

Advanced Surface Engineering

Room 323 - Session SE-MoM

Modern Challenges in Surface Engineering

Moderator: A.A. Voevodin, Air Force Research Laboratory

8:20am **SE-MoM1 Nanomechanical Testing of Films and Coatings, I. Robertson**, University of Illinois **INVITED**

The fundamental deformation and fracture processes of thin metallic films with a nanograined microstructure and of thin hard coatings with a composite nanocrystalline- amorphous structure will be investigated by using the in situ TEM straining technique. For the nanograined materials, a novel uniaxial tensile test device has been fabricated using microelectronic fabrication processes to integrate MEMS force sensors with metallic films on a silicon wafer. The device permits direct correlation of the measured mechanical properties with the observed deformation mechanisms. The importance of grain boundaries as sources and sinks for dislocations will be demonstrated for a 200-nanometer thick freestanding aluminum film. For the hard coatings, a TiC coating supported on a stainless steel substrate was fabricated. Preliminary results suggest that the failure mode for coatings with the same C/Ti ratio is dependent on the percentage of crystalline TiC and the oxygen content, demonstrating the importance of optimizing the composition and structure. Results from these studies will be compared with model predictions.

9:00am **SE-MoM3 Molecular-Scale Tribology in Model SAMs and Amorphous Carbon Films, J.A. Harrison, G.M. Chateaufneuf, P.T. Mikulski, G.T. Gao**, US Naval Academy **INVITED**

With the rapid development of MEMs and NEMs, protection of the surfaces of these devices has become an urgent issue. In recent years, much effort has been devoted to methods for passivating the surfaces of MEMs. Amorphous carbon films (a-C) and self-assembled monolayers (SAMs) are both possible candidates for the passivation and lubrication of MEMs. The fundamental problem associated with minimizing friction and wear mechanisms is to gain a better understanding of the underlying chemical and physical processes at the atomic scale. Over the past several years, we have done extensive molecular dynamics (MD) simulations that examine the compression and friction of model hydrocarbon SAMs attached to diamond and amorphous carbon films attached to diamond. Recently, compression and shear-induced polymerization have been modeled in unsaturated hydrocarbon films. The effects of polymerization on friction will be discussed. In addition, we have also done extensive simulations that analyze the structure and friction of a-C and a-CH films. These results will also be discussed. @FootnoteText@ **Supported by The Office of Naval Research & The Air Force Office of Scientific Research.

10:20am **SE-MoM7 Thin Film Growth by PVD in the Presence of Residual Gas, J.M. Schneider**, RWTH-Aachen, Germany **INVITED**

Vacuum based synthesis techniques are characterized by the presence of residual gas. It is well known that the residual gas in high vacuum mainly consists of water. Depending on the affinity of the residual gas to the growing film material, incorporation during thin film growth has recently been reported.@footnote 1@ Here, a review on residual gas - growing film interactions is presented. Sources@footnote 2@ for residual gas incorporation as well as incorporation mechanisms@footnote 1@ are described. Furthermore the effect of impurity incorporation on the film structure and film properties is discussed.@footnote 3@ @FootnoteText@ @footnote 1@ J. M. Schneider, A. Anders, I. G. Brown, B. Hjorvarsson, and L. Hultman, Applied Physics Letters 75, 612 (1999). @footnote 2@J. M. Schneider, A. Anders, G. Yushkov, Applied Physics Letters 78, 150 (2001). @footnote 3@J.M. Schneider, K. Larsson, J. Lu, E. Olsson and B. Hjorvarsson, Applied Physics Letters 80, (2002) 1144.

11:00am **SE-MoM9 John A. Thornton Memorial Award Address: Advances in Reactive Sputtering Processing Technology, W.D. Sproul¹**, Advanced Energy Industries **INVITED**

Reactive sputtering is the sputtering of an elemental target in the presence of a gas that is purposely added to the system to react with the sputtered species to form a compound film. Although simple in theory, reactive sputtering can be difficult to carry out if one wants to obtain high deposition rates and good properties in the deposited films. The classic problem with reactive sputtering when the flow control of the reactive gas

is used to regulate the inlet of the reactive gas into the chamber is that the surface of the target will suddenly change from the elemental state to a compound state when the flow of the gas is increased beyond a certain point. When this happens, the target becomes covered with the compound ("poisoned state"), and the sputtering rate drops precipitously while the composition and properties of the deposited film change. To avoid the problems associated with flow control of the reactive gas, it is possible to increase the pumping speed of the system, which will prevent avalanching from the metallic state to the poisoned state for most materials. However, this technique will not prevent the loss in deposition rate. To avoid the loss of rate from target poisoning and a degradation of film properties, it is necessary to control the partial pressure of the reactive gas. Partial pressure control is more involved than flow control of the reactive gas, but it does provide high deposition rates, good composition control, and excellent film properties. For partial pressure control to be effective, a feedback signal that varies as the partial pressure changes is required. Common feedback signals are the cathode voltage, a partial pressure signal from a mass spectrometer, or an optical emission signal from the sputtering plasma. Each has its advantages and disadvantages. Signal acquisition, processing, and response times are all very important for partial pressure control. If the update time of the feedback signal or if the response to a change in the control signal are too long, it may not be possible to maintain a stable reactive gas partial pressure. The feedback signal must be obtained and processed quickly, and the response to any change must also be quick. If this is done, it is possible to operate at any point along the transition from the metallic state to the poisoned state of the target, which means that it is now possible to achieve both high deposition rates and good film properties. Reactive sputtering of insulating films presents special problems because arcing can occur on the target surface, which leads to instabilities in the process. Fortunately, arcing can be eliminated by using a power supply that can suppress or prevent arcing. For deposition of insulating films, it is necessary to combine the correct type of power and with partial pressure control of the reactive gas to generate a stable, high-rate reactive sputtering process. One without the other will not produce the optimum results

¹ John A. Thornton Memorial Award Winner

Advanced Surface Engineering Room 323 - Session SE-MoA

Hard Coatings: Preparation, Properties, Wear, and Nanotribology

Moderator: L. Hultman, Linköping University, Sweden

2:00pm SE-MoA1 High-resolution TEM Study the Microstructure of W-Si-C Films in the Vicinity of the Crystalline-Amorphous Transition, *J.E. Krzanowski, J. Wormwood*, University of New Hampshire

