Full length article

Effects of phase stability, lattice ordering, and electron density on plastic deformation in cubic TiWN pseudobinary transition-metal nitride alloys

D.G. Sangiovanni [a, *], L. Hultman [a], V. Chirita [a], I. Petrov [a, b], J.E. Greene [a, b]

[a] Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-58183 Linköping, Sweden
[b] Department of Materials Science and the Materials Research Laboratory, University of Illinois, 104 South Goodwin, Urbana, IL 61801, USA

ABSTRACT

We carry out density functional theory calculations to compare the energetics of layer glide, as well as stress vs. strain curves, for cubic $Ti_{0.5}W_{0.5}N$ pseudobinary alloys and reference B1-structure TiN. Irrespective of the degree of ordering on the metal sublattice, the hardness and stiffness of $Ti_{0.5}W_{0.5}N$, as estimated by stress–strain results and resistance to layer glide, are comparable to that of the parent binary TiN, while ductility is considerably enhanced. After an initial elastic response to an applied load, the pseudobinary alloy deforms plastically, thus releasing accumulated mechanical stress. In contrast, stress continues to increase linearly with strain in TiN. Layer glide in $Ti_{0.5}W_{0.5}N$ is promoted by a high valence-electron concentration which enables the formation of strong metallic bonds within the slip direction upon deformation. [111]-oriented $Ti_{0.5}W_{0.5}N$ layers characterized by high local metal-sublattice ordering exhibit low resistance to slip along <110> directions due to energetically favored formation of (111) hexagonal stacking faults. This is consistent with the positive formation energy of <111>-ordered $Ti_{0.5}W_{0.5}N$ with respect to mixing of cubic-B1 TiN and hexagonal WC-structure WN. In the cubic pseudobinary alloy, slip occurs parallel, as well as orthogonal, to the resolved applied stress at the interface between layers with the lowest friction. We suggest that analogous structural metastability (mixing cubic and hexagonal TM nitride binary phases) and electronic (high valence electron concentration) effects are responsible for the enhanced toughness recently demonstrated experimentally for cubic single-crystal pseudobinary $V_{0.5}W_{0.5}N$ and $V_{0.5}Mo_{0.5}N$ epitaxial layers.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Transition-metal (TM) nitride coatings [1–4] are presently used in a wide variety of applications due to their unique properties including high hardness [5–7], excellent scratch and abrasion resistance [8,9], low coefficient of friction [9–11], high-temperature oxidation resistance [12–14], electrical conductivity ranging from metallic to semiconducting [15–18], optical adsorption which can be tuned across the visible spectrum [19–21], and superconductivity [15,22,23]. Unfortunately, these materials are typically characterized by extreme brittleness which reduces their potential utility.

In previous density functional theory (DFT) investigations, we have shown that alloying TiN or VN with WN or MoN significantly improves ductility while maintaining high hardness, equating to enhanced toughness [24,25]. This is due to a selective mechanical response to applied stresses, i.e., the pseudobinary alloys respond in a hard manner to tensile/compressive stresses, while being more compliant to shearing than their parent binary compounds TiN and VN [24,25].

The empirical elastic-constant-based classifications of Pugh [26] and Pettifor [27] (the metallic-bonding character in cubic crystals increases with the ratio of the bulk to shear moduli B/G [26] and with the Cauchy pressure $(C_{12} - C_{44})$ [27]) indicate that, irrespective of the degree of ordering on the cation sublattice [28], ductility in cubic B1-structure TM nitride pseudobinary alloys increases with valence electron concentration (VEC) [25,29–31] up to maximum VEC of $\simeq$ 10.5. See, for example, the table in Ref. [32] showing an initial increase, followed by saturation, of B/G and $(C_{12} - C_{44})$ values for cubic single-crystal $V_{1-x}W_xN(001)$ epitaxial

layers as a function of WN content x from 0 to 0.6. DFT bonding analysis results are consistent with Pugh and Pettifor empirical criteria. Charge transfer maps and crystal orbital overlap population (COOP) [33] calculations consistently show that VEC $\simeq$ 10.5 results in fully-occupied metallic σ-bonding d-t_{2g} states located at the Fermi level. This, in turn, lowers the resistance to shear and favors dislocation glide [24,25,28,29].

