Topical Symposia
Room Sunrise - Session TS4

Materials Modeling and Simulation

Moderators: Thomas Mussenbrock, BTU Cottbus, David Holec, Montanuniversität Leoben, Austria

1:30pm **TS4-1 From the Atomic Interaction to Thermodynamic and Mechanical Properties of Materials**, ***Ralf Drautz,*** Ruhr-Universität Bochum, Germany **INVITED**

Density functional theory (DFT) provides a solid basis for the simulation of materials properties. In some cases the computational expense of DFT makes the sampling of thermodynamic observables or the calculation of dynamic variables difficult. We coarse grain the interatomic interaction from DFT at two levels of approximation to allow for faster and larger simulations. First, a tight-binding model is derived from a second-order expansion of DFT in a minimal basis. The parameters in the tight-binding model are obtained directly from minimal basis DFT calculations. In a second step the tight-binding model is approximated locally and analytically, resulting in the analytic Bond-Order Potentials (BOPs). Because of the derivation of BOPs from DFT, the contributions of magnetism and charge transfer to bond formation are directly taken into account. The BOPs are orders of magnitude faster than DFT and allow for the direct sampling of thermodynamic observables.

I will discuss the application of the BOPs to simulating finite temperature magnetism in iron, in particular the ferromagnetic to paramagnetic phase transformation and the alpha-gamma transition and the prediction of some mechanical properties. I will further discuss atomic simulations for phase stability, nucleation and solid-solid transformations with relevance to high-temperature materials.

2:10pm **TS4-3 Molecular Dynamics Study of Titanium Oxynitride Surface Properties**, ***Tobias Gergs,*** *J Trieschmann,* Ruhr University Bochum, Germany*; T Mussenbrock,* BTU Cottbus, Germany

Mechanical properties of metal oxynitride hard coatings depend on the preceding film growth through fundamental surface processes and thermodynamic driving forces. While the latter aspects were recently studied for titanium nitrides, the influence of substitutional oxygen requires further investigation. The absence of theoretical approaches reported in the literature is mainly due to unavailable purely classical potentials to describe titanium oxynitrides. A second reason might be computational limitations of ab-initio methods. So far solely the bulk properties have been addressed by means of density functional theory in the literature. Initially in this work, on the basis of these referenced calculations [1], the recently published COMB3 (3rd generation charge optimized many body) semi-classical potential for heterogeneous titania/titanium nitride systems is characterized and validated. Subsequently, the validated potential is utilized to systematically investigate the inherent thermodynamic driving forces for varying nitrogen/oxygen compositions at the surface. For this study, independent atom configurations are generated with a modified version of the combinatorial SOD (site-occupancy disorder) code, taking into account the broken symmetries of the (001), (110) and (111) surfaces. The resulting slabs are relaxed and characterized with the molecular dynamics code LAMMPS (large-scale atomic/molecular massively parallel simulator). With the validation of the semi-classical potential for titanium oxynitride and a discussion of the influence of a substitutional oxygen contribution, a first step towards the modeling of the corresponding film growth is presented.

[1] J. Graciani, S. Hamad, and J. F. Sanz, Phys. Rev. B **80**, 184112 (2009).

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2:30pm **TS4-4 Distribution of O Atoms on Partially Oxidized Metal Surfaces According to Ab-initio Calculations, and the Consequences for Sputtering of Individual Metal Oxides**, ***Jiri Houska,*** *T Kozak,* University of West Bohemia, Czech Republic

We investigate the oxidation of a wide range of metal surfaces by density functional theory. The metals of interest will include those studied in Ref. 1 (Al, Ag, Cu, Ti, Zr, Hf) as well as those studied more recently. We go through a wide range (235 per metal) distributions of O atoms on a partially oxidized metal surface. First, we focus on the qualitative information whether the preferred distribution of O atoms is heterogeneous (stoichiometric oxide + metal) or homogeneous (substoichiometric oxide). We find that the former is energetically preferred e.g. for Al, while the latter is energetically preferred e.g. for Ti, Zr and Hf. Second, we correlate these qualitative results with the known formation enthalpies of oxides of various compositions. Third, we provide the quantitative values of adsorption energies corresponding to the energetically preferred O atom distribution for various partial coverages of various metals by O. We find that the absolute values of the adsorption energies increase with the surface oxygen coverage e.g. for Al, and decrease e.g. for Ti, Zr and Hf. Fourth, we demonstrate one use of these results by presenting Monte Carlo simulations of sputtering. Fifth, we utilize the theoretical results in order to explain the experimental results, such as the time dependence of the magnetron voltage during sputter cleaning of oxidized metal targets (monotonous e.g. for Al but non-monotonous e.g. for Ti).

