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Computational and experimental studies on structure and mechanical properties of Mo–Al–N

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ABSTRACT

Ab initio calculations show that with increasing N-vacancy content of $Mo_{1-x}Al_xN_y$ solid solutions, the cubic structure is increasingly preferred over the wurtzite-type hexagonal structure. While $Mo_{1-x}Al_xN$ solid solutions, without N-vacancies, energetically favor the wurtzite-type structure over the whole composition range, $Mo_{1-x}Al_xN_{0.5(1+x)}$ and $Mo_{1-x}Al_xN_{0.5}$ solid solutions energetically prefer the cubic structure up to ~45 and 65 at.% Al at the metal sublattice.

Detailed *ab initio* calculations in combination with detailed elemental and phase composition analyses and nanoindentation experiments of reactively sputtered $Mo_{1-x}Al_xN_y$ coatings prove the formation of face-centered cubic structures for Al-contents $x \leq 0.57$. These $Mo_{1-x}Al_xN_y$ coatings exhibit an Al-dependent population of the nitrogen sublattice, following the $MoN_{0.5}$–AlN quasi-binary tie line. For Al-contents $x \geq 0.79$ the coatings crystallize in the wurtzite-type hexagonal phase, while in the intermediate composition range both phases, cubic and wurtzite-type hexagonal, coexist. As long as the cubic structure is maintained, the hardness increases from ~33.0 to 38.4 GPa with increasing Al-content, but drops to ~22 GPa for $x \geq 0.67$, when the films contain hexagonal wurtzite-type phases.

1. Introduction

Face-centered cubic-structured γ-Mo_2N (B1, NaCl-type with half-populated N-sublattice, hence, actually $MoN_{0.5}$ [1]) exhibits excellent mechanical and tribological properties [2] and is therefore an ideal candidate for wear-resistant coatings. The major limitation of Mo–N coatings is their low resistance against oxidation, resulting in the formation of molybdenum oxides having a high vapour pressure [3]. To overcome these limitations, we have developed Mo–Al–N coatings, since Al typically increases the oxidation resistance of transition metal (TM) nitrides by forming dense oxides. Moreover, an increasing Al-content is known to improve the tribological and mechanical properties of TM nitrides by solid solution strengthening and age hardening [4–9]. Although the binary phases γ-Mo_2N and hexagonal-structured (ZnS wurtzite-type) w-AlN are not miscible in thermodynamic equilibrium, $Mo_{1-x}Al_xN$ solid solutions can be prepared by physical vapour deposition. Since the face-centered cubic-structured (c-) modification of AlN is a highly unstable high-pressure allotrope of the thermodynamically stable w-AlN structure [10], we expect the Al-content to play a crucial role in the formation of cubic-structured c-$Mo_{1-x}Al_xN_y$ and wurtzite-type w-$Mo_{1-x}Al_xN_y$ phases, similar to the cases of $Ti_{1-x}Al_xN$ [11–13] and $Cr_{1-x}Al_xN$ [13–15].

There is only a limited number of studies on coatings within the Mo–Al–N system and the reported maximum Al-content, $x = Al/(Mo + Al)$, achieved within single-phased c-$Mo_{1-x}Al_xN_y$ coatings is x ~0.3 [16–18]. Two recent publications even present deteriorating mechanical properties with increasing Al-content [17,18]. This rather unusual behavior and the limited information about sputtered Mo–Al–N coatings available, motivated us for a detailed study of this material system.

By combining *ab initio* and experimental studies of $Mo_{1-x}Al_xN_y$ we show that the metal sublattice population as well as the nitrogen sublattice population is crucial for the formation of face-centered cubic-structured solid solutions. Our experimental investigations clearly evidence that sputter-deposited $Mo_{1-x}Al_xN_y$ coatings with a face-centered cubic structure and chemical compositions close to the $MoN_{0.5}$–AlN quasi-binary tie line exhibit strongly improved mechanical properties with increasing aluminum content.

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2. Computational and experimental details

The respective energetic stability of face-centered cubic (c-) and hexagonal wurtzite-type (w-) solid solutions along the three quasi-binary tie lines, MoN–AlN, $MoN_{0.5}$–AlN, and $MoN_{0.5}$–$AlN_{0.5}$, was calculated using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) [19,20].