The theoretical predictions described above have recently been experimentally validated by comparing the mechanical response of single-crystal NaCl-structure $V_{0.5}Mo_{0.5}N$ and $V_{0.5}W_{0.5}N$ alloys with those of single-crystal TiN and VN reference samples [32,34,35]. Berkovich nano-indentation was used to determine hardness and elastic-moduli, while massive deformation via sharp cube-corner indentation through the film and into the substrate was used to assess resistance to brittle crack formation. In all fracture-toughness tests, which were performed at constant penetration depths exceeding the film thickness, VN and TiN films systematically crack along <110> directions. In contrast, $V_{0.5}Mo_{0.5}N$ samples never exhibit crack formation [34]. Instead, material pile-up is observed in regions adjacent to indented areas. The latter demonstrates the ability of these pseudobinary systems to release internal stress by plastic flow [34,35]. Strong metal(d-e_g)–N(p) nearest-neighbor bonds provide cubic TiWN, TiMoN, VMoN, and VWN alloys with hardnesses [32,34–38] comparable to, or higher than, that of B1-structure TiN (~22 GPa) [34]. The hardness of $V_{0.5}Mo_{0.5}N_x$ was shown to be further increased, while maintaining ductility (i.e. toughness) significantly higher than that of TiN and VN, by reducing the N/(V + Mo) fraction x from 1 to ~0.6 across the single-phase region [35]. Indications of enhanced toughness have also been reported for polycrystalline cubic TM nitride alloys TaWN and MoWN [39,40], and for two-phase ZrTaN and TiTaN coatings containing both cubic- and hexagonal-structure grains [3,41].

Our original investigations into the electronic origins of ductility and toughness in single-crystal TM nitride pseudobinary alloys [24,25,29] were based on analyses of the electronic structures of unstrained and uniformly-strained lattices. The development of a deeper atomic-level understanding of plastic-deformation mechanisms in single-crystal and polycrystalline TM nitride ceramics requires additional investigation of dynamic phenomena including dislocation glide, grain sliding, and grain rotation under stress.

In experiments guided by DFT results, Hugosson et al. employed VEC tuning of pseudobinary TM carbides [42] and nitrides [43] to set the cubic-B1 and hexagonal structures to equal energies, thus promoting the formation of stacking faults, during crystal growth, which increased hardness by hindering dislocation slip across the faults. At room temperature, TiN and VN crystallize in the cubic-B1 structure, while stoichiometric WN and MoN are hexagonal. The positive formation energies of cubic $Ti_{0.5}W_{0.5}N$, $Ti_{0.5}Mo_{0.5}N$, $V_{0.5}W_{0.5}N$, and $V_{0.5}Mo_{0.5}N$ (higher for ordered atomic arrangements), calculated by mixing B1-Ti(V)N and h-W(Mo)N binary phases [24,28], indicate that the presence of (111) hexagonal stacking faults should be thermodynamically favored for these metastable pseudobinary alloys. This is supported by the experimental observation of stacking faults along (111) W-rich planes in $V_{0.6}W_{0.4}N$ thin films exhibiting local metal-sublattice ordering [44]. In the present work, we carry out DFT calculations to show that the energetically-favored formation of hexagonal (111) stacking faults in cubic pseudobinary TM nitrides with VEC $\gtrsim$ 10 is beneficial not only for hardness, as demonstrated by Hugosson and coworkers [42,43] and later by Kindlund et al. [32,44], but also for ductility. The latter is due to strain-induced faulting along the slip-direction.