2:50pm **TS4-5 First-principles Study of Adsorption and Diffusion of Oxygen on the Surface of TiN, ZrN, HfN and the Effect of Al on Oxidation Resistance of TiN Coatings**, ***Fangyu Guo,*** Central South University, China

Using first-principles calculations based on the density functional theory, we systematically study the adsorption and diffusion behaviors of single oxygen (O) atom on the (001) surface of nitride coating s of TiN, ZrN and HfN. When adsorbing at the top(N) site, the adsorption energy of TiN is much lower than the value of ZrN and HfN. The O atom is more likely to stabilize adsorbed on the ZrN and HfN surfaces. The diffusion behavior of O atom is investigated through determining the minimum energy pathways (MEP) and diffusion barrier on the (001) surface of these metal nitrides. O atom tends to diffuse on the (001) surface from one top(N) site to neighboring top(N) sites via the hollow site for all the three nitrides. It is also found that diffusion of O atom on the (001) surface of TiN is easier than that of ZrN and HfN. On the three nitrides surface, the adsorption of O on the TiN(001) surface is most unstable. This is a good explanation for a experimental phenomenon that the oxide thickness of TiN is smaller than that of ZrN under the same oxidation conditions.

In order to further increase oxidation resistance of TiN coating, the third elements are added to the TiN coating. TiAlN is widely used as protective coating for cutting and forming tools due to the high hardness combined with good oxidation and wear resistance. We used the special quasirandom structure (SQS) approach to represent the random Nacl structure TiAlN systems and address the effect of Al on the oxidation resistance of TiN by means of *ab initio* molecular dynamics simulations. The forming process of oxides of TiAlN coatings was investigated at 1123k and 773k.

3:10pm **TS4-6 Metastable Phase Formation of Pt-X (X= Ir, Au) Thin Films**, ***Aparna Saksena,*** *Y Chien, K Chang, P Kuemmerl, M Hans,* RWTH Aachen University, Germany*; B Völker,* Max-Planck-Institut für Eisenforschung GmbH, Austria*; J Schneider,* RWTH Aachen University, Germany

The dependence of phase formation and mechanical properties on the chemical composition has been investigated for Pt-Ir and Pt-Au combinatorial thin films. Composition spreads are deposited at substrate temperatures ranging from room temperature to 950°C and are subsequently characterized using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning transmission electron microscopy (STEM), atom probe tomography (APT) and nanoindentation. The formation of a single, metastable Pt-Ir solid solution phase has been observed for all experimentally probed compositions and growth temperatures. Upon Ir addition to Pt the experimentally determined changes in lattice parameter and Young's modulus display the expected rule of mixture behavior which is in very good agreement with our *ab initio* data. Whereas, in the Pt-Au system, the single metastable solid solution phase is seen to decompose into two solid solution phases as the growth temperature is raised to ≥ 600°C. The lattice parameters of the single metastable phase grown at temperatures < 600°C increase linearly as Au is added, showing rule of mixture behavior in good agreement with *ab initio* predictions. However, the lattice parameters of the phases in the dual phase region are independent of chemical composition displaying phase formation behavior consistent with the CALPHAD results. The substrate temperature and chemical composition dependent phase formation in Pt-Ir and Pt-Au thin films can be rationalized based on CALPHAD calculations combined with estimations of the activation energy required for surface diffusion: The metastable phase formation during film growth is caused by kinetic limitations, where Ir atoms (in Pt-Ir) need to overcome an up to factor 6 higher activation energy barrier than Au (in Pt-Au) to enable surface diffusion.

3:30pm **TS4-7 From Plasmas Towards Surfaces: How Plasma Simulation Supports Materials Development**, ***Mark J. Kushner,*** University of Michigan, USA **INVITED**

New materials development and fabrication often have the goals of new functionality or smaller dimensions. In many cases, thermal or equilibrium processes are challenged to achieve this functionality. The inherent non-equilibrium reactivity available from low-temperature plasma materials processing addresses both the prospect of new functionality, by enabling new structures to be fabricated, and smaller dimensions, due to the precision available to plasma produced fluxes to surfaces. An example of achieving both new functionality and finer precision is plasma enabled atomic layer deposition (ALD) and atomic layer etching (ALE). The broad parameter space available to plasma enhanced materials processing has motivated integrated plasma-materials modeling to help narrow the scope. In this talk, contributions of modeling of plasmas and plasma-surface-interactions to the development of new functionality and greater precision will be discussed. Examples will be shared from the low pressure, modeling enhanced development of new plasma excitation schemes with the goal of customizing fluxes; and feature scale modeling for ALE and high aspect ratio processes. Modeling enabled insights to atmospheric pressure plasma functionalization of surfaces will also be discussed.

