

Advanced Surface Engineering Division

Room On Demand - Session SE-Contributed On Demand

Advanced Surface Engineering Contributed On Demand Session

SE-Contributed On Demand-1 Electrodeposition of Mn⁺³ Rich Layered δ -Phase MnO₂ Nanofibers on Epitaxial Graphene-Silicon Carbide Heterostructures for Fast Selective Gas Sensing, *Michael Pedowitz, S. Kim,*

Department of Electrical and Computer Engineering, University of Maryland, College Park; *B. Uppalapati,* 3Holcomebe Department of Electrical and Computer Engineering, Clemson University, Clemson; *D. Khan,* Holcomebe Department of Electrical and Computer Engineering, Clemson University; *F. Bayram, G. Koley,* Holcomebe Department of Electrical and Computer Engineering, Clemson University, Clemson.; *R. Myers-Ward,* Naval Research Laboratory, USA; *K. Daniels,* Department of Electrical and Computer Engineering, University of Maryland, College Park

Mixed valence manganese oxides (MnO_x) have attracted significant research interest in recent years due to the easily reversible redox reactions between manganese oxidation states (Mn⁺², Mn⁺³, and Mn⁺⁴) which enable applications in catalysis², energy storage³, and gas sensing⁴. Of the MnO_x compounds, manganese dioxide (MnO₂) has been of particular interest due to its wide variety of structural polymorphs, which allow for enhanced control over the available surface area and reactive properties of MnO₂. Among these crystalline phases, the δ -phase contains a large number of Mn⁺³ defects, as Mn⁺³ content has been found to increase the catalytic activity of MnO₂ films we selected the δ -phase to be the optimal phase to produce highly reactive MnO₂ thin films⁵. However, MnO₂'s reactivity is limited by its low inherent conductivity⁴. To overcome this limitation, heterostructures have been formed between MnO₂ and graphene, seeking to couple the conductivity of graphene with the reactivity of MnO₂. We selected quasi-freestanding epitaxial graphene on silicon carbide (EG/SiC) as the substrate for the electrodeposition. In this work, we present the electrodeposition of δ -MnO₂ on (EG/SiC) and then demonstrate its reactive properties by processing the resulting film into a room temperature gas sensor. The electrodeposition was carried out in a three-electrode electrochemical cell with an Ag/AgCl reference electrode, a Pt counter electrode, and an EG/SiC working electrode utilizing 0.1M manganese acetate solution. The resulting δ -MnO₂/EG/SiC was then characterized through Raman spectroscopy, photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) to determine its crystalline phase and surface morphology. Raman spectroscopy confirmed the formation of δ -MnO₂, and the XPS indicated it was Mn⁺³ rich with an average oxidation state of 3.3. The SEM revealed that the surface was made up of microplates \sim 160 μ m² coated in nanofibers in nanofibers. AFM confirmed this and indicated the nanofibers were \sim 10nm thick. Following characterization, we deposited 4 Ti/Au(30nm/120nm) contacts on the δ -MnO₂ to form a simple gas sensor that was tested against 5ppm NO₂, 5ppm NH₃, 1000ppm IPA, and 1000ppm methanol. In preliminary room temperature testing, the sensor displayed a response time <2s for NO₂ and NH₃ and no response for IPA and methanol, demonstrating the reactive potential of the produced heterostructure.

References:[1]L. Spinelle et al. *Sensors* 17(7), 1520(2017)[2] F. Cheng et al. *Chem. Mater* 22(3), 898-905(2010)[3] Y.J. Huang et al. *Electrochim Acta* 99, 161-165(2013)[4]N. Joshi et al. *Microchim. Acta* 185, 213(2018)[5]Z. Chang et al. *Proc Natl Acad Sci USA* 115(23), 5261-5268(2018)

SE-Contributed On Demand-4 Fabrication of Hydrogenated Tungsten Carbide Coatings by Reactive Superimposed Hipims-Mf Deposition System: Effect of Target Poisoning Ratio, *B. Lou,* Chang Gung University, Taiwan; *I. Moirangthem, Jyh-Wei Lee,* Ming Chi University of Technology, Taiwan

