New Horizons in Coatings and Thin Films
Room Town & Country B - Session F5-1-MoM

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

Moderators: David Holec, Montanuniversität Leoben, Austria, **Ivan G. Petrov**, University of Illinois at Urbana-Champaign, USA

10:00am **F5-1-MoM-1 Competition between Plasticity and Brittleness in Refractory Ceramics**, ***Davide Sangiovanni (davide.sangiovanni@liu.se)***, *F. Tasnadi, I. Abrikosov,* Linköping University, Sweden **INVITED**

Understanding the competition between brittleness and plasticity in refractory ceramics is of fundamental importance for screening and design of hard materials with enhanced resistance to fracture from room to elevated temperature.

Ab initio and classical molecular dynamics (AIMD & CMD) simulations are used to investigate fracture mechanisms in defect-free, as well as notched B1 $Ti_{1-x}Al_xN$ ($0 \le x \le 0.75$) supercells subject to tensile and shear deformation as a function of temperature. The interatomic potential employed in CMD – thoroughly validated for several structural, mechanical, and thermodynamic properties of Ti-Al-N systems – accurately reproduces the results of AIMD simulations obtained for *small* (1100 atoms) supercells. Hence, the results of relatively large ($\approx 10^5$ atoms) CMD simulations of notched crystals subject to mode-I tension allow gaining a comprehensive understanding of the competition between unstable crack growth vs plasticity mechanisms at crack tips in Ti-Al-N systems.

The talk also briefly introduces an AIMD database (24 investigated systems) of B1-structure ceramic properties calculated for $300 \le T \le 1200$K. The database includes both raw *ab initio* data – $\approx 10^9$ phase-space configurations with associated energies, forces, total stresses, and magnetic moments – as well as mechanical properties including elastic constants, tensile and shear strengths, moduli of tensile toughness, Schmid vs non-Schmid lattice-slip mechanisms, and strain-mediated lattice transformation pathways. Taking Ti-Al-N systems as representative case, it is illustrated how indicators (determined from the *ideal* properties of single-crystal ceramics) can reliably predict statistical trends in mechanical performance evaluated for systems that contain native structural flaws.

Sangiovanni, Inherent toughness and fracture mechanisms of refractory transition-metal nitrides via density-functional molecular dynamics, Acta Materialia (2018).

Sangiovanni et al, Strength, transformation toughening, and fracture dynamics of B1 Ti-Al-N alloys, Physical Review Materials (2020).

Mei et al, Adaptive hard and tough mechanical response in single-crystal B1 VNx ceramics via control ofanion vacancies, Acta Materialia (2020).

Almyras et al, Semi-Empirical Force-Field Model for the Ti-Al-N System, Materials (2019).

Sangiovanni et al, Enhancing plasticityin high-entropy refractory ceramics via tailoring valence electron concentration, Materials &Design (2021).

Sangiovanni et al, Temperature-dependent elastic properties of binary and multicomponent high-entropyrefractory carbides, Materials & Design (2021).

10:40am **F5-1-MoM-3 Intriguing Deformation Mechanisms in Nanolayered Ceramics**, ***Nikola Koutná (nikola.koutna@tuwien.ac.at)***, TU Wien, Austria*; L. Löfler,* RWTH Aachen University, Germany*; D. Holec,* Montanuniversitat Leoben, Austria*; Z. Chen, Z. Zhang,* Austrian Academy of Sciences, Austria*; L. Hultman,* Linkoping University, Sweden*; P. Mayrhofer,* TU Wien, Austria*; D. Sangiovanni,* Linkoping University, Sweden

Nanolayered ceramic materials exhibit fascinating properties and can easily overshadow their individual layer components. An excellent example are the superhardening and supertoughening effects experimentally shown for series of nitride superlattices, such as cubic-based TiN/VN, TiN/WN, or TiN/CrN films. Advancing applicability of nanolayered ceramics in extreme conditions—including high mechanical loads—calls for atomic-level understanding of their response to stress. In this talk, we employ multi-method/multi-(length)scale approach that combines density-functional ab initio molecular dynamics, classical molecular dynamics, and experiments to identify elementary mechanisms responsible for tensile strength, plastic deformation, and fracture in transition metal nitride superlattices. The AlN/TiN system—a paradigm protective coating for industrial machining and engine components—represents our model platform. The predicted bilayer-period-dependent trends closely relate to different strain-mediated phase transformations initiating in AlN layers. In particular, the B1-to-B3 transformation is clearly confirmed also by transmission electron microscopy analyses of AlN/TiN superlattice films. The key message of our study is that a simultaneous increase in hardness and toughness can be achieved if the superlattice layer thickness is such that slip across the SL interfaces is impeded at initial stages of deformation, while lattice transformations within AlN layers are gradual and/or local, rather than full polymorph transitions. The AlN/TiN system is well-established and widely studied, however, other TiN-based superlattices, e.g. TaN/TiN, offer even better basis for plasticity enhancement: not only via phase transformations but also via vacancy and valence electron concentration engineering. Different deformation mechanisms arising in these superlattices will be discussed, especially in contrast to AlN/TiN.

