New Horizons in Coatings and Thin Films
Room Town & Country C - Session F5-2-MoA

In-Silico Design of Novel Materials by Quantum Mechanics and Classical Methods II

Moderators: David Holec, Montanuniversität Leoben, Austria, **Davide G. Sangiovanni**, Linköping University, Sweden

3:40pm **F5-2-MoA-7 Theoretical Investigation of Sluggish Diffusion in Nitride Films of High-Entropy Alloys**, ***Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at)***, Montanuniversität Leoben, Austria*; A. Kretschmer, P. Mayrhofer,* TU Wien, Austria*; D. Holec,* Montanuniversität Leoben, Austria

The concept of alloying was revolutionized in multi-component or high-entropy alloys (HEA), where five or more elements are distributed randomly on a crystalline lattice in equiatomic or near-equiatomic composition. Thereby, no element acts as a principal component and four core effects have been postulated to stem from this configuration: high configurational entropy, severe lattice distortion, sluggish diffusion, and cocktail effects. Since we still lack a proper quantification of the sluggish diffusion, this work focuses on this topic applied to the case of high-entropy nitrides (HENs). These ceramic materials possess high hardness and good thermal stability and are hence attractive for high-temperature applications.

The HEN systems that have been considered for this ab initio study are non-magnetic and structurally stable systems with the metals distributed on the metal sublattice by special quasi-random structure (SQS) methods. For each HEN system and each species, we determined migration barriers corresponding to vacancy-driven elementary point-defect migration mechanisms for crystalline solids. The change in diffusion w.r.t. migration barrier, while going up from ternary to hexinary systems, will be presented. Our results suggest that the impact of the local composition and increasing high-entropy environment can significantly alter these results. Our analyses focus on comparing low and high entropy systems (as measured by the number of elements) for systems exhibiting low and large local distortions, and similar and different nominal bond lengths of the forming binary nitrides. From our preliminary results, the claimed sluggishness of the diffusion in HENs should be more composition and/or environment-specific rather than generalizing for all high entropy systems.

4:00pm **F5-2-MoA-8 Simulation of Transport and Mechanical Properties of TiSiN:Ag Self-Lubricating Coatings With Machine Learned Force Fields**, ***Veniero Lenzi (veniero.lenzi@fisica.uminho.pt)***, University of Minho, Portugal*; F. Fernandes,* University of Coimbra, Portugal*; L. Marques,* University of Minho, Portugal

The quest for the environmental impact mitigation of aerospace industry passes through the use of lightweight and high-performance novel materials. However, these materials are hard to work/machine with standard tools. In this regard, a promising solution is the use of nanocomposite self-lubricating thin films on cutting and machining tools, which might enhance their lifetimes while reducing the use of lubricant, with clear economic and environmental advantages.

Titanium Silicon Nitride and Silver (TiSiN:Ag) nanocomposite thin films have been shown to provide good performance as self-lubricating coatings.[1,2] Their performance depends critically on the release rate of silver, the lubricating agent, which is influenced by the nanoscale structure of the thin film. Atomistic simulation methods are thus necessary to investigate and understand the Ag diffusion within the coating. [3] Moreover, it is important to consider the effects of the high temperatures and stresses encountered during the operation conditions on the coating's structure and stability.

To tackle the complexity of this material, we are currently employing machine learning (ML) techniques to obtain force fields capable of ab-initio level accuracy while enabling large-scale simulations. In particular, we are using the FLARE package [4] to perform on-the-fly training over ab-initio calculations. In this way, we obtained force-fields for TiN/Ag, SiN/Ag and TiSiN systems, which we used to calculate not only the diffusion constants for the different transport processes of Ag within the coating, but also the evolution of the nanocomposite structure under high temperatures and stresses. The obtained force fields show a very high degree of accuracy, within range of ab-initio calculations.

This work highlights the importance of ML methods for the simulation of complex materials. Our results shed light into the Ag transport in TiSiN coatings and in their mechanical properties, thereby providing a unique tool to optimize the thin film processing parameters to achieve the best possible performance.

References:

1: S. Calderon Velasco, A. Cavaleiro and S. Carvalho, *Progress in Materials Science*, 84:158-191, 2016.
2: D. Cavaleiro, *et al.*, *Surface and Coatings Technology*, 399:126176, 2020.
3: V. Lenzi, *et al., Applied Surface Science,* 556:149738, 2021.
4: Y. Xie,*et al., Nature Computational Materials,* 7:40, 2021.

4:20pm **F5-2-MoA-9 Machine Learning Assisted Ab Initio Thermodynamics of Novel Materials**, ***Prashanth Srinivasan (prashanth.srinivasan@imw.uni-stuttgart.de)***, University of Stuttgart, Germany*; F. Körmann,* Max-Planck Institut für Eisenforschung, Germany*; B. Grabowski,* University of Stuttgart, Germany **INVITED**

Recent developments in machine learning techniques has immensely benefited *ab initio*modeling of materials. Interatomic potentials such as the moment tensor potential (MTP) (Shapeev, 2016) that are trained to high temperature density-functional theory (DFT) data are able to predict energies and forces of atomic configurations highly accurately. They are thus able to statistically sample a much wider part of the phase space in a fast and efficient manner. In combination with a systematic thermodynamic integration method (Direct Upsampling), they can be used to calculate total free energies of even complicated systems such as high entropy alloys (HEAs) to 1 meV accuracy (Grabowski et al., 2019, Ferrari et al., 2020) up to the melting point. Apart from static and electronic energies, this also includes vibrational contributions including anharmonicity which significantly affect thermodynamic properties such as specific heat capacity and bulk modulus at high temperatures.

Here, firstly, we demonstrate these results for a bunch of refractory BCC systems ranging from single- to five-component alloys. We break-down the total free energies into various individual contributions. We compare a contrasting trend in the anharmonic free energies beyond the quasi-harmonic approximation in certain BCC refractories, some of which show a positive contribution and some a negative contribution. We narrow this feature down to the density of states (DOS) and the first- and second-neighbor forces and illustrate a difference in bonding behavior between the two sets of BCC elements. Secondly, we also show the applicability of the MTPs to design novel shape memory alloy materials, where a MTP trained to DFT data predicts the stress- and temperature-induced phase transformations in these alloys.

5:00pm **F5-2-MoA-11 Materials Design Principles of Amorphous Cathode Coatings for Lithium-ion Battery Applications**, ***Jianli Cheng (jianlicheng@lbl.gov)***, *K. Persson,* Lawrence Berkeley National Laboratory (LBNL), USA **INVITED**

Cathode surface coatings have been the foremost solution to suppress cathode degradation and improve cycling performance of lithium-ion batteries (LIBs). In this work, we carry out an extensive high-throughput computational study to develop materials design principles governing amorphous cathode coating selections for LIBs. Our high-throughput screening includes descriptors to evaluate the thermodynamic stability, electrochemical stability, chemical reactivity with electrolytes and cathodes, and ionic diffusivities in the cathode coatings. We consider the commonly used Li_3PS_4 and $LiPF_6$ as the solid and liquid electrolytes, respectively, and categorize the coating materials based on their chemical reactivity with the electrolytes. We reveal the formidable challenge of mitigating oxygen diffusion when selecting an ideal cathode coating, and suggest a few promising materials that pass all the criteria in our high-throughput study. Combining the screening results and detailed ionic diffusion analysis of the selected cathode coatings, we summarize the general guidelines for selecting amorphous cathode coatings.

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