The research of tungsten carbide coatings has attracted lots of interest from academia and industry due to their outstanding properties such as high hardness, high wear resistance, chemical stability and low coefficient of friction. In this study, the hydrogenated tungsten carbide coatings were fabricated by a superimposed high power impulse magnetron sputtering (HiPIMS)- middle frequency (MF) deposition system. The W target poisoning status was controlled using a plasma emission monitoring (PEM) system by adjusting the gas flow ratios of Ar and acetylene (C₂H₂). The morphology and microstructure of coatings were evaluated by scanning electron microscope (SEM) and transmission electron microscope (TEM). The crystallinity of films was studied using an X-ray diffractometer (XRD).

The electron probe micro analyzer (EPMA) was used to determine the chemical compositions of thin films. The hardness, adhesion and tribological properties of coatings were explored. The corrosion resistance of tungsten carbide coated AISI304 stainless steel plates was evaluated in 0.1 M H₂SO₄ solution. We found that the peak power density of the HiPIMS increased with increasing target poisoning ratio. The deposition rates and carbon concentrations of coatings also increased with increasing target poisoning ratio. The crystalline β -WC_{1-x} phase was transformed into an amorphous phase when target poisoning ratio of coating increased from 50% to 70%. We can conclude that the hydrogenated tungsten carbide coating with the highest hardness of 32.3 GPa, high critical load (L_{CI}) of 34.3 N, high resistance to plastic deformation index (H³/E²) of 0.53, excellent corrosion resistance, and a quick deposition rate of 21.9 nm/min/kW was grown by the superimposed HiPIMS-MF power supply at the target poisoning ratio of 30% in this work.

SE-Contributed On Demand-7 In-Situ Raman Approaches for Studying Tribological Surfaces, *Andrey Voevodin, A. Shirani, E. Cairns, K. Jacques, M. Dockins, A. Killam, S. Aouadi, D. Berman,* University of North Texas; *J. Mogyonye, S. Berkibile,* DEVCOM Army Research Laboratory

The study provides examples of in-situ Raman spectroscopy use to investigate adaptive tribological surfaces lubricated with solid and liquid materials. The in-situ Raman spectroscopy is shown to capture tribologically induced changes of adaptive surfaces inside the lubricated sliding contact in response to applied mechanical and thermal stresses. For solid lubricated adaptive contacts, duplex plasma-electrolytic oxidation (PEO) and chameleon coating produced on Al alloys were investigated. These were composed of a 80-160 mm thick hard load-supporting Al-Si-O coating and a 5–8 μ m top layer of a chameleon coating made of graphite or BN, MoS₂ or WS₂, and Sb₂O₃. For liquid contacts, 52100 steel coupons were tested under lubricant starvation regimes using low viscosity hydrocarbons. The counterpart pins were made of 52100 steel and Si₃N₄. The tests were performed at temperatures ranging from room (liquid lubrication) to 600 °C (solid lubrication). In-situ Raman spectroscopy revealed that the lubricating phases, i.e. MoS₂, WS₂, and graphite, were protected from oxidation by the porous PEO structure. It also revealed a gradual evolution of chameleon composition with diminishing orthorhombic Sb₂O₃ phase presence at the surface in favor of hexagonal lubricating phases of chameleon components. The low shear strength of MoS₂, WS₂, and graphite and the integration of the chameleon coating with the PEO sublayer were responsible for the ultra-low friction behavior. In all examples, the in-situ Raman spectroscopy was shown to reliably detect contact chemical change correlated with the observed friction behavior.

SE-Contributed On Demand-10 Advances in Fatigue Testing of Protective Coatings: A Case Study on Cr-Based Ceramics, *L. Zauner, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; *M. Alfreider,* Department of Materials Science, Montanuniversität Leoben, Leoben, Austria; *P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany; *O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Leoben, Austria; *Helmut Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Thermomechanical fatigue phenomena strongly limit the life time of modern high-performance components and therefore demand innovative coating materials extending the life-time through predictable crack propagation. Especially, an in-depth knowledge on the decisive failure criteria of ceramic thin film materials – generally associated with an intrinsic lack in ductility – under long-term mechanical loading is paramount to enhance limited bulk material properties. Literature reports on fatigue resistance, especially of hard coatings but also thin films in general, are relatively rare. Thus, an extensive analysis of different coatings – meaning prevalent bonding states, i.e. altered ratio of ionic, covalent, or metallic bonds – with respect to fatigue phenomena (e.g. LCF, HCF, or extrusion formation) is of great interest.