The addition of silicon to transition metal nitride and carbide thin films has generated considerable interest due to reports of greatly enhanced mechanical properties. It has been proposed that the effect of adding Si is to gradually reduce the crystallite size while introducing a thin amorphous interlayer between crystallites, ultimately resulting in an amorphous structure. In our work, we have examined a series of WC/SiC thin films over a composition range where the crystalline to amorphous transition occurs. By using high-resolution transmission electron microscopy, we have obtained a detailed picture of the mechanisms of this transformation in the W-Si-C system. These experiments have led to observations of novel microstructures not previously reported for Si-containing carbide/nitride thin films. A series of WC-SiC thin films has been deposited by RF magnetron co-sputtering, with compositions ranging from 15 to 38% SiC. X-ray diffraction analysis of these films confirmed the crystalline-to-amorphous transition in this compositional range. HRTEM observations revealed the following microstructural changes as the Si content increases: first, we observed fully crystalline nano-crystallites embedded in an amorphous matrix. Next, we observed the formation of larger (~50 nm) domains within which a novel droplet-like morphology of an amorphous phase is found. As Si is further increased, the droplets adopt a morphology where they appear to be strung together as the matrix phase becomes increasingly disordered. Finally, at yet higher Si contents, a spinodal-like two-phase structure is observed where one phase is amorphous and the second is best described as highly disordered. Despite the presence of these extensive microstructural changes, the hardness of the films within this compositional range was essentially constant.

2:20pm SE-MoA2 Metrology of 1-10 nm Thick CN_x Films: Thickness, Density and Surface Roughness Measurements, *D.J. Li*, Northwestern University, Tianjin Normal University; *Y. Chen, Y.W. Chung*, Northwestern University

Ultrathin nitrogenated carbon (CN_x) films were synthesized using pulsed dc magnetron sputtering. The influence of substrate tilt angle and rotation speed on surface roughness was explored. Atomic force microscopy studies showed that the smoothest films were obtained at substrate tilt of 45°, and rotation speed 20-25 rpm, corresponding to 2-3 rotations per deposited atomic layer. The root-mean-square surface roughness under these optimum conditions is ~0.3 nm when sampled over 20i, 20 i-m2 areas, increasing to ~0.4 nm when sampled over ~0.05i, 3 cm2 using x-ray reflectivity measurements. In addition, x-ray reflectivity measurements showed that the mass density of these CN_x films is ~2.0 gm/cc, independent of film thickness from ~1 to 10 nm, consistent with ion beam analysis.

2:40pm SE-MoA3 Reactive Magnetron Sputtering of Hard Si-C-N and Si-B-C-N Films and Their Properties, *J. Vlcek, J. Cizek, S. Potocky, M. Kormunda, J. Houska, P. Zeman, Z. Soukup*, University of West Bohemia, Czech Republic

INVITED

Based on the results obtained for C-N films a systematic investigation of reactive magnetron sputtering of hard ternary Si-C-N and quaternary Si-B-C-N materials has been carried out. The Si-C-N and Si-B-C-N films were deposited on Si(100) substrates by dc magnetron co-sputtering of silicon and carbon (Si-C-N films) and silicon, boron and carbon (Si-B-C-N films) in nitrogen-argon gas mixtures using a composed C-Si and C-Si-B (at a fixed 20% boron fraction in the erosion track area) target, respectively, with variable Si/C area ratios. Elemental compositions of the films (determined by RBS and ERD), their bonding structure, and mechanical (hardness and friction coefficient) and optical (refractive index and extinction coefficient) properties were controlled by the Si fraction (5-80%) in the magnetron erosion track area, by the Ar concentration (0-75%) in the gas mixture, by the rf induced negative substrate bias voltage (from a floating potential to -500V) and by the substrate temperature (135-800°C). The total pressure and the discharge current on the magnetron target were held constant at 0.5Pa and 1A, respectively. The energy and flux of ions bombarding the

target and the growing films were estimated on the basis of the discharge characteristics measured for both the dc magnetron discharge and the rf discharge dominating in a deposition zone. Mass spectroscopy was used to explain differences between sputtering of carbon, boron and silicon from the composed targets in nitrogen-argon discharges. The films, typically 1-2µm thick, were found to be amorphous with a very smooth surface (R_a less than 1nm) and good adhesion to substrates at a compressive stress less than 1.2GPa. They exhibited hardness up to 35GPa (Si-C-N films) and 50GPa (Si-B-C-N films), enhanced high-temperature oxidation resistance and very high optical transparency (at a high Si content), and promising tribological properties (at a high C content).

3:20pm SE-MoA5 Using NMR to Probe the Bonding in Amorphous Carbon Nitride Thin Films, *W.J. Gammon*, College of William & Mary; *O. Kraft*, Inst. für Materialforschung II, Germany; *G.L. Hoatson, A.C. Reilly, B.C. Holloway*, College of William & Mary

In this study the chemical bonding in hard and elastic amorphous carbon nitride (a-CN_x) films is investigated with 15N, 13C, and 1H nuclear magnetic resonance (NMR) spectroscopy. Nanoindentation yields an elastic recovery of 80%, a hardness of 5 GPa, and an elastic modulus of 47 GPa. Our 13C NMR study demonstrates the lack of sp³ bonded carbon in this material. Furthermore, the 13C and 15N NMR data imply a film-bonding model that has an aromatic carbon structure with sp² hybridized nitrogen incorporated in heterocyclic rings and in pentagons; a suggestion that is supported by our preliminary total energy calculations of graphite defect structures. Results from 15N and 13C cross polarization (CP) and 1H magic angle spinning (MAS) NMR experiments also suggest that the nitrogen bonding sites are susceptible to protonation. The most likely source of protons is from water absorbed during sample preparation for the NMR experiments. The sensitivity of the surface of a-CN_x to water absorption may impact tribological applications for this material.

