mg, and typical Mg surface treatments include anodizing and chemical conversion. Anodic oxidation treatment is used industrially because corrosion resistance is improved by using sealing treatment and painting in combination. However, for Mg anodizing treatment, unlike the alumite treatment for Al alloys, an electrolytic solution for maintaining current-carrying holes, such as a sulfuric acid bath, has not been developed. As a result, to form a thick film on the magnesium surface, it is necessary to grow an oxide film with dielectric breakdown due to spark discharge during its formation. Therefore, it is necessary to increase the current density, and accordingly the cost of the power supply and cooling equipment increases. Chemical conversion treatment is a method for chemically treating a metal surface and forming a coating of an insoluble compound. This method combines high versatility and low cost, and it is applied industrially. In typical chemical conversion treatment of Mg alloys, a liquid containing a large amount of hexavalent chromic ions, such as anhydrous chromic acid and dichromic acid salt, is used. However, due to growing "green" social demands, such as the

EC Restriction of Hazardous Substances Directive, to limit the use of hazardous substances for electronic devices, chromic-free chemical conversion is required. At present, there are two types of practical chromic-free chemical conversion treatments: phosphate and permanganate. Between them, the phosphate type is more commonly applied to Mg alloys. The most proven coating system is the calcium phosphate-X system (where X denotes a metal such as Mn and V). The film formed by this system is excellent for resisting corrosion. However, the corrosion resistance of the produced calcium phosphate-manganese type film is not sufficient and needs improvement. To improve the corrosion resistance of the Mg alloy, a new processing technique is required. In this study, basic research on the formation of a film for improving the corrosion resistance of a Mg alloy (AZ31) surface was carried out by the addition of dilute phosphoric acid during water jet peening (WJP) and multifunction cavitation (MFC).

E-6: Formation of TiO_2/ZrO_2 Nanotube/Nanoporous Heterostructure on Silicon Substrates Using an Anodization Process(1234983)

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Metal oxide nanostructures display unique electrical, optical and chemical properties. Among various methods of processing nanostructured metal oxides, anodization is generally known as a useful method for modifying the surface structures to obtain the nanoporous or nanotubular structures. However, most of the work focuses on the anodization of metal or alloy foils, which structure are inflexible and difficult to apply the micro and nano device. In this work, Ti/Zr/Ti multilayer film as an anodized substrate was prepared by magnetron sputtering. Subsequently, the TiO_2/ZrO_2 nanotube/nanoporous heterostructure was obtained by anodizing. In this work, Ti/Zr/Ti multilayer films were deposited on single-crystal Si wafers using DC magnetron sputtering then anodized. The TiO_2/ZrO_2 nanotube/nanoporous heterostructure were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS).

For the results of scanning electron microscope (SEM), the cross-section morphology of the Ti/Zr/Ti multilayer films prepared by magnetron sputtering show a columnar structure and Ti layers are more dense than the Zr layer. And a flake-like surface morphology of the top Ti layer can be observed. After the anodizing treatment, the upper and lower Ti layer are transformed into a nanotube structure. The nanotubes are open on the top while on the bottom they are closed, and the tubes diameter are about 90nm. Different from the Ti layer, the Zr layer in the middle is transformed into a nanoporous structure. Because of Zr layer with more inter-columnar voids, the electrolyte has access not only to the top surface, but also to the side walls of the columns. Each column would individually experience the typical anodization process, involving pit nucleation and growth resulting in a sponge-like structure. The EDS and XRD results indicate the formation of a TiO_2/ZrO_2 nanotube/nanoporous heterostructure.

