Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Royal Palm 4-6 - Session E2-2

Mechanical Properties and Adhesion

Moderators: Gerhard Dehm, Max-Planck Institut für Eisenforschung, Megan Cordill, Erich Schmid Institute of Materials Science, Ming-Tzer Lin, National Chung Hsing University, Taiwan

1:30pm **E2-2-1 Controlling the Chemomechanical Effects in Sapphire by Ion-implantation***, **Steve Bull**, A Yadav,* Newcastle University, UK

Modification of the chemomechanical behaviour of the surface of sapphire by ion implantation has been investigated to improve its near-surface mechanical properties (i.e. hardness). 300keV Ti^+ ions at various doses have been implanted and the concentration and damage profiles characterised using Rutherford Backscattering (RBS). At high doses (≥3×10^{16} Ti^+cm^{-2}), a surface amorphous layer has formed due to implantation-induced damage. Nanoindentation has been used to determine the hardness behaviour of the ion-implanted single crystal sapphire. It has been found that hardness increases at low implanted doses, which is associated with implantation-induced damage but that also chemomechanical softening of the surface is reduced due to the removal of adsorbed water layer. In-situ Raman scattering measurements demonstrate the removal of the adsorbed water at low doses, and existence of the readsorbed water at high doses. For the optimum implanted dose the water readsorption does not recur even several years after the implantation treatment. Based on this study, it is concluded that ion implantation with an appropriate ion species and dose can control the chemomechanical effect and improve the hardness of ceramics such as sapphire.

1:50pm **E2-2-2 Magnetron Sputtering of Refractory Metal Thin Films on NiTi Shape Memory Alloy Sheets***, **Fabian Seifried**,* Karlsruhe Institute of Technology (KIT), Germany*; H Riedl,* Technische Universität Wien, Austria*; S Baumgaertner, H Leiste, R Schwaiger, S Ulrich, H Seifert,* Karlsruhe Institute of Technology (KIT), Germany*; P Mayrhofer,* Technische Universität Wien, Austria*; M Stüber,* Karlsruhe Institute of Technology (KIT), Germany

In this study, pseudo-elastic Ni 50.8 at.%-Ti alloy sheets of 1000 microns thickness were coated with 10 microns thick refractory metal thin films (e.g. Mo, Ta and Nb thin films), by non-reactive d.c. magnetron sputtering. These thin films were characterized with regard to their microstructure and selected mechanical properties. Microstructural characterization of the thin films included X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analyses. Mo thin films grow in a densely packed, (110) textured b.c.c. structure with columnar grains and large crystallite size (columnar width: 280-300 nm) on the NiTi substrate. Ta and Nb thin films grow as well in a dense columnar structure; however they show X-Ray diffraction peaks of various lattice planes of the b.c.c. structures (i.e. no texture) and exhibit much smaller crystallite sizes (columnar width: 30-40 nm). Considering the specific thin film/substrate thickness ratio (1:100) of the samples, the mechanical properties of both the thin films and thin film/substrate composites were investigated on different length scales, using nano- and microindentation techniques. Nanoindentation results confirm that the values of the Young's modulus of all thin film materials are identical with the values of the related bulk metals. Microindentation revealed that the Young`s modulus of the Nb/NiTi composite is closest to that of the pure NiTi substrate. Progressive scratch tests indicate excellent adhesion of all metal thin films on NiTi. To further evaluate the elasticity of the metal films and the integrity of the composites during elastic deformation tensile tests were performed on the thin film/NiTi composites. These pre-strained samples were subsequently used for cycle fatigue testing. To evaluate the potential impact of the surface coating and the deposition process on the phase transformation behaviour of the NiTi shape memory alloy, differential scanning calorimetry (DSC) analyses were done. We will discuss in detail the correlation of microstructure and static and dynamic mechanical properties of metal coated NiTi shape memory alloys. Conclusions and recommendations will be given for a material selection of refractory thin films design as radiopaque coatings on NiTi substrates for medical applications.