The energy of formation, E_f, was determined with respect to the elemental constituents, fcc-Al, bcc-Mo and molecular nitrogen, applying the following Eq. (1) [21]:

$$E_f = \frac{1}{\sum_i n_i}\left(E_{tot} - \sum_i n_i E_i\right) \quad (1)$$

Here E_{tot} and E_i are the total energy of the compound and its elemental constituents, respectively, as determined from DFT, while n_i denotes the number of atoms of species i. For a stability comparison between different structure types the configurational entropy can be neglected, since at a given concentration the configurational entropy is the same and independent of the structure type. Supercells with different chemical compositions were constructed using the special quasi-random structure (SQS) approach [22]. The high cooling rates in PVD and the fact that no heat treatment was applied, in combination with the absence of super-structure reflections in our XRD data, make ordering rather unlikely. Therefore, ordering tendencies were not investigated in our simulations. Wurtzite-type phases were studied with $2 \times 2 \times 4$ supercells using a $6 \times 6 \times 4$ kpoint mesh. The cubic phases were investigated with a $2 \times 2 \times 1$ supercell (along the MoN–AlN and $MoN_{0.5}$–AlN tie lines) and $2 \times 2 \times 2$ supercells (along the $MoN_{0.5}$–$AlN_{0.5}$ tie line) using $4 \times 4 \times 8$ and $4 \times 4 \times 4$ kpoint meshes, respectively. All computations were performed with the projector augmented wave method and the generalized gradient approximation (PAW-GGA) using an energy cutoff of 700 eV. Together with the chosen kpoint mesh, these settings guaranteed for an accuracy of a few meV/atom.

A modified Leybold Heraeus magnetron sputtering system Z400 was used to deposit Mo–Al–N thin films in Ar and N_2 atmosphere (purity above 99.999% for both gases). Mo-rich Mo–Al–N thin films were synthesised from a molybdenum target (99.97% purity, Ø75 mm) by covering the race track with different numbers of small Al-cubes (99.85% purity, $3 \times 3 \times 3$ mm^3). Al-rich Mo–Al–N coatings were prepared from an aluminum target (99.5% purity, Ø75 mm), where small Mo-cubes (99.99% purity, $3 \times 3 \times 3$ mm^3) uniformly covered the race track. Primarily to the deposition processes, the chamber was evacuated to a high vacuum of $p_{base} \leq 5 \cdot 10^{-4}$ Pa. The sputter depositions were performed with a constant total pressure, p_T, of 0.35 Pa and a N_2-to-total pressure ratio of $p_{N2}/p_T = 0.32$, based on our previous study [1]. All depositions were carried out with a target current of 0.4 A DC while keeping the substrates at floating potential (~-15 V) and at 450 ± 20 °C.

The crystal structures of the as-deposited thin films were analyzed by X-ray diffraction (XRD), using a Philips X'Pert diffractometer with monochromatic Cu $K\alpha$ radiation in Bragg Brentano geometry. The stress-free lattice parameters were obtained with the "$\sin^2\psi$" method [23] using a PANalytical Empyrion diffractometer in glancing angle mode with an angle of incidence $\gamma = 2°$.

The film growth morphology was investigated by scanning electron microscopy (SEM) of fracture cross-sections. Energy dispersive X-ray spectroscopy (EDS) allowed for a chemical characterization of the thin films. The EDS measurements were calibrated with Mo–N thin film standards that have been characterized by elastic recoil detection analyses [1]. Mechanical properties, such as indentation modulus and hardness were determined by nano-indentation using an ultra micro indentation system (UMIS) equipped with a Berkovich type indenter. The obtained load–displacement curves were evaluated after Oliver and Pharr [24] as described in detail in Refs. [1] and [25].