3:40pm SE-MoA6 DLC and CN_x Coatings Produced by Pulsed Laser and Filtered Vacuum Arc Techniques, *A.A. Voevodin, J.G. Jones, T.C. Back, J.S. Zabinski*, Air Force Research Laboratory; *V.E. Strelitzki, I.I. Aksenov*, Kharkov Physical Technical Institute, Ukraine

Unhydrogenated amorphous diamond-like carbon (DLC) and fullerene-like carbon nitride (CN_x, N/C ratio ~ 0.2) are rival surface protection coatings with exceptional mechanical and tribological properties. A comparative study was performed on their benefits for sliding wear protection. The coatings were grown in the same deposition system, using similar substrates, surface preparation procedures, functionally graded interlayers (Ti-TiC-C), and top layer thicknesses. They were produced using pulsed laser deposition (PLD) and filtered cathodic arc deposition (FAD). Samples of laser-DLC, laser-CN_x, arc-DLC, and arc-CN_x coatings were prepared. Comparisons of coating chemistry, structure, hardness, elastic modulus, internal stress, coefficient of friction (c.o.f.) against steel and SiC balls, wear rate, and wear mechanism in humid and dry environments were performed. PLD and FAD provided very similar coating chemistry, structure and properties. Independent of the growth technique, DLC coatings had hardnesses within 52-57 GPa and elastic moduli within 490-560 GPa. The CN_x coatings offered a reasonably high hardness of 28-30 GPa, while their elastic modulus was as low as 160 GPa. There was a clear difference in tribological behavior of DLC and CN_x, which depends on the environment humidity. In humid air, DLC coatings had a c.o.f. of 0.1, a very low wear rate, and formed a graphitic transfer film in friction contact. In the same tests, CN_x coatings had a c.o.f. of 0.3-0.4, a higher than DLC wear rate, and did not form a transfer film. In this environment, wear tracks on CN_x coatings were polished by abrasion wear. In dry nitrogen, DLC coatings had a c.o.f. of about 0.15 and a higher wear rate, while CN_x coatings had a c.o.f. 0.03-0.04 and a lower wear rate with formation of a graphitic-like transfer film. The observed difference in mechanical response and tribological performance can be used to optimize selection between DLC and CN_x, depending on application requirements.

4:00pm SE-MoA7 Fabrication and Properties of Ultra-nano, Nano, and Polycrystalline Diamond Membranes and Sheets, *D.K. Reinhard*, Michigan State University and Fraunhofer Center for Coating and Laser Applications; *M. Becker*, Fraunhofer Center for Coating and Laser Applications; *R.A. Booth*, Michigan State University and Fraunhofer Center for Coating and Laser Applications; *T.P. Hoepfner*, Michigan State University; *T.A. Grotjohn, J. Asmussen*, Michigan State University and Fraunhofer Center for Coating and Laser Applications

Thin diamond membranes and free-standing sheets are of interest for a variety of potential applications. One such application is the motivation of this research, i.e. achieving diamond electron-stripping foils for use in

Monday Afternoon, November 3, 2003

heavy ion (1 - 11 MeV total energy) accelerators. The objective of this research is to produce large area free-standing foils/membranes of diamond. Stripping foils have areas of approximately 1 cm by 1 cm and thickness of approximately 1 μm . They must be positioned and mounted to a metal frame, supported on three sides. This paper describes the film nucleation, synthesis, and subsequent fabrication steps required to make large area free-standing diamond foils. Films are deposited on silicon wafers as ultra-nano (10 nm or less grain size), nanocrystalline (100 nm grain size), and as polycrystalline (micrometer grain size) diamond by varying gas composition, nucleation, power, substrate temperature, growth rate, and pressure. Large area foils are fabricated from each of these film types. Subsequently the diamond is separated from the substrate and mounted as a supported foil. Mechanical properties of the foils before and after mounting are described as a function of film morphology and thickness (0.5 μm to 5 μm). Examples of stripping foils and associated frames are presented. C. J. Liaw, Y. Y. Lee, and J. Tuozzolo, "Lifetime of Carbon Stripping Foils for the Spallation Neutron Source, Proceedings of the 2001 Particle Accelerator Conference, Chicago, (2001), 1538.

4:20pm **SE-MoA8 Nanotribological Properties of Nanocomposite and Amorphous CrBN Thin Films**, *D.M. Mihut, J. Turner, T.P. Butler*, University of Nebraska, Lincoln; *S.M. Aouadi*, Southern Illinois University; *S.L. Rohde*, University of Nebraska, Lincoln

Thin films with nanocomposite and/or amorphous CrBN structures can be successfully used for applications where high hardness, good wear resistance, low roughness and good corrosion resistance are required. CrBN films were deposited on to silicon substrates using reactive unbalanced magnetron sputtering. The deposition was monitored in-situ using spectroscopic ellipsometry. Films were characterized using X-Ray diffraction (XRD), atomic force microscopy (AFM), Auger electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS). Nanotribological behavior of CrBN thin films with differing composition were studied using a Hysitron Triboscope in conjunction with an AFM. Microscratch measurements were carried out in both constant and ramped load modes, after which the wear tracks were imaged and measured using AFM. The failure modes were also investigated using scanning electron microscopy (SEM). The measured friction coefficient, residual wear depth, and percent elastic recovery were compared for CrBN films of differing deposition conditions to begin to develop an understanding of process-property relationships in these new materials.

Advanced Surface Engineering Room 323 - Session SE-TuM

Nanostructured, Nanocomposite, and Functionally Gradient Coatings

Moderator: Y.W. Chung, Northwestern University

8:20am **SE-TuM1 Influence of Sputtering Condition and Target Material on the Microstructure and Properties of Ti-Si-N Coatings Prepared by r.f.-reactive Sputtering**, *M. Nose*, Takaoka National College, Japan; *Y. Deguchi*, Toyama University, Japan; *T. Mae*, Toyama National College of Technology, Japan; *E. Honbo*, Toyama Industrial Research Center, Japan; *W.A. Chiou*, University of California, Irvine; *K. Nogi*, Osaka University, Japan

Since Veprek et al. presented a theoretical concept to design super-hard nano-crystalline composite materials on the TM-Si-N (TM = transition metal) systems consisting of nano-crystalline transition metal nitrides embedded in amorphous Si@sub 3@N@sub 4@, many studies on these kinds of films deposited by PVD have been reported. Although most of them used r.f.- or d.c.-reactive sputtering in an Ar/N@sub 2@ gas mixture, the results were not always consistent with each other. This suggests that the structure of films depends sensitively on the deposition conditions. Hence, we decided to examine the effect of sputtering condition and target material on the microstructure and mechanical properties of Ti-Si-N coatings prepared by r.f.-reactive sputtering. We used the composite targets consisting of Ti (99.99%) plate and Si@sub 3@N@sub 4@ chips as well as the target consisting of Ti plate and Si chips. Thin films were synthesized by r.f. sputtering machine in a facing target-type (FTS) on the substrates of high speed steel. During the deposition, the substrate was heated from room temperature up to ~300 °C and a d.c. bias up to -100V was applied. In the case of films deposited from the Ti-Si target without bias application, the hardness of high Si films (containing ~20 at %Si) showed the lower value of 20 GPa. The hardness of the films increased and reached to a maximum value of 40 GPa around a bias of -30V, but the crystallite size of the film increased to ~30nm. On the other hand, the hardness of the films (containing ~20 at %Si) deposited from the Ti-Si@sub 3@N@sub 4@ target increased with increasing negative bias voltage, being saturated at a level of ~40 GPa over -80V. Although the crystallite size of the films increased gradually with increasing negative bias, it still remains about 7nm at -80V. The characteristics of the latter film could be attributed to the formation of nano-composite structure defined by Veprek et al.