4:10pm **TS4-9 Numerical Estimation of Intrinsic Stress in Physical Vapor Deposited Thin-Films**, ***Anurag Chakraborty,*** *R Anderson, J Ash,* South Dakota School of Mines and Technology, USA*; F Kustas,* Arbegast Materials Processing and Joining Laboratory (AMP), USA*; S Ahrenkiel,* South Dakota School of Mines and Technology, USA

A method of numerically quantifying the intrinsic stress estimates has been developed for physical vapor deposited thin-film coatings prepared at 250°C. This method involved constructing a prototype of a dedicated optical setup for measuring the curvatures of thinly coated samples with a film thickness ranging from 3-5 microns. A portable fixture was made which was clamped onto the translation stage of an optical microscope and this could be potentially usable with any commercial microscope that has 40 mm or more of vertical stage travel. Characterizations were performed on the optical instrument to enhance the sensitivity of detecting curvature changes over a given range of radii for the samples. The optical setup is compatible with reverse-mounted thin-film samples across a range of radii and it was modeled in Autodesk Inventor. A finite element model was developed in Abaqus where the deformation due to the residual stress in the thin-film sample was modeled as a pure thermal load. Subsequently, the initial stress state parameter was incorporated into the original model and systematically varied until the finite element model showed a deflection and a curvature which was in the range of 1-3% of the actual values obtained from the optical setup. The difference in the S11 and S22 principal stress values generated by the two models could be considered as equivalent to the actual intrinsic contribution to the eventual residual film stress in the coating responsible for the physical deflection. A test model with fixed constraints in Abaqus was also developed to capture the pre-deformed state of stress. Finally, this method was used to observe the intrinsic stress variations across 20 samples which were placed in a rectangular array formation over an 8" by 6" area of an aluminum supporting plate as a function of their separation distance from the target material. All 20 coatings were developed in a single deposition run to eliminate the process variables from having a non-uniform impact on the intrinsic stress development.

4:30pm **TS4-10 Modeling of UHMWPE Surface Texture for Reducing Wear on a Knee Prosthesis**, ***Tomas De la Mora Ramírez,*** Universidad Autónoma Metropolitana, Mexico*; I Hilerio Cruz,* Universidad Autónoma Metropolitana- Azcapotzalco, Mexico*; M Doñu Ruiz,* Universidad Politécnica del Valle de Mexico, Mexico*; N Lopez Perrusquia,* Universidad Politecnica Del Valle De Mexico, Mexico*; E García Bustos,* Universidad de Guadalajara, CUCEI, Mexico, México*; D Maldonado Onofre,* Tecnológico de Estudios Superiores de Jocotitlán, Mexico

The objective of the research is to improve tribological properties of UHMWPE through the morphological modification of its surface texture with the analysis of stress distribution, contact stress, volume loss and coefficient of friction. Test specimens were made through 3D printing to produce hexagonal geometric textures at depths of 18, 25, 36 and 50 micrometers at different geometric densities with respect to a uniform distribution on the surface of the specimen of 5, 10, 20 and 40%. Microabrasion tests were performed using a UHMWPE specimen and a ball of 52100 steel material one inch in diameter. Throughout 3D perfolometry the wear rate and the wear constant of the test specimens with and without texture were obtained. A dynamic simulation was performed by finite element analysis of the tribometer microabrasion test using a subroutine in fortran language linked to Abaqus V6.12 finite element software. With the simulation a rate of wear is obtained; comparing with the experimental results. With the experimental results and the simulation the subroutine was applied to predict its lifetime.

4:50pm **TS4-11 Perturbation Analysis Of Glassy Alloy Film Formation**, ***Rahul Basu,*** Adarsha Insitute of Technology, VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated incorporating surface convective effects. These equations which are non linear due to the moving interface are linearised and decoupled. Effects of the Biot, Fourier and Stefan numbers are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for several alloys in various groups of the Periodic Table. Earlier work by Duwez (1) and Spaepen & Turnbull (2) is analysed in light of the present analysis.

References:

1) P. Duwez, Annual Review of Materials Science, 1976

2) F Spaepen and D Turnbull, Scripta Met, 8,563, 1974

5:10pm **TS4-12 First Principles Study of the Nb-Al Intermetallic System**, ***David Holec,*** Montanuniversität Leoben, Austria*; N Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; K Preininger, S Zoehrer, R Franz,* Montanuniversität Leoben, Austria

Physical-vapour-deposited materials exhibit a variety of interesting and useful properties. Often, however, the actual behaviour strongly depends on the specific synthesis method and conditions. For revealing such synthesis-property relationships, understanding of the deposition process, which in turn is influenced by the target material used for the deposition, is critical.

In this contribution we will use first principles calculations to assess the stability of phases in a model binary intermetallic Nb-Al system. The convex hull constructed using the USPEX code yields Al_3Nb and $AlNb_2$ as the stable phases along with $AlNb_3$ being slightly metastable. These phases appear in published phase diagrams, in which the $AlNb_3$ is nevertheless a stable phase. Surprisingly, the reported compositional window for $AlNb_3$ does not contain the nominal x=0.75 composition.

Cohesive energies are calculated as representatives for the bonding strength and hence ease of the evaporation during an arc evaporation process. Additionally, we propose to use vacancy formation energies instead of cohesive energies as they provide species-specific information as well as their temperature dependence can be estimated. The vacancy formation energies are further on studied as a function of distance from the surface as well as the surface orientation. A correlation with experimental measurements of cathodic arc behaviour is attempted.

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