Within this study we present a methodical approach towards a general understanding on the failure behaviour of PVD deposited thin films from the aspect of the bonding nature between the atomic constituents using model systems – Cr and Cr-based ceramics, respectively. The DC magnetron sputtered thin films were analysed with respect to structure, thermo-mechanical properties, and morphology by means of micro-mechanical testing, X-ray diffraction, as well as electron imaging techniques. The influence of the stress state was quantified through high-temperature wafer-curvature measurements. Static fracture characteristics

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such as fracture toughness KIC and -stress of have been evaluated during cantilever bending of pre-notched beams. Low and high cycle fatigue tests of unstrained micro-cantilevers were subsequently performed under various loading scenarios based on the critical stress intensities observed during the quasi static tests. These results are also correlated with dynamic-mechanical analysis to get insights on the size effects during fatigue testing. Through this comprehensive approach we are able to identify the most critical aspects with respect to fatigue life of these protective coating materials.

Keywords: Fatigue; Thin films; Cr-based compounds; Micro cantilever; LCF; HCF

SE-Contributed On Demand-13 Structural, Nanomechanical and Tribological Properties of Plasma Electrolytic Oxide Coatings for Sliding Contact Applications, Esteban Broitman, SKF B.V. , Netherlands; J. Dzwonczyk-Mertzanis, S. Geerts, SKF B.V., Netherlands; G. Dennis, SKF Ltd., UK

Plasma electrolytic oxidation (PEO) is a method that promotes the formation of a high-hardness ceramic coating on the surface of light metals. The process involves an anodic oxidation of the metallic substrate by subjecting the alloy to high voltages in an electrolytic bath.

In this work, PEO Keronite® coatings were fabricated on a AA7075-T73 aluminum alloy. This lightweight surface finishing solution is targeting self-lubricating sliding contact applications where conditions request low to medium ranges of loads and medium to high motion frequencies.

The microstructure and composition of the as-received coatings were characterized by SEM and EDS. Nanomechanical properties (hardness H_{IT} and elastic modulus E_{IT}) were studied by nanoindentation on samples cross-sections confirming a bi-modular coating composition. Toughness and macroscale hardness were derived from classic Vickers indentation. The sliding friction and wear responses were assessed by pin-on-disc tests where the counterface was a commercial lining compound available on the market for self-lubricating applications. Furthermore, the coated samples were also characterized by an oscillating dynamic load test that replicates load behavior from real applications. In addition, a modeling exercise has been performed to analyze distribution of contact pressures in the system with a coated interface. The tribological results obtained on Keronite® were compared to an electroless Ni plated coating, highlighting pros and cons of this type of coating being used for self-lubricating sliding applications.

SE-Contributed On Demand-16 The Struggles to Compare Coatings Hardness by Vickers and Instrumented Nanoindentation Techniques, Esteban Broitman, SKF B.V., Netherlands

It is widely accepted to define the hardness of a solid material as its resistance to a permanent shape change when a constant compressive force is applied. At macro- and microscale, the Vickers hardness test is assessed from the size of an impression left under a load by a four-sided pyramid-shaped diamond indenter. The Vickers hardness number, H_V , is then calculated as the indenter load L divided by the actual surface area of the impression A_c measured after the indentation. On the other hand, the instrumented nanoindentation hardness H_{IT} , using a three-sided pyramid-shaped diamond indenter, is calculated as the maximum indenter applied load L_{max} divided by the projected area of contact at maximum load A_{proj} , i.e., during the indentation [1].

