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Inherent toughness and fracture mechanisms of refractory transition-metal nitrides via density-functional molecular dynamics

D.G. Sangiovanni [a, b, *]

[a] Atomistic Modelling and Simulation, ICAMS, Ruhr-Universität Bochum, D-44801 Bochum, Germany
[b] Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-58183 Linköping, Sweden

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ABSTRACT

Hard refractory transition-metal nitrides possess unique combinations of outstanding mechanical and physical properties, but are typically brittle. Recent experimental results demonstrated that single-crystal NaCl-structure (B1) $V_{0.5}Mo_{0.5}N$ pseudobinary solid solutions are both hard (~20 GPa) and ductile; that is, they exhibit toughness, which is unusual for ceramics. However, key atomic-scale mechanisms underlying this inherent toughness are unknown. Here, I carry out density-functional *ab initio* molecular dynamics (AIMD) simulations at room temperature to identify atomistic processes and associated changes in the electronic structure which control strength, plasticity, and fracture in $V_{0.5}Mo_{0.5}N$, as well as reference B1 TiN, subject to <001> and <110> tensile deformation. AIMD simulations reveal that $V_{0.5}Mo_{0.5}N$ is considerably tougher than TiN owing to its ability to (*i*) isotropically redistribute mechanical stresses within the elastic regime, (*ii*) dissipate the accumulated strain energy by activating local structural transformations beyond the yield point. In direct contrast, TiN breaks in brittle manner when applied stresses reach its tensile strength. Charge transfer maps show that the adaptive mechanical response of $V_{0.5}Mo_{0.5}N$ originates from highly populated *d-d* metallic-states, which allow for counterbalancing the destabilization induced via tensile deformation by enabling formation of new chemical bonds. The high ionic character and electron-localization in TiN precludes the possibility of modifying bonding geometries to accommodate the accumulated stresses, thus suddenly causing material's fracture for relatively low strain values.

1. Introduction

Refractory transition-metal (TM) nitrides, a class of technologically important materials characterized by unique combinations of properties [1–5], are widely employed as protective coatings for industrial machining [6,7], diffusion-barrier layers in electronic devices [8–12], and biocompatible coatings [13–15]. More recently, it has also been shown that these materials are promising candidates for applications in catalysis [16], energy storage and conversion [17,18], and plasmonics [19]. As most ceramics, however, TM nitrides are generally brittle: thermally- or mechanically-induced stresses rapidly lead to fracture, thus limiting their potential use. Toughness in TM nitrides is typically enhanced in extrinsic manner, e.g., by nanoengineering superlattice or nanocomposite structures, which block or deflect propagating cracks at grain boundaries or interfaces to prevent brittle failure [20–22]. Recent experiments [23,24], motivated by *ab initio* theoretical predictions [25], demonstrated that single-crystal NaCl-structure (B1) $V_{0.5}Mo_{0.5}N$ solid solutions (denoted below as VMoN) are inherently *both* hard and ductile (i.e. tough). This surprising finding addressed a long-standing question in materials science on whether high hardness/strength and good ductility/plasticity are necessarily mutually exclusive properties in a single-crystal ceramic phase.

Density-functional theory (DFT) investigations have indicated that the intrinsic ductility of VMoN, as well as of nearly isoelectronic TM nitride solid solutions, is primarily an effect of optimized occupation of bonding metallic *d-d* states near the Fermi energy, which renders the material more compliant to shearing [25–27]. Recently, it has also been suggested that metastable B1 TM nitride alloys formed upon mixing cubic and hexagonal binary phases possess enhanced ductility due to energetically-favored formation of stacking faults that allows for dissipating accumulated stresses during $\{111\}\langle 1\bar{1}0\rangle$ slip [28]. However, previous theoretical

* Atomistic Modelling and Simulation, ICAMS, Ruhr-Universität Bochum, D-44801 Bochum, Germany.
E-mail addresses: davide.sangiovanni@ruhr-uni-bochum.de, davsan@ifm.liu.se.

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investigations were carried out at 0 K. The explicit inclusion of temperature in *ab initio* modeling is necessary to reveal atomistic processes with associated changes in electronic structures that govern the ductile vs. brittle mechanical behavior of single-crystal TM nitrides.

In this work, I carry out density-functional *ab initio* molecular dynamics (AIMD) simulations to clarify the synergistic effects of lattice vibrations and electronic structures on the onset of plastic deformation, as well as of crack formation in bulk $V_{0.5}Mo_{0.5}N$ and TiN (here considered as reference hard but brittle nitride system [23]) subject to tensile strain. I identify atomistic pathways leading to materials' structural transformation and fracture, thus providing novel insights into the modalities by which mechanical yielding, plastic deformation, and bond rupture take place in intrinsically brittle (TiN) vs. inherently ductile (VMoN) transition metal nitride ceramics.

2. Computational details and methods

Density-functional *ab initio* molecular dynamics (AIMD) [29] simulations are carried out using the VASP code [30] implemented with the projector augmented wave method [31]. The electronic exchange and correlation effects are treated with the Armiento-Mattsson approximation [32]. The Newton's equations of motion are integrated at 1-fs timesteps by sampling the *NVT* canonical phase space. At each time-step, the total energy is evaluated to an accuracy of 10^{-5} eV/atom, employing Γ-point sampling of the Brillouin-zone and a plane-wave cutoff energy of 300 eV.