2:10pm **E2-2-3 Quantitative *In Situ* SEM MEMS High Cycle Fatigue: the Critical Role of Oxygen on the Nanoscale-Void-Driven Nucleation and Propagation of Small Cracks in Ni Microbeams***, A Barrios Santos, S Gupta,* Georgia Institute of Technology, USA*; G Castelluccio,* Cranfield University, UK*; **Olivier Pierron**,* Georgia Institute of Technology, USA **INVITED**

Small-scale fatigue is an active research area due to the widespread use of metallic films and micrometer-scale structures in applications such as flexible/stretchable electronics, micro and nano electromechanical systems (MEMS and NEMS), and microelectronics. This work presents an advanced small-scale, *in situ* scanning electron microscope (SEM) fatigue testing technique to characterize the fatigue behavior of electroplated Ni microbeams (with an ultrafine grained microstructure) subjected to high / very high cycle fatigue loading conditions, with and without a protective Au coating. The fatigue devices consist of MEMS microresonators that are driven at resonance inside the SEM, leading to fully-reversed loading of the microbeams at a frequency of ~8 kHz. The fatigue damage leads to a decrease of the microresonator's resonance frequency, which can be measured and used as a metric to quantify the crack growth rates. In addition, the *in situ* SEM observations allow direct evaluation of fatigue crack nucleation and propagation rates. Fatigue tests on the Ni microbeams provided direct measurement of ultraslow fatigue crack growth (average values down to 10^{-14} m/cycle) that have heretofore not been reported and highlighted strong environmental effects on fatigue lives that are three orders of magnitude longer in air than in vacuum. This ultraslow fatigue regime does not follow the well documented fatigue mechanisms that rely on large cyclic plastic zones and that are associated with larger crack growth rates (>~10^{-10} m/cycle). Instead, our study reveals fatigue nucleation and propagation mechanisms that mainly rely on room temperature vacancy condensation leading to voids, whose nucleation process is strongly affected by oxygen. The presence of a protective Au coating also increased the fatigue life in air by one order of magnitude, by delaying the crack nucleation process in the underlying Ni microbeam. The improvement in fatigue life is related to the fatigue degradation of the Au coating and its delamination from Ni once a fatigue crack reaches the interface. This work highlights significant size-dependent fatigue behaviors, whose origin will be discussed in this talk.

2:50pm **E2-2-5 Role of Microstructure on the Interface Stability of Copper Thin Films on Brittle Substrates***, **Alice Lassnig**,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; V Terziyska,* Montanuniversität Leoben, Austria*; C Gammer,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; D Kiener, C Mitterer,* Montanuniversität Leoben, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Thin ductile films on brittle substrates are widely used in different technological applications such as in microelectronics and energy sectors. Of particular interest is the stability of the interface between the two materials, since it is the weakest site determining the overall reliability of the material system. To decouple extrinsic from intrinsic size effects, a model ductile thin film on a brittle, chemically inert substrate was investigated. Therefore, 100 nm copper thin films were deposited by magnetron sputtering where the deposition process was optimized to maintain the same thin film thickness but a significant variation of the microstructure (bimodal). Further variations of the microstructures could be achieved by means of heat treatments leading to a uniform, coarse-grained microstructure. A thorough characterization of the film microstructures and interfaces was conducted by means of SEM and TEM.

To determine the adhesion, stressed overlayers were deposited, leading to the formation of spontaneous buckles with straight and telephone cord buckle morphologies. These buckles were measured by means of confocal laser scanning microscopy, allowing for the determination of the adhesion energy with the well-known Hutchinson & Suo model.

We could show that the adhesion values of the same thin film – brittle substrate system increased a factor of almost 2 with decreasing grain size but same thin film thickness.

A detailed study explaining the change of interface adhesion energy by means of a thorough characterization of the thin films will be presented, including a TEM study to reveal the delamination processes in-situ.