There are many publications where authors try to compare their coating hardness values measured by nanoindentation with bulk hardness values that have been measured by Vickers tests. The comparison is usually made through a formula that is supposed to give an exact mathematical equivalence of hardness values between both methods: $H_V = 0.09 H_{IT}$, with H_V having units of kgf/mm^2 and H_{IT} having units of MPa. In this presentation, I demonstrate that an exact mathematical equivalence can be established only for materials with 0% indentation elastic recovery. In other cases, I will show that it is impossible to establish such mathematical relationship.

[1] "Indentation Hardness Measurements at Macro-, Micro-, and Nanoscale: A Critical Overview" Esteban Broitman - Tribology Letters 65 (2017) 23.

SE-Contributed On Demand-19 Alloying of Period VI Transition Metal Boride-Based Coatings for Ultra-High Temperature Oxidation Protection, Thomas Glechner, R. Hahn, A. Bahr, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; T. Wojcik, Institute of Materials Science and Technology, TU Wien, Austria; M. Weiss, Institute of Chemical Technologies and Analytics, TU Wien, Austria; J. Ramm, O. Hunold, Oerlikon Surface Solutions AG, Liechtenstein; S. Kolozsvári, Plansee Composite Materials GmbH, Germany; H. Riedl, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Various challenges in the field of environmental sustainability as well as emission reduction in general are closely linked to the usage of ultra-stable materials. Protective coatings sustaining harsh environments, involving highest temperatures accompanied by abrasive and corrosive media, are therefore of great interest. Transition metal ceramics are a suitable class to resist such conditions. Especially, period VI borides, nitrides and carbides stand out due to their extraordinary mechanical properties and highest thermal stability making them interesting for ultra-high temperature applications. However, their high temperature stability is strongly limited due to their strong tendency to form volatile oxides.

In particular, to improve the oxidation resistance of period VI based transition metal diborides, it is important to first have a profound knowledge on the scale formation of the binary systems – such as HfB_{2-z} , TaB_{2-z} and WB_{2-z} , in oxidative environments. Here, especially the influence of the stoichiometry and constitution of the grain boundary interior is of major interest. Based on that knowledge, we developed alloying strategies which tremendously enhance the oxidation resistance of these coating materials and enable temperature regimes up to 1600 °C. The coating materials were deposited using an unbalanced magnetron sputtering system and consequently oxidized in a DTA/TG setup (using coatings on substrates) to study the oxidation kinetics. These results were verified with long-term oxidation tests at 1200 °C (various time periods up to 60 h) using a conventional chamber furnace. To gain a comprehensive insight on the relation between chemical composition, crystal structure, as well as morphology, we applied a broad set of high-resolution characterization techniques (e.g. HR-TEM, APT, SIMS, as well as XRD) to correlate the as deposited with the annealed states.

SE-Contributed On Demand-22 Influence of the Nature of the Terminal Group on the Rate of Tribochemical Reaction of Carboxylic Acids on Copper, Resham Rana, W. Tysae, University of Wisconsin Milwaukee

Lubricant additives reduce friction and wear by reactively forming a thin tribofilm at the rubbing contacts in machines. Carboxylic acids are often used as both boundary lubricants and also as lubricant additives that undergo tribochemical reactions to form a tribofilm on the surfaces. It has been suggested that the terminal group on the carboxylic acids could influence their tribochemical reaction rate. This was studied on a well-characterized clean copper sample in an ultrahigh vacuum tribometer capable of measuring friction, load, and electrical contact resistance to follow the tribochemical reaction by analyzing the surface by microfocus Auger electron spectroscopy. An atomic force microscope (AFM) is also used to measure the friction, and pull-off forces, and tribochemical reaction rates of a carboxylic acid on a copper (100) surface. The microscale tribochemical reactions are carried out using a tungsten carbide ball under a normal load of ~0.44 N, and the nanoscale tribochemical reactions with a silicon tip applying a normal load of ~56.0 nN where both result in similar contact stresses. C-C, C=C, and C≡C terminated carboxylic acids were studied and no effect on the tribochemical reaction rates was found despite the difference in friction and pull-off forces being measured in AFM.