AIMD tensile-deformation testing is performed by sequentially elongating [001]- and [110]-oriented defect-free cubic-B1 TiN and $V_{0.5}Mo_{0.5}N$ supercell boxes [denoted below as TMN(001) and TMN(110)] along their vertical axis (z) at strain steps of 1.5%, while maintaining unvaried lateral supercell sizes. All simulation supercells are formed of 24 atomic layers for a total of 192 nitrogen and 192 metal atoms, applying periodic boundary conditions in x, y, and z directions. The relationship between simulation-box vs. crystallographic in-plane directions are $x = [\bar{1}10]$ and $y = [110]$ for structures of vertical [001]-orientation, whereas $x = [1\bar{1}0]$ and $y = [001]$ for [110]-oriented supercells. Short- and long-range CuPt-like 111 cation ordering has been observed in B1 $V_{0.5}W_{0.5}N$ [33] and rhombohedral (111-distortion of the B1 structure) $Ti_{0.5}W_{0.5}N$ [34] solid solutions. On the contrary, lattice ordering has not been reported for B1 $V_{0.5}Mo_{0.5}N$ samples [23,24,35,36]. Thus, the special quasirandom structure approach [37] is used to minimize the degree of short-range ordering on the $V_{0.5}Mo_{0.5}N$ cation sublattice. At each strain step, the supercells are first (*i*) rapidly equilibrated at 300 K via an isokinetic thermostat (velocity rescaling for 300 time steps) to compensate for sudden volume changes, then (*ii*) maintained at room temperature for additional 2.7 ps using the Nosé-Hoover thermostat. The model systems are elongated up to materials' fracture. Fracture, identified in AIMD runs as abrupt variations in atomic velocities and stresses, is characterized by a rapid sequence of bond snapping. AIMD videos are created with the software Visual Molecular Dynamics [38] and can be found in the supplemental material [39]. The normal and shear stresses induced in the materials by tensile deformation are directly extracted from VASP output. Integration of the area underlying vertical-stress (σ_z) vs. strain curves allows evaluating the ideal tensile toughness of defect-free B1 TiN and B1 $V_{0.5}Mo_{0.5}N$ ceramics.

The use of defect-free bulk structures provides qualitative comparisons between the ideal resistances to fracture in different TM nitrides; a fundamental step for subsequent investigations of the mechanical behavior in defective lattices. Below, the following notations are used: tensile toughness = U_T, moduli of resilience = U_r, strain along [h k l] crystallographic direction = $\delta^{[h\ k\ l]}$, elongation at fracture points = δ_f, yield strengths = γ, and stress components: lateral (σ_x and σ_y), vertical (σ_z), and shearing (σ_{xy}, σ_{yz}, and σ_{xz}) stresses. All stresses are given in absolute values. Bond-angle analyses, based on the approach described in Ref. [40], are used to identify the changes in local atomic coordination induced by tensile strain. The percentage of fcc, bcc, and hcp local atomic environments are calculated at each timestep by using the software Ovito [41]. The percentages are separately determined for the anion and cation sublattices, and then averaged. The bond-angle analysis is performed on fractional atomic coordinates in order to eliminate the effects of uniaxial supercell stretching on local lattice symmetries.

Electron transfer maps, determined via DFT for lattice configurations extracted directly from AIMD trajectories, are obtained by subtracting the superposition of non-interacting atomic electron densities from self-consistent charge densities. For these calculations, the Brillouin zone is integrated on $3 \times 3 \times 3$ k-point grids while the cutoff energy is set to 400 eV.

3. Results and discussion

Ductility, materials' ability to deform plastically, can be assessed as the elongation at the fracture point (δ_f) during tensile deformation. Good ductility combined with high mechanical strength (γ) equates to high toughness, a measure of the energy (per unit volume) required to deform a material up to rupture.

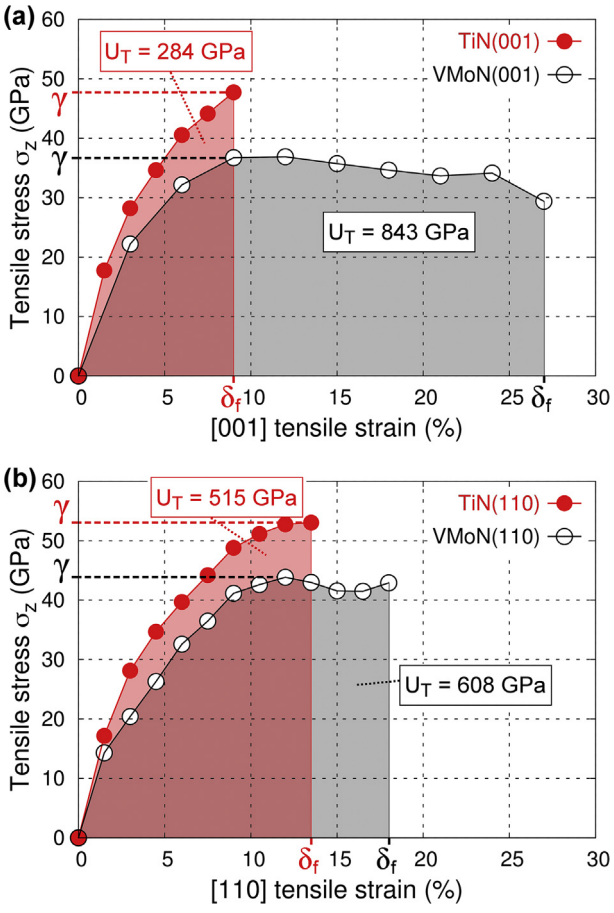

Fig. 1. Tensile stresses as a function of tensile strain obtained for (a) [001]-oriented and (b) [110]-oriented TiN and VMoN supercells during AIMD simulations at 300 K. U_T, γ, and δ_f indicate tensile toughness, yield strengths, and maximum elongations, respectively. Stresses are given in absolute values.