8:40am **SE-TuM2 Growth and Physical Properties of Epitaxial CeN and Nanocrystalline Ti@sub 1-x@Ce@sub x@N Layers**, *T.-Y. Lee*, University of Illinois at Urbana-Champaign, United States; *D. Gall*, Rensselaer Polytechnic Institute; *C.-S. Shin*, Hynix Corporation; *N. Hellgren*, Intel Corporation; *J.G. Wen*, *R.D. Twisten*, *I. Petrov*, *J.E. Greene*, University of Illinois at Urbana-Champaign

While NaCl-structure transition-metal nitrides have been widely studied over the past two decades, little is known about the corresponding NaCl-structure rare-earth nitrides. Polycrystalline CeN, for example, has been reported by different groups to be both a wide bandgap semiconductor and a metal. To address this controversy, we have grown epitaxial CeN layers on MgO(001) and measured their physical properties. CeN is metallic with a positive temperature coefficient of resistivity and a temperature-independent carrier concentration of $2.8 \pm 0.2 \times 10^{22} \text{ cm}^{-3}$ with a room temperature mobility of $0.31 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. At temperatures between 2 and 50 K, the resistivity remains constant at $29 \mu\text{ohm-cm}$, while at higher temperatures it increases linearly to reach a room-temperature value of $68.5 \mu\text{ohm-cm}$. The hardness and elastic modulus of CeN(001) were determined from nanoindentation measurements to be 15.0 ± 0.9 and 330 ± 16 GPa. We further explore the possibility to alter the microstructure evolution in metastable Ti@sub 1-x@Ce@sub x@N quasi-binary alloys by controlling, using low-energy ion irradiation, the kinetics of phase separation driven by the large lattice mismatch of the two components ($a_{\text{sub CeN}} = 0.504 \text{ nm}$, $a_{\text{sub TiN}} = 0.424 \text{ nm}$). We observed nanophase films with $x > 0.1$. During reactive sputter-deposition of alloys, we observe nanophase films with $x > 0.1$. Under conditions of low ion-irradiation, the nanostructure consists of equiaxed nanometer-size grains which form due to continuous reannealing induced by CeN segregation, which is analogous to the one observed in the nanocomposites of TiN/Si@sub 3@N@sub 4@. In contradistinction, a nanocolumnar structure forms when the alloys are grown under intense ion-irradiation with $J_{\text{sub i}}/J_{\text{sub Me}} \sim 15$ and

$E_{\text{sub i}} = 45 \text{ eV}$. The intense ion mixing in the near surface area allows sufficient adatom mobility to form local TiN- and CeN-rich areas that propagate along the growth direction.

9:00am **SE-TuM3 Fabrication of Nanostructured Metallic Thin Films by Femtosecond Pulsed Laser Ablation**, *M. Jaime Vasquez*, *T. Fiero*, *G.P. Halada*, *C.R. Clayton*, State University of New York at Stony Brook

Pulsed laser ablation is a well-known technique used for deposition of a variety of thin films for various applications. A major disadvantage of the use of excimer lasers has been the deposition of irregular melted droplets on the deposited film attributed to heterogeneities of the target, fluctuations in the laser fluence and other difficulties of process control. The extremely short pulse duration of femtosecond lasers results in reduction or complete prevention of lateral thermal damage as well as lower and more precise threshold fluences of ablation. This presentation focuses on both the mechanism of material ablation using femtosecond lasers as well as a number of examples of nanostructured metallic films of significance to analytical surface studies and catalysis. The femtosecond laser deposition process involves a high intensity laser pulse (10@super - 15@ s range) that passes through an optical window of a vacuum chamber (10@super - 6@ torr) and is focused onto the target, which can be a single metal, a mix of powders or a reactively arc melted coin. The partially ionized ejected material or ablation plume is then allowed to settle and form a thin film on a Si substrate. The plume itself was studied through analysis of the kinetics of ejected material from a Pt target and through charge screening methods to aid in determination of ionic character. In addition to Pt films, a nanostructured Al@sub 2@CuMg intermetallic thin film was formed (to study corrosion issues in Al aerospace alloys). Films were characterized by Secondary Electron Microscopy (SEM), Energy Dispersive Analysis of X-rays (EDAX), X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). Thin films were polycrystalline and of the same composition as targets and chemically homogeneous. Observations of the morphological and structural features of the ablated films indicate that the technique can be used to reliably create nanostructured thin films.

9:20am **SE-TuM4 Self-adaptation Processes in Nanostructured Hard Coatings**, *C. Mitterer*, *P.H. Mayrhofer*, University of Leoben, Austria; *E. Badisch*, *M. Stoiber*, *G. Gassner*, Materials Center Leoben, Austria **INVITED**

Hard coatings deposited by plasma-assisted vapor deposition are widely applied to reduce tool wear. In the last decade, nanocomposite coatings have attracted increasing interest, due to the possible design of superhard coatings. Recently, it has been shown that nanostructured coatings also allow the realization of self-adaptive properties. This work summarizes recent developments in this field. The unavoidable Cl impurities in TiN coatings deposited by PACVD using TiCl@sub 4@ as precursor is known to deteriorate mechanical coating properties when exceeding several at.-%. However, small and tolerable Cl concentrations of about 3 at.-% cause a reduction of the friction coefficient against various steels and alumina from 0.8 to 0.15. This is due to the formation of an interfacial lubricant film on top of the coating caused by Cl-stimulated rutile formation in humid air. These coatings have been shown to improve the lifetime of metal forming tools significantly. Low-friction behavior at elevated temperatures, which is a pre-requisite for dry cutting operations, can be achieved by liquid oxide lubrication. This can be realized by various nitride phases, e.g. VN, WN, Mo@sub 2@N or MoN, which form low-melting oxides in the temperature range between 400 and 550°C. Melting of these phases occurs between 650 and 850°C. Using a nanoscaled arrangement of these phases in a hard matrix results in a self-adaptation of the friction coefficient to values of 0.18-0.4 at 700°C. Self-hardening to increase the wear resistance can be observed in metastable (Ti,Al)N coatings due to spinodal decomposition into fcc TiN and AlN domains. These nanoscaled coherent domains introduce additional stresses into the coating resulting in a hardness increase in the temperature range between 600 and 1000°C. These nanoscale design approaches allow the utilization of functional properties facilitating the development of next generations hard coatings.