E-7: Effect of TiO_2 Doping on the Mechanical and Thermo-Physical Properties of Y_2O_3 Stabilized HfO_2 (1258411)

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The fracture toughness of ceramics has an important influence on the service life of thermal barrier coatings. 8 mol% Y_2O_3 stabilized HfO_2 (YSH) ceramics doped with different TiO_2 contents ((Hf1-xTix)0.92Y0.08O1.96 , x=0, 0.05, 0.1, 0.15, 0.2 and 0.25) were synthesized by solid-state reaction at 1550℃ for 5h. The phase composition, mechanical properties and thermal conductivity of TiO_2-doped YSH were investigated. The ceramics were composed of monoclinic phase and cubic phase when the TiO_2 concentration varied from 0 to 0.1. As TiO_2 concentration was between 0.15 and 0.2, more oxygen deficient $YTiO_{2.085}$ phase was observed. As TiO_2 content reached 0.25, hafnium titanate was detected. The fracture toughness of (Hf1-xTix)0.92Y0.08O1.96 ceramic increased as Ti^{4+} ion concentration increased, and reached 3.2MPa·$m^{1/2}$ when x=0.25, nearly 52% higher than that of Hf0.92Y0.08O1.96. This enhancement of fracture toughness of the (Hf1-xTix)0.92Y0.08O1.96 ceramic by emerging the residual stress as a result of the increased amount of the second phase when TiO_2 doping content increased. The thermal conductivity of (Hf1-xTix)0.92Y0.08O1.96 ceramics decreased as Ti^{4+} ion concentration increased. Specifically, 25mol%TiO_2-doped YSH had the lowest thermal conductivity (1.8W/m*K at 1200℃), which was about 24% lower than that of Hf0.92Y0.08O1.96. This reduction was due to the lattice distortion of the unit cell, upon substituting Ti^{4+} for the Hf^{4+} cation with a mismatch in atomic mass and ionic radius. Lattice defects scattered the phonon transmission effectively, resulting in the phonon mean free path as well as the thermal conductivity reduced. Meanwhile, 25mol% TiO_2-doped YSH kept good phase stability between room temperature and 1400℃. Considering the comprehensive properties, 25mol% TiO_2 doped YSH was considered as a promising thermal barrier coating ceramic.

E-8: Synthesis and Characterization of Gadolinium Zirconate Feedstocks for PS-PVD(1260091)

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Plasma spray-physical vapor deposition (PS-PVD) is an advanced coating fabrication technology which can produce multiple microstructures, such as "columnar structure", "dense lamellar structure", and "quasi-columnar structure". Recently, columnar structured thermal barrier coatings made of yttria stabilized zirconia (YSZ) manufactured by PS-PVD has been reported presenting excellent thermal cycling lifetime. Gadolinium zirconate (GZO) is very promising ceramic material suggested as a substitute of YSZ. In this study, pyrochlore structured GZO feedstocks for PS-PVD were successfully synthesized. Two kinds of starting powders were prepared by reverse titration coprecipitation and solid-state reactions, which were in nanoscale (NP) and microscale (MP), respectively. Afterwards, GZO feedstocks for PS-PVD were obtained through spray drying. The characteristics of the two feedstocks were studied by Laser particle size analyzer (LPSA), Scanning electron microscope (SEM), X-ray diffraction (XRD), and Hall funnel. Results revealed that the phase composition, the size distribution and their flowability of the NP and MP feedstocks were similar while the porosity of the NP feedstocks was lower than that of MP feedstocks. GZO coatings were fabricated by PS-PVD with same spraying parameters. It showed that the coating deposited from MP feedstock was typical columnar structure and was thicker, which indicates that the MP feedstock was more suitable for PS-PVD.

E-9: Study on the Preparation Process and Microstructure of Yb_2SiO_5 Environment-Barrier Coating Prepared by Plasma Spray Physical Vapor-Deposited (1458868)

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In this paper, the spraying parameters of Yb_2SiO_5 environmental barrier coating prepared by PS-PVD were optimized and determined by orthogonal experiments. The typical morphologies of the coating under different spraying parameters were analyzed. The variation of the morphology and thickness of the coating along the radial direction of the jet was studied, and the deposition mechanism of the coating prepared under the optimal spraying parameters was analyzed. The results show that the coatings prepared by spraying parameters of 1200A gun current, 10mbar vacuum and 900mm spraying distance have high density, high hardness and fast deposition rate. With the increase of beam heating, small solid particles, large solid particles, liquid phase layered structure, silicon-poor particles and silicon-rich gas cylinders can be formed separately. The farther away from the center of the beam flow, the heating ability of the beam on the powder is weakened, and the solid and liquid particles will migrate downward under the influence of gravity. Under the optimum parameters, the coating is mainly liquid phase deposition. With the increase of deposition thickness, the liquid layer becomes uniform gradually, and the proportion of gas and solid phase deposition is small.