SE-Contributed On Demand-25 Enhanced Oxidation Resistance of Cr₂AlC MAX Phase Coatings through Tailoring of Substrate Microstructure, Clío Azina, Materials Chemistry, RWTH Aachen, Germany; J. Gonzalez-Julian, Forschungszentrum Jülich GmbH, Germany; P. Eklund, Thin Film Physics Division, Linköping University, Sweden; J. Schneider, Materials Chemistry, RWTH Aachen, Germany

MAX phases are a family of layered ternary ceramics, characterized by a hexagonal structure, which are considered for high temperature applications. In particular, Al-based MAX phases have attracted significant attention because of their self-healing behavior. Indeed, weakly-bonded Al is able to diffuse and react with the oxidizing atmosphere to form a protective Al_2O_3 scale. In the case of Cr_2AlC , the loss of Al, which leads to the formation of the alumina scale, is accompanied by the local decomposition of the MAX phase into Cr_7C_3 just below the Al_2O_3 scale

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resulting in the formation of pores in the vicinity of the interface. The presence of pores has an adverse effect on the mechanical and thermal stability of the component and often results in its premature failure. To avoid the Cr₇C₃ formation, Al would need to be supplied to the oxide scale continuously. To this end, we deposited Cr₂AlC coatings on Cr₂AlC substrates and focused on the interfacial interaction to prove the concept of continuous Al supply from the Cr₂AlC substrate to the Cr₂AlC coating.

Cr₂AlC substrates were produced by spark plasma sintering of either elemental or Cr₂AlC powders. The substrates produced contained different amounts of secondary phases and exhibited different grain sizes. Cr₂AlC coatings were deposited on the produced substrates using high power pulsed magnetron sputtering (HPPMS) to obtain dense films. The Cr₂AlC / Cr₂AlC assemblies were then oxidized at 1100 °C in air for different times to investigate the effect of the microstructural variations of the substrate on the oxidation behavior.

SE-Contributed On Demand-28 Corrosion Induced Diffusion Pathways in Thin Film Materials Investigated by Atom Probe Tomography, Oliver E. Hudak, E. Aschauer, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria; V. Dalbauer, Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; L. Shang, O. Hunold, M. Arndt, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; P. Polcik, Plansee Composite Materials GmbH, Germany; P. Felfer, Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; H. Riedl, Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Corrosion phenomena have a large impact in almost all of today's technological fields. A ubiquitous interplay between material and its environment challenges material-engineers in selecting materials that provide a safe and work effective implementation. In this regard, protective thin films and surface modifications have opened up new avenues in aviation and power generation sectors. In particular, physical vapor deposited (PVD) coatings have been specifically developed to elicit superior material properties, as well as extend the longevity and work performance of machining components. Unfortunately, due to a deficient understanding of corrosion related processes in PVD coatings, industrial demands for high performance corrosion resistant thin films remain sparse.

This study intends to take a closer look at corrosion driven diffusion pathways in aqueous solutions at an atomic scale. As many technical alloys used in marine environments, aviation and energy sectors are prone to pitting corrosion, a demand for tailored corrosion protective coatings seems quite overdue. A three-electrode cell potentiostat was utilized for conducting potentiodynamic polarization measurements, and enabled precise control over the corrosion test parameters. With a systematic approach on highlighting preferred diffusion pathways, this study displays a thorough exploration of the effect of grain size, macro-particle formation and crystallinity on the diffusion mechanism in arc-PVD thin films. For better tracing the corrosive species, a novel marker architecture was developed for eliciting chemical and structural changes upon arrival of the diffused media. Consequently, this allows for improved application of high-resolution analytical methods, such as APT and TEM, to help identify preferential diffusion paths.