10:00am **SE-TuM6 Design of Functional Coatings**, *D. Hegemann*, Swiss Federal Laboratories for Materials Testing and Research EMPA, Switzerland, Germany; *A. Fischer*, Swiss Federal Laboratories for Materials Testing and Research EMPA, Switzerland

Since materials are commonly chosen with respect to their bulk characteristics, availability, mechanical properties, and costs, their surface characteristics often do not meet the demands for special applications. The plasma technology is an appropriate method to tailor surface properties selectively and offers a convenient way to design even functionally gradient

Tuesday Morning, November 4, 2003

surface coatings. Using low pressure plasmas, various materials and geometries can be treated in batch or reel-to-reel reactors. When long-term stable surface properties such as wettability are of great interest, well-adherent, stable coatings can be provided minimizing aging effects. Using low power inputs in the course of chemical vapour deposition (CVD) processes, monomer structures can be retained in the gas phase yielding dense and homogeneous functional gradient films. The evaluation of the deposition rate of these radical-dominated plasmas was proven to be an appropriate way to design functionally gradient coatings, since also hints for the optimum deposition conditions are given. Chemicals containing functional groups such as amino, carboxy or epoxy are used to mediate the adhesion between substrate and coating. Siloxane-based plasma coatings enable the deposition of hydrophobic, polymer-like layers or hydrophilic, quartz-like films. Gradient layers are suitable to enhance the adhesion of the functional coatings e.g. by adaptation of the mechanical properties, when an inorganic coating is deposited on a polymeric substrate or an organic coating on a non-polymeric material. These gradient layers can be designed considering the reaction parameters power per gas flow and plasma potentials, which control deposition rate, chemical composition, and mechanical properties. Finally, an example of a physical vapour deposition (PVD) process is given, in which a nm-thin silver film has been coated continuously onto the surface of multifilament yarns to enhance the discharging of a textile surface.

10:20am **SE-TuM7 Functional Profile Coatings and Film Stress**, *C. Liu, R. Conley, A.T. Macrander*, Argonne National Laboratory

In recent years we have developed a profile-coating technique to obtain functional thickness-profiled thin films and multilayers. This technique uses a linear motion of the substrate in a dc magnetron sputter system and a contoured mask to obtain the desired profile perpendicular to the substrate-moving direction. The shape of the contour is determined according to the desired profile and the knowledge of the film-thickness distribution at the substrate level. Applications of this technique include laterally graded multilayers and elliptical x-ray Kirkpatrick-Baez (KB) mirrors. An elliptical shape is essential for aberration-free optics. The use of profile coating to make x-ray-quality elliptical KB mirrors overcomes the obstacle of polishing asymmetrical mirror surfaces and provides the x-ray community with a practical way to obtain monolithic KB mirrors for microfocusing. Previously we have used gold as a coating material and cylindrical Si mirrors as substrates to obtain elliptical KB mirrors. More recently we are using flat Si substrates to fabricate elliptical KB mirrors. Substantially thicker and steeper gradients of Au films are needed to obtain an elliptical profile from a flat substrate. The Au films may relax to droplets when the stress in the film is too large. The challenges and solutions for this problem will be discussed.

10:40am **SE-TuM8 The Effect of Surface Finish on Field Emission in Nitrogen-implanted, Silicon Dioxide-Coated Stainless Steel**, *N.D. Theodore, D. Manos*, College of William and Mary; *C. Hernandez, T. Wang, H.F. Dylla*, Jefferson Lab; *R. Moore*, University at Albany Institute for Materials

The purpose of this study was to assess the changes in tunneling parameters associated with field emission from processed stainless steel surfaces, as a function of their prior surface finish. According to Fowler-Nordheim theory (FNT), field emission from a material is governed by two parameters, alpha and beta, which relate to the work function of the material and to its surface morphology. Thus surface roughening may lead to large changes in field emission due to geometrical enhancements associated with sharp features. In this paper, six 304 stainless steel disks were hand-polished to different finishes, ranging from 1 micron to 30 microns rms roughness. These disks were then coated with a nitrogen-implanted silicon dioxide layer. @footnote1@ Depth Auger electron spectroscopy revealed that the thickness of the coating is approximately 240 nm. Field emission spectroscopy maps, STM maps, and AFM and DekTek scans were also taken of each sample. Data from these scans as well as the compositional character of the coating will be presented. Results show that despite surface morphology, each sample possessed 1-3 emission sites, producing current of 2nA at each emitter at threshold electric fields above 85 MV/m. The coated samples have comparable field emission I-V curves. An interpretation of these data in terms of a total electron energy FNT model will be discussed.@footnote 1@C. Sinclair, et al. Proceedings of the 2001 Particle Accelerator Conference. Chicago, IL, 2001.