E-10: Structure, Magnetic and Dielectric Properties of Co-$SrTiO_3$ Nano-Composite Films(1235669)

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The magnetoelectric effect in materials that consist of magnetic and dielectric components has been demanded for the magnetoelectric applications such as sensors, and tunable devices. Although many candidate materials were previously studied, the magnetoelectric effects are too weak at room temperature because of their low magnetic transition temperature. In our group, the tunneling magneto-dielectric (TMD) effect was observed in FeCo-MgF nano-composite films for the first time(1). These films comprise two-phase components with the room temperature TMD effect, which holds high potential for device application. In this study, we prepared Co-$SrTiO_3$ nano-composite films using differential pressure sputtering (DPS), that can control Co (ϕ3") and $SrTiO_3$ (ϕ3") sputtering condition, respectively. Metal-oxide nano-composite systems, which are expected to expand the application range of TMD effect, has been used instead of metal-fluoride composite. The Si(100), Si/Ti/Pt, Si/Ti/Au and quartz were used. Magnetic property was observed by Vibrating Sample Magnetometer. Electric resistivity was tested by resistivity meter. Dielectric constant was analyzed by LCR meter. The Co-$SrTiO_3$ films exhibit nano-composite structure, with Co granules embedded in $SrTiO_3$ matrix. At Co=29 at.%, film shows super-paramagnetic properties and the electric resistivity is more than $1.0 \times 10^4\ \Omega \cdot m$. TMD effect at room temperature has been found in Co-$SrTiO_3$ nano-composite films.

E-11: Highly Conductive and Stable Silver Nanowire Transparent Electrodes Fabricated by Electrodeposition (1222756)

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Transparent conducting electrodes (TCEs) have been one of key components in various electronic and energy applications such as photovoltaic devices, flat panel display devices, and light emitting diodes. So far, Indium tin oxide (ITO) has been the most commonly used material for TCEs owing to its high transmittance (T >90%) and low sheet resistance (R_s <10 Ω/m). Despite the high transmittance, however, the inherent brittleness of ITO proves to be insufficient for flexible device application. Furthermore, the relatively high cost of ITO in materials and processing has still been problematic to wider the application of TCE. Thus, various materials such as carbon nanotubes, graphene and metal nanowires, have been studied as alternatives to ITO thin films. Among them, metal nanowire networks including silver nanowire has attracted tremendous interests, due to the capability of solution process that enable to reduce processing time and cost as well as its flexibility resulting from the networks structure and ductility of metal. On the other hands, the critical properties of AgNWs network as a TCE such as the sheet resistance, transparency, surface roughness and thermal stability need to be improved with reliable processes in order to be commercially utilized in the market. Here we demonstrate a method to improve aforementioned properties in silver nanowire network by using electrodeposition. The electrodeposition enhanced the conductance of silver nanowire by increasing diameter of nanowire and lowering the contact resistance between each silver nanowire. Our experimental data demonstrate that the silver nanowire network with larger diameter showed lower sheet resistance than with smaller diameter at the same transparency, implying that electrodeposition is the effective method to improve optical and electrical properties of nanowire transparent electrode. In addition to the enhancement of optical and electrical properties, electrodeposition method also improved surface roughness and thermal stability of silver nanowire network. Additional silver is uniformly deposited on the surface of the nanowires to smooth the surface morphology of the silver nanowire network. By increasing the diameter of silver nanowire up to 300nm, the silver nanowire network preserves its conductance up to 550˚C, proving that the thermal instability of silver nanowires due to surface diffusion was greatly improved by electrodeposition. A CIGS thin-film solar cell with an electrodeposited sliver nanowire TCE shows nearly equal device performance to that of a cell with a sputtered AZO TCE. We expect that electrodeposited sliver nanowire networks can be used as high-performance and robust TCEs for various optoelectronic applications.