11:00am **F5-1-MoM-4 In Silico Testing of AlN/TiN Superlattices Using Molecular Dynamics**, ***Lukas Löfler (loefler@mch.rwth-aachen.de)***, Montanuniversität Leoben, Austria*; N. Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; Z. Chen,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; G. Nayak,* Montanuniversität Leoben, Austria*; O. Renk,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; L. Hultman,* Linköping University, Sweden*; Z. Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; D. Sangiovanni,* Linköping University, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversität Leoben, Austria

The mechanical strength and fracture toughness of thin films can be tuned by microstructure. Superlattices, for example, have shown an increase in both hardness and fracture toughness at small layer thicknesses for a variety of materials. The introduced interfaces in these systems govern the mechanical response of the coating. However, their key role during mechanical loading is not yet understood. In this work, classical molecular dynamics simulations were performed to study the behavior of rocksalt cubic-structured AlN(001)/TiN(001) superlattices under mechanical loading in the form of uniaxial tension and indentation.

The tensile loading simulations aimed at revealing mechanisms behind plasticity and crack growth. Cells with layer thicknesses between 1.25 and 10 nm were put under tensile loading in different crystallographic directions. Depending on the load direction different mechanisms for plastic deformation are activated resulting in anisotropic behavior. Tensile loading perpendicular to the (001)-interface shows only minor plasticity accompanied by the nucleation of only a few dislocations and fracture parallel to the layers near the interface. Strain applied along the [100] and [110] directions on the other hand reveals a significant increase in toughness due to B1-to-B3 or B1-to-B4 phase transformations in AlN and later the development of shear bands. Under these load scenarios, networks of dislocations form that can, for small layer thicknesses, span over the interfaces. The findings were supported by ab initio molecular dynamics and nanoindentation and transmission electron microscopy experiments. From the joint results, we could conclude that the layer thickness of superlattices can impede the formation of cracks.

The indentation simulations focused on the intermixing of the alternating layers in superlattices under the load of the indenter. We were able to reveal that with ongoing deformation, a single phase starts to form near the indenter, degrading the coherent interface. The findings were supported by nanoindentation and high-resolution transmission electron microscopy experiments.

These cutting-edge simulations provided novel insights into the deformation mechanisms and processes of thin bi-layer superlattices at the atomistic level, hence complementing information available through high-end sophisticated experiments.

11:20am **F5-1-MoM-5 Advancing Computational Methods for Heterogeneous Material Systems**, ***Susan Sinnott (sinnott@matse.psu.edu)***, Penn State University, USA **INVITED**

Heterogeneous systems are challenging to investigate with high fidelity at the atomic scale across length scales that are not accessible by first-principles methods. This presentation describes recent developments of classical reactive potentials to enable the modeling of phenomena such as metal catalyst absorption to graphene and carbide-derived carbon supports, the interactions of metal catalysts with water, and the growth of thin films on oxide substrates. The classical simulations that are used to investigate these phenomena are complementary to first-principles,

quantum mechanical calculations and experimental measurements. The new insights gained from these investigations are key to enabling the design of new materials and their utilization in applications of technological importance.

12:00pm **F5-1-MoM-7 On the Interplay between Stacking and Stability of Transition-Metal Diborides*, David Holec (david.holec@unileoben.ac.at),*** *T. Leiner,* Montanuniversität Leoben, Austria*; N. Koutná, P. Mayrhofer,* TU Wien, Austria

Transition-metal diborides are a hard and brittle type of materials, which, among others, find their use as protective coatings, because of their excellent heat conductivity, oxidation stability and wear resistance.

In this work, we apply first-principles calculations to investigate the interplay between the structural properties (stacking of metal planes, puckering of the boron planes), mechanical properties (elasticity) and stability. For the latter, we assessed chemical, mechanical and vibrational stability. The investigated diborides XB_2 included *X*=Cr, Hf, Mn, Mo, Nb, Re, Ta, Ti, V, Zr. We probed (among others) also the three stackings corresponding to the stable structures of our XB_2, namely the A-A-A-A stacking of, e.g. TiB_2, the A-B-A-B stacking of ReB_2 and the A-B-B-A stacking of WB_2.

We could reveal chemical trends (i.e. related to the position of X element in the periodic table of elements) on the stability and transformation barriers between different stackings.

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