Advanced Surface Engineering Room 323 - Session SE-TuA

High Temperature Protective Coatings

Moderator: A. Matthews, University of Hull, UK

2:00pm SE-TuA1 Synthesis and High Temperature Performance of SiAlON Thin Film Coatings, J.I. Krassikoff, G.P. Bernhardt, M. Call, R.J. Lad, University of Maine

SiAlON ceramics made by alloying Al₂O₃ and Si₃N₄ possess oxidation resistance, high strength, and thermal shock resistance, which make them extremely attractive for high temperature coating applications. However, most work to date has emphasized bulk sintered SiAlONs rather than thin coatings. We have synthesized well-defined SiAlON thin films using rf magnetron sputtering of Al and Si targets in Ar / O₂ / N₂ mixtures on sapphire substrates. By manipulating the relative amounts of the deposition fluxes, homogenous versus multilayer or gradient SiAlON structures with a range of stoichiometries were produced. The films remain amorphous even with post-deposition annealing in vacuum or air up to 1000°C. Moreover, the film stoichiometries remain stable at high temperature in vacuum but lose nitrogen during air annealing. A thin film Ni-Cr corrosion sensor was embedded at the SiAlON / substrate interface, and the rate of oxygen penetration through the SiAlON film structures was measured in situ during accelerated thermal cycling tests in 1000°C oxidative environments. The time to failure ranges from hours to weeks depending on the exact SiAlON composition. Multilayer films with an Al₂O₃ overlayer exhibit the best oxidation resistance. Pin-on-disk wear tests indicate that the wear rate is also a function of the SiAlON stoichiometry. Our results yield important information that can be used to design and fabricate multifunctional SiAlON environmental barrier and thermal barrier coatings. @footnote 1@ @FootnoteText@@footnote 1@ Supported by AFOSR Grant #F49620-02-1-0323.

2:20pm SE-TuA2 Synthesis and Characterization of Nanolayered TiO₂/Al₂O₃ Coatings for Possible Elevated Temperature Applications, K.W. Lee, M. Sturino, Y.W. Chung, L.M. Keer, Northwestern University

It was demonstrated from previous studies that nanolayered coatings with the correct choice of components and layer thicknesses have enhanced hardness, due to interfaces providing barriers against dislocation motion and multiplication. We expect superlattice coatings made of two immiscible components to be stable against interdiffusion. Therefore, the layer structure and reasonable hardness for such nanolayered coatings should be preserved at high temperatures. These thermally stable coatings are desirable for protection of cutting tools in dry machining applications, which may operate at temperatures in the 800-1000°C regime or higher. For this reason, TiO₂ and Al₂O₃ were chosen for this investigation. Nanolayered coatings made of these two immiscible components were synthesized by dc dual-cathode reactive magnetron sputtering. Substrate rotation was used to enhance uniformity of the coating. Substrates include M2 steel and Si(001). These coatings were exposed to air at 1000°C. Coatings deposited on silicon were characterized before and after the heat treatment in terms of surface roughness, residual stress, and nanoindentation hardness. Actual dry machining will be performed to evaluate the performance of these coatings. These results will be presented and discussed in terms of the coating potential in dry machining and high-temperature tribological applications.

2:40pm SE-TuA3 Advances in Surface Engineering for High Temperature and Wear Resistant Applications, A. Inspektor, Kennametal Inc. INVITED

Many components, when exposed to aggressive environments like high temperatures and cyclic stresses, fail when their surfaces have degraded beyond a predetermined limit. Thus, the demand for improved performance requires early integration of coatings into product design in order to assemble a functional surface tailored to resist the particular environment in which the component is working. This functional surface, with a unique combination of bulk and surface properties, is vital to the successful performance of the component. The corresponding surface engineering technique is an integral part of the manufacturing process. This paper will review present and future trends in surface engineering with an emphasis on the design and on the preparation of functional surfaces for high temperature and for wear resistant applications. Topics to be covered

are nanostructured coatings architecture and substrate-surface integration for improved hardness, thermal stability, oxidation resistance and tribological properties of cutting tools and of wear parts. An effort will be made to identify performance needs in these applications and the corresponding surface engineering solutions. A discussion will be held how to meet the challenge of surface engineering and of substrate-coating integration in materials design.

3:20pm SE-TuA5 Processing and Properties of NiAl-Hf Coatings via DC Magnetron Sputtering, B. Ning, M.L. Weaver, The University of Alabama

Crystalline NiAl-0.1Hf coatings (20 μm thick) were deposited onto CMSX-4 substrates at temperatures ranging from room temperature up to 300 °C using direct current (DC) magnetron sputtering. The microstructures of the coatings were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The as deposited coatings were single phase, and exhibit dense columnar Zone T microstructures. Column sizes were observed to increase from approximately 250 nm at room temperature to more than 2 μm in diameter at 250 °C. Annealing in argon at 1000°C for 1h resulted in densification of the coatings and in increased adhesion between the coatings and the substrate. Microstructural and compositional changes of the coating system after isothermal oxidation were studied using SEM and energy dispersive spectroscopy (EDS) techniques. The mechanical properties of the coatings were studied via nanoindentation in the as deposited condition, after annealing, and following various oxidation heat treatments. The hardness and modulus of the coatings were observed to correlate with oxidation time. Extended oxidation resulted in decreased hardness due to grain growth and diffusion induced precipitation and phase transformations. The results are discussed relative to conventional CVD aluminide coatings.

4:20pm SE-TuA8 Surface Alloying of Aluminum Films by Electron Beam Evaporation on Zirc-4 Substrates and Hydrothermal Crystal Growth in Sub-critical Condition, S.T. Park, R.H. Baney, University of Florida

Waterside corrosion of the Zircaloy cladding encasing the uranium oxide pellets is one of the primary factors limiting high "burn up" of nuclear fuel in pressurized water reactor (PWR) nuclear reactors. High "burn up" can significantly impact plant safety and economics. This research has been performed to develop ceramic coating corrosion protection system. Aluminum films were deposited on Zircaloy substrates by electron-beam evaporation and surface-alloyed by controlled oxidation at near the melting temperature of aluminum. Two different oxidation procedures were employed to make compositional gradient compound layers. These gradient compound layers can increase the corrosion resistance and minimize the interface defects like grain boundaries that can occur in multilayer coatings. The substrate surface roughness, aluminum film thickness, and air oxidation time and temperature were varied. The durability of films was tested through the use of an autoclave test in sub-critical condition that is the same condition as in actual PWR. The samples were then evaluated to determine the film condition. Deposited films were characterized for morphology and elemental composition using field emission scanning electron microscopy (FE SEM), energy dispersive x-ray analysis (EDX), and auger electron spectroscopy (AES). AES analysis of the oxidized coatings showed that gradient compositions were obtained as expected, with Al, Zr, and O content varying through the coating thickness. Glancing angle x-ray diffraction (GAXRD) analysis also showed that variety of intermetallic and oxide phases (such as Al₃Zr, Al₂Zr₃, Al₂O₃, ZrO₂ and Zr₃O₅) were formed in the coatings during processing. Hydrothermal growth of well-faceted particulates was observed after autoclave test. They were identified to be hydrothermal synthesized aluminum hydroxide, Boehmite by GAXRD and transmission electron microscopy (TEM).