3. Results

Fig. 1a, b, and c present the energy of formation, E_f, of $Mo_{1-x}Al_xN_y$ with face-centered cubic (red squares) and wurtzite-type (green hexagons) crystal structures along the three quasi-binary tie lines, MoN–AlN, $MoN_{0.5}$–AlN, and $MoN_{0.5}$–$AlN_{0.5}$, respectively. Solid solutions along the MoN–AlN quasi-binary tie line, hence, with fully occupied N-sublattices, energetically prefer the wurtzite-type structure, w-$Mo_{1-x}Al_xN$, over the whole composition range, see Fig. 1a. Solid solutions along the $MoN_{0.5}$–AlN tie line exhibit a crossover between cubic- and wurtzite-type $Mo_{1-x}Al_xN_{0.5(1+x)}$ at Al-contents of x ~0.45 (see Fig. 1b), where lower Al-contents favor the cubic structure. Compositions along the $MoN_{0.5}$–$AlN_{0.5}$ tie line, hence, with half-occupied N-sublattices over the whole composition range, provide a crossover between cubic-structured and wurtzite-type $Mo_{1-x}Al_xN_{0.5}$ at x ~0.65.

The energies of formation for the cubic and wurtzite-type solid solutions $Mo_{1-x}Al_xN$, $Mo_{1-x}Al_xN_{0.5(1+x)}$, and $Mo_{1-x}Al_xN_{0.5}$, are very similar over a wide concentration range. These x-regions (with ≤50 meV/at differences between the polynomial fits to the cubic and wurtzite-type data points) are 0.3–0.75 for $Mo_{1-x}Al_xN$, 0.3–0.6 for $Mo_{1-x}Al_xN_{0.5(1+x)}$, and 0.55–0.8 for $Mo_{1-x}Al_xN_{0.5}$, see the vertical dashed lines within Fig. 1a, b, and c, respectively, Consequently, within these Al-contents, the preference for cubic or wurtzite-type phases is very sensitive to small changes in structure and atomic arrangements.

Our *ab initio* data clearly suggest increasing Al-solubility of the cubic phase with increasing N-vacancy content, Fig. 1a, b, and c, respectively. Therefore, we have selected the relatively low N_2-to-total pressure ratio of 0.32 during sputtering of our $Mo_{1-x}Al_xN_y$ coatings, which guaranties the formation of single-phase cubic-structured $MoN_{0.5}$ [1]. For lower nitrogen partial pressures, the Mo–N coatings also contain metallic Mo-based phases and for higher nitrogen partial pressures, the N-vacancy concentration decreases.

The nitrogen content of our sputtered $Mo_{1-x}Al_xN_y$ coatings increases nearly linearly from 35 to 49 at% with increasing Al-content x from 0 to 0.79, following the $MoN_{0.5}$–AlN quasi-binary tie line, see Fig. 2. Thus, the relationship between y and x can be described with $y = 0.5(1 + x)$ and $Mo_{1-x}Al_xN_{0.5(1+x)}$ solid solutions are formed, corresponding to the results obtained for $Mo_{1-x}Cr_xN_{0.5(1+x)}$ [1]. This chemical variation suggests that the theoretical vacancy content of the nitrogen sublattice continuously decreases from 50% ($MoN_{0.5}$) to 0% (AlN) when Al substitutes for Mo.

XRD analyses prove that our $Mo_{1-x}Al_xN_y$ coatings crystallize in a face-centered cubic structure with preferred (200)-orientation for Al/(Mo + Al)-ratios up to ~0.57, see Fig. 3a. Higher aluminum contents energetically prefer the formation of wurtzite-type $Mo_{1-x}Al_xN_y$ solid solutions. Both phases, cubic and wurtzite-type $Mo_{1-x}Al_xN_y$ coexist with x between 0.67 and 0.79, and the coating is predominantly wurtzite-type structured (with traces of the cubic phase) for $x = 1$. Fig. 3b is the corresponding color-coded XRD intensity map, based on our 13 different $Mo_{1-x}Al_xN_y$ coatings. This graphical representation is obtained by using a linear interpolation scheme between the experimentally obtained XRD patterns.

The stress-free lattice parameters of the experimentally obtained single-phased cubic-structured $Mo_{1-x}Al_xN_y$ coatings only slightly decrease from 4.18 ± 0.02 to 4.16 ± 0.02 Å with increasing Al-content x from 0 to 0.57, see Fig. 4. The comparison with the *ab initio* obtained averaged lattice parameters of face-centered cubic solid solutions along the three quasi-binary tie lines, MoN–AlN (1),