Abstract #3863

3:10pm **E2-2-6 Mechanical Reliability of Barrier Films for Flexible Electronics***, **Kyungjin Kim**, H Luo, T Zhu, S Graham, O Pierron,* Georgia Institute of Technology, USA

PECVD SiN_x thin film coatings have been developed to protect flexible electronics devices from environmental exposure. While most of the study has leaned on water vapor transport properties, the mechanical reliability during flexural deformation is another critical aspect for the coatings. Previously, we investigated the time-dependent channel crack growth behavior of silicon nitride (SiN_x) barrier films on polyethylene terephthalate (PET) substrates in humid and dry air and showed that crack growth can occur at strains that are much lower than the standard measured crack onset strains. In this work, we demonstrate the long-term time dependent fracture of PECVD SiN_x barrier films on polyethylene terephthalate (PET) and polyimide (PI) substrates by measuring crack growth rates under fixed strain as a function of time using in-situ microscopy tensile test. Our study highlights the interplay between neighboring cracks and substrate damage on the long term crack growth rates. For isolated cracks in SiN_x with PET damage, the growth rates were found to increase with time due to the loss of constraint on the $SiN\text{-}_x$ channel cracks as the corresponding crack grew in the PET. For multiple cracks growing on PET, decrease in the subcritical crack growth rates was found by up to 2 orders of magnitude until reaching steady-state rates due to substrate cracking in the interacting cracks. For SiN_x on PI, crack growth rates were observed to be nearly constant due to the lack of substrate cracking in PI as compared to PET.

3:30pm **E2-2-7 Molecularly Grafted, Structurally Integrated Multifunctional Polymer Thin Films with Improved Adhesion***, A Lassnig,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; P Smith,* Carnegie Mellon University, USA*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; **B.Reeja Jayan**,* Carnegie Mellon University, USA

We present a novel molecular scale grafting technique using chemical vapor deposition (CVD) polymerization to enhance the adhesion of thin polymer films to various substrates. Such engineered coatings can find applications in structurally integrated batteries and sensors that can carry mechanical loads in addition to performing energy conversion functions. Conventional un-grafted polymer thin films are loosely anchored to surfaces by weak physical interactions like Van der Walls forces or physisorption, which are easily disrupted by mechanical forces. We show that grafting can deploy strong chemical bonds or chemisorption to permanently anchor the film to the substrate. Until now, direct measurements of these bonds have not been possible because the materials used are very thick (typically 10-100 µm) and are difficult to access by surface characterization methods like x-ray photoelectron spectroscopy. Also, in previous attempts these bonds were made on small (localized) scale (e.g., polymer brushes grafted on nanoparticles) and thus large spatial variations in stresses that arise under real operating conditions in a device could not be investigated.

Herein, we use a novel non-line-of-sight oxidative CVD (oCVD) polymerization technique to simultaneously graft and polymerize monomers of EDOT onto radical (reactive) sites present on a Silicon substrate, resulting in conducting poly(3,4-ethylenedioxythiophene) (PEDOT) films. This grafting improves adhesion of coatings to the substrate surface. Films without the graft spalled and delaminated in the form of spontaneous buckles, after the application of Molybdenum stressed overlayer. Similar PEDOT films with the graft only spontaneously delaminated after the same stressed overlayer was added. From the spontaneous buckling the adhesion energy of the PEDOT-Silicon interface can be evaluated using the well-known Hutchinson and Suo model. It will be demonstrated that the addition of the graft significantly increases the adhesion of the PEDOT to a Silicon substrate

3:50pm **E2-2-8 Thin-film Adhesion Characterization by Colored Picosecond Acoustics***, **Arnaud Devos**,* IEMN UMR CNRS 8520 / MENAPiC, France*; P Emery,* MENAPiC, 41 Bd Vauban, France

Thin-film characterization is a main issue for a broad range of industrial applications related to the microelectronic industry or coatings for optics or glass industry or photovoltaics. All these technologies have in common to develop new products based on complex stacks made of various thin-film materials thinner and thinner. Thickness, elasticity, composition and adhesion at interfaces must be controlled if possible in a non-destructive way. Increased efforts are being made to develop measurement methods compatible with “real life conditions”.

This paper will present a new technique so-called the Colored Picosecond Acoustics (APiC), a unique combination of optics and acoustics, which implements a SONAR at the nanoscale using a tunable ultrafast laser. From the experimental point of view, it is a full optical setup, acoustics taking place in the sample only. Very high frequency acoustic waves are emitted and detected using ultra-short laser pulses. The acoustic waves propagate indifferently in transparent or opaque materials. These “hypersonic waves” have such a short wavelength that they suit very well the characterization of thin films, multi-layers, nanostructures and interfaces.[1-2]

In this paper, we will present some results to show useful can be the APiC technique for controlling thin-film thickness and adhesion at interface on complex samples related to various industrial objects: radio-frequency filters, thin-film solar cell, advanced mirrors, semiconductor lasers.