4:40pm SE-TuA9 Surface Studies of the High Temperature Corrosion of Stainless Steel by Oxygen Controlled Lead-Bismuth Eutectic, A.L. Johnson, D. Parsons, J. Manzerova, D. Koury, B. Hosterman, University of Nevada, Las Vegas; D.L. Perry, Lawrence Berkeley National Laboratory; J.W. Farley, University of Nevada, Las Vegas

There has been a resurgence of interest in the use of oxygen controlled Lead/Bismuth Eutectic (LBE) and similar high Z liquid metals as neutron spallation targets and coolants in advanced technology reactors. LBE was used in the Russian Alpha class nuclear submarines, with encouraging results. We have been investigating the corrosion of some western steels by oxygen controlled LBE in a Russian test loop using a number of techniques including SEM, EDAX, XPS and sputter depth profiling. We found for some mixtures of composition and surface preparation an order

Tuesday Afternoon, November 4, 2003

of magnitude lower oxidation and dissolution, associated with a change in morphology of the protective oxide layer. We shall discuss the effects of surface and near surface preparation and composition on this interesting oxidation/dissolution corrosion system.

Tuesday Evening Poster Sessions, November 4, 2003

Advanced Surface Engineering Room Hall A-C - Session SE-TuP

Poster Session

SE-TuP1 Synthesis and Elastic Properties of Polycrystalline Thin Films with Cr₂AlC Structure, *J.M. Schneider, Z. Sun, R. Mertens, F. Åæstel*, RWTH-Aachen, Germany; *R. Ahuja*, Uppsala University, Sweden

We report the synthesis and characterization of polycrystalline thin films with Cr₂AlC structure by magnetron sputtering. Ab initio total energy calculations using the Projector Augmented-Wave (PAW) was used to investigate the electronic structure. Our estimated d spacing values agree well (within 3 to 6 Å) with glancing incidence X-ray diffraction data of the as deposited films. No peaks other than the ones of Cr₂AlC were observed.

SE-TuP2 Growth of PACVD c-BN Films and c-BN/Diamond Bilayers, *M.S. Wong*, National Dong Hwa University, Taiwan, ROC, Taiwan, R.O.C; *J.B. Cheng, T.S. Yang, S.S. Chu*, National Dong Hwa University, Taiwan, ROC

The synthesis of c-BN films was carried out by the reaction of BF₃ and N₂ in the hydrogen and argon mixture using microwave plasma-assisted chemical vapor deposition (PACVD). The effects of N₂/BF₃ ratios, hydrogen addition, DC substrate-bias voltage and diamond as bufferlayer on the formation of c-BN were investigated. As-grown films are characterized by FTIR, grazing-incidence XRD, and SEM. The composition of gas mixture and energy of ion bombardment are critical to the formation of c-BN phase in the BN films. Under optimal growth conditions and using nanocrystalline diamond film as bufferlayer, the growth of high c-BN content up to ~85 % c-BN was achieved.

SE-TuP3 Kinetics of Boron Nitride Thin Film Formation using Low Energy Ion Beam Assisted Deposition, *W. Otaño*, University of Puerto Rico at Cayey

Cubic boron nitride (cBN) is a superhard material, which is defined as a material with microhardness over 40 GPa, and offers the best combination of high hardness, low friction coefficient, resistance to oxidation, and resistance to chemical degradation with iron-based materials. Other applications of cBN take advantage of its high density, high thermal conductivity, good transparency in the visible and infrared portion of the spectrum, and high electrical resistivity. Cubic BN is also a wide band gap semiconductor, which can be n- and p-type doped. Several models have been proposed to describe the nucleation and growth of cBN thin films based on the observation of the necessity of energetic bombardment of the growing film for the stabilization of the cubic phase. These models include the concept of thermal spikes, the subplantation model, stress-induced stabilization, and resputtering of the BN hexagonal phase. Several authors have been able to correlate the energetic bombardment with P/a , the total momentum imparted to the growing film per arriving boron atom. In this report, the use of a high intensity, low energy ion source, incorporated to an ion beam assisted deposition system to study the kinetics of the cBN thin film nucleation at bombarding ion energies in the 50-100 eV range will be discussed. It will be shown that the control of the ion bombardment and of the incoming boron atom flux is critical for the kinetics of formation of the boron nitride films. The implications for the nucleation process of the BN cubic phase and a comparison with systems using high deposition rates will be discussed.

SE-TuP4 Mechanistic Studies of the Wet Chemical Oxidation of Hydrogen-terminated Si(100), *C.A. Shea, K.T. Queeney*, Smith College

Wet chemical cleaning of the Si(100) surface is a critical step in wafer processing for microelectronics. Oxidation of HF-etched (hydrogen-terminated) Si(100) surfaces occurs both intentionally (via peroxide solution) and unintentionally (e.g. during rinsing steps) and can affect both the chemistry and the morphology of the underlying substrate. We have used a combination of surface infrared spectroscopy and contact angle measurement to follow both the microscopic and macroscopic evolution of the H-terminated Si(100) surface during aqueous oxidation. Ex-situ transmission IR experiments allow us to elucidate the role of solution species including dissolved oxygen and OH⁻ on both the rate and the mechanism of oxidation by following changes in both the Si-H and Si-O regions of the infrared spectrum. Contact angle hysteresis provides a measure of surface heterogeneity during these processes; comparison with the more uniform Si(111) surface provides a benchmark for the degree of inhomogeneity inherent to the rougher H:Si(100) substrate.