Cubic VWN and VMoN crystals are natural choices as model-systems, due to their excellent mechanical properties [32,34,35], to investigate the mechanisms controlling plastic deformation in hard, tough TM nitrides. However, stoichiometric defect-free B1 VN

exhibits imaginary phonon frequencies at the Brillouin-zone X point at 0 K [45]. The room-temperature stability of VN in the NaCl-structure [46] is due to a significant vibrational entropy contribution to the Gibbs free-energy of formation [47]. Because of this, reliable estimates of dislocation-glide energetics in cubic VN and VN-based materials would require the inclusion of thermal effects [48], which is beyond the scope of this work. Nevertheless, TiN is dynamically stable in the NaCl-phase, even at 0 K [49]. This motivates the use of TiN and TiN-based alloys for the present investigations. Here, cubic $Ti_{0.5}W_{0.5}N$ is chosen as a model-system [48] to gain insight into the mechanisms underlying the ductile behavior of metastable cubic TM nitride solid solutions formed upon mixing cubic and hexagonal binary TM nitride phases. Cubic single-crystal stoichiometric $Ti_{0.5}W_{0.5}N$ thin films, exhibiting ordering on the metal sublattice, have been grown on MgO(001) substrates [50]. Here, we probe the energetics of the primary active slip systems in cubic TM nitrides at room temperature [51,52], $\{110\}\langle1\bar{1}0\rangle$ and $\{111\}\langle1\bar{1}0\rangle$, for ordered and disordered TiWN using stoichiometric B1 NaCl-structure TiN as a reference.

2. Methodology

DFT calculations are carried out using the Vienna *ab-initio* simulation package (VASP) [53] implemented with the generalized gradient approximation (GGA) [54]. The electron−ion interaction is described by the projector augmented wave method [55]. Structural optimizations are achieved, upon minimizing the total energy to within 10^{-5} eV/atom, using planewave basis-set energy cutoffs of 500 eV and integrating the Brillouin zone on $6 \times 6 \times 6$ **k**-point grids. The equilibrium structures, starting points for both crystal-glide and stress−strain calculations, are determined by relaxing the atomic positions, cell shape, and volume. The visual molecular dynamics (VMD) code [56] is used to generate crystal structure images. Charge transfer maps are obtained by subtracting atomic electron densities from the self-consistent electron density.

In the present work, we probe the mobility of $\{110\}\langle1\bar{1}0\rangle$ and $\{111\}\langle1\bar{1}0\rangle$ slip systems in $Ti_{0.5}W_{0.5}N$ alloys with various degrees of lattice ordering and, as a reference, in binary TiN. This is accomplished using two different approaches to progressively deform [110] and [111]-oriented crystals along the $[1\bar{1}0]$ direction.

(i) Induced slip (as proposed by Frenkel [57]). *Rigid* crystal blocks are allowed to glide against each other, along the interface between two layers, to quantify lattice friction energetics.

(ii) Stress/strain calculations. Uniform shear of all lattice layers is used to probe the degrees of crystal elasticity and plasticity.

The mechanical properties of disordered and ordered lattices are investigated separately. Alloy configurations with negligible short-range order (referred to as *disordered*) are generated using a modified version of the special quasirandom structure (SQS) method [58] (Fig. 1(a) and (d)). As detailed in our previous study [34], this mimics lattice disorder in single-crystal thin films grown in a layer-by-layer manner. Perfectly-ordered [111] and [110] oriented $T_{0.5}W_{0.5}N$ (referred to as *ordered*) possess alternating Ti/W metal-sublattice (111) and (110) layers orthogonal to the glide direction $[1\bar{1}0]$ (Fig. 1(b) and (e)). Metal-sublattice ordering along (111) planes has been observed experimentally in single-crystal $Ti_{0.5}W_{0.5}N$ [50] and $V_{0.5}W_{0.5}N$ [44] thin films.

Rigid-slip (Frenkel's model [57]) in ordered $Ti_{0.5}W_{0.5}N$ alloys is induced on both the Ti/N and W/N glide-plane interfaces. For stress/strain calculations, we probe, in addition to ordered and disordered pseudobinary $Ti_{0.5}W_{0.5}N$ structures, the mechanical response to <110> shearing of [110] and [111]-oriented cubic TiN/