References:

[1] A. Devos, R. Cote, G. Caruyer, and A. Lefevre, Appl. Phys. Lett. 86, 211903 (2005).

[2] A. Devos, Ultrasonics 56, pp. 90-97 (2015) DOI 10.1016/j.ultras.2014.02.009

4:10pm **E2-2-9 Imaging Thin Film Adhesion with Picosecond Ultrasonics***, **Allaoua Abbas**, X Tridon, J Michelon,* Neta, France

In the middle of the eighties, it has been demonstrated that femtosecond lasers are able to generate and to detect ultrasounds which frequencies can extend up to serval TeraHertz. Thanks to their very small wavelengths, these ultrasounds can perform measurement of the mechanical properties of structures with nanometric resolution. These measurements have serval application in industries which use thin films, as the photovoltaic or the electronic ones.

In this presentation, utilization of these ultra-high frequencies ultrasounds as a tool for nondestructive testing will be overlined. It will be shown how photo-generated and photo-detected ultrasounds are able to probe, without any contact, the bounding quality and the thickness of a thin metallic film deposited on a dielectric substrate. Cartographies, which illustrate the thickness inhomogeneities and the bounding quality adhesion of a 255 nm Tungsten thin film deposited on a Silicon substrate will be presented to support these points.

4:30pm **E2-2-10 Mechanical Property Evaluation of Zr-Ti- Fe Thin Film Metallic Glasses***, **Yi-Jie Liao**,* Ming Chi University of Technology, Taiwan*; D Tseng, T Wu, M Lin,* National Chung Hsing University, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

Recently, thin film metallic glass (TFMGs) have drawn lots of attention from academia and industries due to their unique properties and possible applications. In this study, four ternary Zr-Ti-Fe TFMGs were fabricated on Si wafer and AISI304 stainless steel disk substrates using a magnetron co-sputtering system. The power of iron target was adjusted to grow TFMGs with different Fe contents. The effects of iron content on the microstructure and mechanical properties of Zr-Ti-Fe TFMGs were discussion. The thin film metallic glass materials consisted of an amorphous structure, with an absence of any detectable peak corresponding to crystalline phases. The surface morphology of TFMGs showed a very smooth surface by the analysis of atomic force microscopy. The hardness and elastic modulus of TFMGs were analyzed by nanoindentation. Furthermore, the bulge test was carried out to determine the residual stress, elastic modulus and deformation behavior of TFMGs from the pressure–deflection curves. The influence of Fe concentration on the mechanical property and deformation behavior of ternary Zr-Ti-Fe TFMGs was discussed.

4:50pm **E2-2-11 Mechanical Properties Measurement of Submicron Ti-Ni Shape Memory Alloys Thin Films***, T Wu, **Ming-Tzer Lin**,* National Chung Hsing University, Taiwan*; T Chen,* Chaoyang University of Technology, Taiwan*; T Lin,* National Chung Hsing University, Taiwan

Ti-60at%Ni thin films with thickness of 600nm were deposited on silicon nitride with and without chromium interlayer. Static and dynamic mechanical properties of these films were investigated using bulge test and observed their microstructure and crystalline phase orientation from SEM and XRD. It was found that with the adhesion of chromium interlayer the Ti-Ni films have the lowest residual stress and the highest Young’s modulus. The addition of chromium interlayer between Ti-Ni film and silicon nitrite introduces R phase transformation in room temperature. Microstructure analysis revealed that the surface trenches could be significantly reduced if the film has chromium interlayer, which indicates that chromium interlayer can minimize the stress development on Ti-Ni films during deposition. Thermal cycling stress evolution test results showed that chromium interlayer can be a buffer layer between TiNi and SiNx thermal mismatch. Moreover, the thermal cycling bulge test can be used to measure the thermal expansion coefficient of the films. In addition, the fatigue test showed that the interlayer of Cr can enhance the fatigue strength of TiNi films.

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