Keywords: Corrosion resistance; PVD coatings; Diffusion pathways; Atom probe tomography; pitting corrosion

SE-Contributed On Demand-31 Effects of Magnetic Field Strength on the Structure and Properties of non-hydrogenated DLC Coatings Deposited by HiPIMS, Jianliang Lin, Southwest Research Institute, San Antonio Texas; X. Zhang, Southeast University, China

In this study, non-hydrogenated diamond like carbon (DLC) coatings (3-4 mm) were deposited by sputtering a graphite target in argon (Ar) using high power impulse magnetron sputtering (HiPIMS). The effects of the vertical magnetic field strength (B) in the middle of the target racetrack on HiPIMS deposition parameters, and structure and properties of the DLC coatings were investigated. The coatings were characterized by transmission electron microscopy (TEM), Raman spectroscopy, atomic force microscopy (AFM), scratch test, nanoindentation, and ball on disk wear test. It was found that the deposition at a higher B was associated with a higher peak target current density and an increased ion flux to the substrates. These conditions are beneficial for improving the structure and properties of DLC coatings. The DLC coatings deposited at a higher B exhibited more compact surface, smaller carbon mounds and a higher sp³ bond fraction. The results showed that a B higher than 600 G is needed for obtaining dense DLC coatings with a high sp³ bond fraction and a high

hardness (>35 GPa). However, the deposition rate of DLC coatings decreased as B was increased. The tribological properties of the coatings were evaluated under dry and lubricated conditions. The tribological tests revealed great friction reduction and improved wear resistance of these non-hydrogenated DLC coatings deposited by HiPIMS.

SE-Contributed On Demand-34 Enhancing the Surface Properties of Polymethyl Methacrylate by TiO₂ Atomic Layer Deposition, Mina Shahmohammadi, E. Pensa, H. Bhatia, B. Yang, G. Jursich, C. Takoudis, University of Illinois - Chicago

Polymethyl methacrylate (PMMA) is a widely used polymer in applications such as engineering structural plastics, energy storage materials, and biomaterials. However, its poor surface properties and wear resistance lead to fracture and deformation. Functionalization of the PMMA surface can make it stable in aggressive environments and prevent it from biodegradation, discoloration, and increased surface roughness. Here, thermal Atomic Layer Deposition (ALD) was used to deposit TiO₂ thin films from Tetrakis(dimethylamido)titanium(IV) (TDMAT™) and ozone (O₃) on PMMA substrate, without the need for plasma assistance or alumina interlayer, to improve its surface properties. The depositions were done in a commercial ALD system (Kurt J. Lesker ALD150LE™). The reactor pressure and temperature were kept at 120°C and 1 Torr, respectively and ultra-high purity N₂ was used for both carrier and purging gas. Spectroscopic ellipsometry was used to measure the film thickness on thick PMMA substrate and two different growth regimes were observed for initial and later ALD cycles. Initially, the growth rate on PMMA was 1.39 Å/cycle, which is ~3.5 times higher than that on silicon (0.4 Å/cycle). However, after ~30 nm-thick film on PMMA, the growth rate became similar to that on silicon. Moreover, our results revealed that the presence of PMMA affects the growth rate on silicon reference. These findings were corroborated with Residual Gas Analyzer and X-ray Absorption Near-Edge Structure data. The thermal stability of the PMMA samples used in this study, was examined by Thermogravimetric Analysis. Chemical composition and surface roughness of coated PMMA were studied by X-ray Photoelectron Spectroscopy and optical profilometry, respectively, which corroborated the presence of a uniform conformal film of TiO₂. The TiO₂ coating increased wettability by ~70% and surface hardness by 60%.

SE-Contributed On Demand-37 Development and Scale-up of ALD Coatings for Sulfur Tolerant, Long Lifetime Catalyst Powders, Christopher Gump, J. Burger, D. Lindblad, G. Rojas, K. Buechler, Forge Nano; W. McNear, National Renewable Energy Laboratory (NREL)

As potential applications of atomic layer deposition expand beyond the nano-scale devices of the semiconductor industry, development of larger-scale processes on high surface area substrates are necessary. This is especially true in catalyst coating applications, where ALD has been shown to improve stability, selectivity, and lifetime of catalyst materials. The high surface areas associated with supported catalysts introduce new challenges with regards to processing.