SE-TuP5 Rheological Modeling of Fracture Mechanics of Hard Coatings on Soft Substrates at Hertzian Indentation, *M.V. Kireitseu, L.V. Kireitseu*, Institute of Mechanics and Machine Reliability, Belarus

The present work described rheological modeling of novel coating «chrome carbide nanoparticles – aluminum oxide – soft aluminum substrate» and «steel – viscous-elastic polymer – aluminum – aluminum oxide» at their Hertzian indentation. When the hard aluminum oxide-based coatings are brought into contact with a ceramic or a metal indenter, different stress-deformation modes can be developed between the materials. Strains and forces will depend upon the state of the surfaces, its roughness and the fundamental mechanical properties of the two solids that are both indenter and substrate. Mechanical behaviour between the coatings and another solid indenter are discussed from a theoretical consideration of the mechanical constants (elasticity, plasticity and viscosity) of the coatings and experimentally by relating loading forces and stresses to the interface resulting from the contact. Rheological models were proposed for the coatings and were confirmed by in-suit experiments using principal Hertzian theory. An experimental evidence showed good agreement between the models and mechanical behavior of the coatings. Load rating tests revealed ultimate stresses and stress-deformation modes for both the coatings and their particular layer. The models and its behavior under a few fundamental conditions of loading (triangle, pulse, sinusoidal etc.) are discussed. @FootnoteText@ none

Author Index

Bold page numbers indicate presenter

- A —
Ahuja, R.: SE-TuP1, 8
Aksenov, I.I.: SE-MoA6, 2
— Å —
Åæstel, F.: SE-TuP1, 8
— A —
Aouadi, S.M.: SE-MoA8, 3
Asmussen, J.: SE-MoA7, 2
— B —
Back, T.C.: SE-MoA6, 2
Badisch, E.: SE-TuM4, 4
Baney, R.H.: SE-TuA8, 6
Becker, M.: SE-MoA7, 2
Bernhardt, G.P.: SE-TuA1, 6
Booth, R.A.: SE-MoA7, 2
Butler, T.P.: SE-MoA8, 3
— C —
Call, M.: SE-TuA1, 6
Chateaufneuf, G.M.: SE-MoM3, 1
Chen, Y.: SE-MoA2, 2
Cheng, J.B.: SE-TuP2, 8
Chiou, W.A.: SE-TuM1, 4
Chu, S.S.: SE-TuP2, 8
Chung, Y.W.: SE-MoA2, 2; SE-TuA2, 6
Cizek, J.: SE-MoA3, 2
Clayton, C.R.: SE-TuM3, 4
Conley, R.: SE-TuM7, 5
— D —
Deguchi, Y.: SE-TuM1, 4
Dylla, H.F.: SE-TuM8, 5
— F —
Farley, J.W.: SE-TuA9, 6
Fiero, T.: SE-TuM3, 4
Fischer, A.: SE-TuM6, 4
— G —
Gall, D.: SE-TuM2, 4
Gammon, W.J.: SE-MoA5, 2
Gao, G.T.: SE-MoM3, 1
Gassner, G.: SE-TuM4, 4
Greene, J.E.: SE-TuM2, 4
Grotjohn, T.A.: SE-MoA7, 2
— H —
Halada, G.P.: SE-TuM3, 4
Harrison, J.A.: SE-MoM3, 1
Hegemann, D.: SE-TuM6, 4
Hellgren, N.: SE-TuM2, 4
Hernandez, C.: SE-TuM8, 5
Hoatson, G.L.: SE-MoA5, 2
Hoepfner, T.P.: SE-MoA7, 2
Holloway, B.C.: SE-MoA5, 2
Honbo, E.: SE-TuM1, 4
Hosterman, B.: SE-TuA9, 6
Houska, J.: SE-MoA3, 2
— I —
Inspektor, A.: SE-TuA3, 6
— J —
Jaime Vasquez, M.: SE-TuM3, 4
Johnson, A.L.: SE-TuA9, 6
Jones, J.G.: SE-MoA6, 2
— K —
Keer, L.M.: SE-TuA2, 6
Kireitseu, L.V.: SE-TuP5, 8
Kireitseu, M.V.: SE-TuP5, 8
Kormunda, M.: SE-MoA3, 2
Koury, D.: SE-TuA9, 6
Kraft, O.: SE-MoA5, 2
Krassikoff, J.I.: SE-TuA1, 6
Krzanowski, J.E.: SE-MoA1, 2
— L —
Lad, R.J.: SE-TuA1, 6
Lee, K.W.: SE-TuA2, 6
Lee, T.-Y.: SE-TuM2, 4
Li, D.J.: SE-MoA2, 2
Liu, C.: SE-TuM7, 5
— M —
Macrander, A.T.: SE-TuM7, 5
Mae, T.: SE-TuM1, 4
Manos, D.: SE-TuM8, 5
Manzerova, J.: SE-TuA9, 6
Mayrhofer, P.H.: SE-TuM4, 4
Mertens, R.: SE-TuP1, 8
Mihut, D.M.: SE-MoA8, 3
Mikulski, P.T.: SE-MoM3, 1
Mitterer, C.: SE-TuM4, 4
Moore, R.: SE-TuM8, 5
— N —
Ning, B.: SE-TuA5, 6
Nogi, K.: SE-TuM1, 4
Nose, M.: SE-TuM1, 4
— O —
Otaño, W.: SE-TuP3, 8
— P —
Park, S.T.: SE-TuA8, 6
Parsons, D.: SE-TuA9, 6
Perry, D.L.: SE-TuA9, 6
Petrov, I.: SE-TuM2, 4
Potocky, S.: SE-MoA3, 2
— Q —
Queeney, K.T.: SE-TuP4, 8
— R —
Reilly, A.C.: SE-MoA5, 2
Reinhard, D.K.: SE-MoA7, 2
Robertson, I.: SE-MoM1, 1
Rohde, S.L.: SE-MoA8, 3
— S —
Schneider, J.M.: SE-MoM7, 1; SE-TuP1, 8
Shea, C.A.: SE-TuP4, 8
Shin, C.-S.: SE-TuM2, 4
Soukup, Z.: SE-MoA3, 2
Sproul, W.D.: SE-MoM9, 1
Stoiber, M.: SE-TuM4, 4
Strelnitzki, V.E.: SE-MoA6, 2
Sturino, M.: SE-TuA2, 6
Sun, Z.: SE-TuP1, 8
— T —
Theodore, N.D.: SE-TuM8, 5
Turner, J.: SE-MoA8, 3
Twisten, R.D.: SE-TuM2, 4
— V —
Vlcek, J.: SE-MoA3, 2
Voevodin, A.A.: SE-MoA6, 2
— W —
Wang, T.: SE-TuM8, 5
Weaver, M.L.: SE-TuA5, 6
Wen, J.G.: SE-TuM2, 4
Wong, M.S.: SE-TuP2, 8
Wormwood, J.: SE-MoA1, 2
— Y —
Yang, T.S.: SE-TuP2, 8
— Z —
Zabinski, J.S.: SE-MoA6, 2
Zeman, P.: SE-MoA3, 2