As a part of an effort to improve sulfur tolerance and lifetime in supported palladium catalysts for biomass processing, we used ALD to deposit under- and over-coatings of alumina or titania onto Pd/Al₂O₃- and Pd/TiO₂-supported catalysts. Because of the high surface area of the substrates (140 - 185 m²/g), even low numbers of ALD cycles required large amounts of deposition precursors and resulted in high weight loadings of film on the catalyst. Initial small-scale tests performed on 3 g lots of catalyst powder resulted in 5-15wt% mass gains with fewer than 10 ALD cycles. Precursor transport was a rate limiting step for the deposition, and controlled dosing of the precursor was critical to achieving reproducible deposition.

Using the hydrogenation of naphthalene to tetralin as a model reaction, the productivity, conversion, and turn-over frequency of the coated catalysts was characterized. The titania overcoat on the Pd/Al₂O₃ proved to be the most effective catalyst, increasing the productivity, conversion, and turnover frequency in the model reaction. Although the film increased catalyst performance, carbon monoxide chemisorption testing indicated that the ALD film reduced the number of available Pd metal sites on the catalyst.

The TiO₂ overcoat on Pd/Al₂O₃ was scaled up from the 3 g lot size to a 100 g lot size (~15,000 m² of powder surface area). Coating this quantity of powder required the implementation of a large-scale precursor vaporizer capable of delivering the tens of grams of the titanium (IV) isopropoxide used as the titanium source every cycle. The TiO₂-coated catalyst coated at the large scale showed the same increase in productivity, as well as increased stability after 450 or 750°C thermal treatments, as compared to

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the uncoated materials. The TiO₂-coated catalyst also retained the highest amount of activity (86%) after sulfur poisoning by dimethyl disulfide.

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SE-Invited On Demand-1 Metallic Glass: A Novel and Emerging Coating For Various Industrial Applications, *P. Yiu, Jinn P. Chu*, National Taiwan University of Science and Technology, Taiwan

INVITED

In this presentation, I will first present many unique properties that make thin-film metallic glasses (TFMGs) stand out from other thin film materials: smooth surface, ultra-low coefficient of friction, low surface free energy, non-sticking surface, high plasticity, anti-cell adhesion properties, biocompatibility, and shape recovery. I will also demonstrate a number of applications where TFMGs have outstanding performance over the existing materials, such as surgical blades and various types of diffusion barriers that boosted the lifetime of their corresponding device. We also showcase a number of innovative attempts to put TFMG in commercial products and industrial applications. Furthermore, we would like to showcase that due to the variety of composition and thus properties of TFMGs, they have a wide range of applications from consumer products like kitchen cutlery to the cutting edge MEMS, to be explored. The ease of TFMG fabrication by magnetron sputtering is also favorable for industries and manufacturers to transfer the technologies from laboratory to factory. Our research and development of TFMG is still ongoing and making a remarkable progress and hopefully it could open up even more new research works in the near future. In addition, new perspectives in the research and development of TFMGs and opportunities for commercialization will also be highlighted.

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Riedl, H.: SE-Contributed On Demand-10, **1**; SE-Contributed On Demand-19, **2**; SE-Contributed On Demand-28, **3**
Rojas, G.: SE-Contributed On Demand-37, **3**
— S —
Schneider, J.: SE-Contributed On Demand-25, **2**
Shahmohammadi, M.: SE-Contributed On Demand-34, **3**
Shang, L.: SE-Contributed On Demand-28, **3**
Shirani, A.: SE-Contributed On Demand-7, **1**
— T —
Takoudis, C.: SE-Contributed On Demand-34, **3**
Tysoe, W.: SE-Contributed On Demand-22, **2**
— U —
Uppalapati, B.: SE-Contributed On Demand-1, **1**
— V —
Voevodin, A.: SE-Contributed On Demand-7, **1**
— W —
Weiss, M.: SE-Contributed On Demand-19, **2**
Wojcik, T.: SE-Contributed On Demand-19, **2**
— Y —
Yang, B.: SE-Contributed On Demand-34, **3**
Yiu, P.: SE-Invited On Demand-1, **4**
— Z —
Zauner, L.: SE-Contributed On Demand-10, **1**
Zhang, X.: SE-Contributed On Demand-31, **3**