

Regular article

Ab initio-guided development of super-hard Mo–Al–Cr–N coatings



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ABSTRACT

The ab initio-guided adjustment in N_2 -partial pressure during reactive magnetron sputtering allowed the preparation of single-phase cubic-structured $Mo_{1-x-y}Al_xCr_yN_z$ coatings with Al-contents up to even $x \approx 0.6$. Combining with low Cr-concentrations, Al-enrichment significantly enhances material strength. The highest hardness, H , of 41.2 ± 2.9 GPa in combination with a low indentation modulus, E , of 440 ± 15 GPa is obtained for $Mo_{0.39}Al_{0.52}Cr_{0.09}N_{0.98}$, possessing also the highest H/E - and H^3/E^2 -ratios of 0.1 and 0.36 GPa, respectively. Further Al-enrichment ($x > 0.6$) favours, however, the hexagonal phase formation, drastically decreasing the hardness to ~ 20 GPa. Therefore, the combination of excellent mechanical properties with a high Al-content suggests fcc- $Mo_{1-x-y}Al_xCr_yN_z$ for severe applications.

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The application area of hard cubic molybdenum nitride, γ - $MoN_{0.50}$, showing also excellent tribological properties due to the formation of possible Magnéli phases, is basically restricted to the temperatures below $500^\circ C$ [1]. At elevated temperatures, the relatively weak bonds between molybdenum and nitrogen – resulting from the filling of anti-bonding electron states [2] – easily break, leading to the loss of nitrogen and pronounced oxidation, where the volatile MoO_3 forms. Improved thermal stability and oxidation resistance are very often obtained by alloying with aluminium and/or chromium. These easily form very dense protective oxide scales, Al_2O_3 , Cr_2O_3 , or even mixtures thereof, $(Al,Cr)_2O_3$. Synthesis of single-phased quaternary materials also increases the mixing entropy, leading to high thermal stability as reported for high entropy alloys [3,4].

Based on our previous studies on the binary Mo–N system [5] and its ternaries Mo–Al–N [6] and Mo–Cr–N [7], we developed quaternary Mo–Al–Cr–N coatings with the highest Al-content dissolved in the cubic-structured Mo–N-based phase. The key parameter for this development is the knowledge-driven incorporation of N-vacancies at the N-sublattice of the NaCl-based cubic structure. Thereby, even super-hard coatings could be developed.

The quaternary Mo–Al–Cr–N thin films were synthesised using a modified (3") magnetron sputtering system, Leybold Heraeus Z400, in mixed Ar and N_2 glow discharges (both gases with purity above 99.999%). Three different powder metallurgically prepared targets (99.95% purity, $\varnothing 75$ mm, PLANSEE SE) were used: the two most common Cr/Al-compositions with 40/60 at.-%-ratio ($Cr_{0.40}Al_{0.60}$) and 30/70 at.-%-ratio ($Cr_{0.30}Al_{0.70}$), and a target with Mo/Al of 40/60 at.-%-ratio ($Mo_{0.45}Al_{0.55}$), which was especially developed by PLANSEE SE based

on our recent findings [6]. In order to synthesise quaternary nitrides, additional small cubes (4, 8, 12, 16, 20, or 36 pieces with a size of $3 \times 3 \times 3$ mm³) of the alloying elements (either Mo, Cr, or $Cr_{0.40}Al_{0.60}$ or $Cr_{0.15}Al_{0.85}$ compounds, all with 99.95% purity) were uniformly arranged on the racetrack of the corresponding targets, without coupling them together (the effective contact area was due to, e.g., the surface roughness and racetrack curvature < 9 mm²). All depositions were prepared using the constant target current (DC, 0.4 A), floating potential at the substrates (~ -15 V), and substrate temperature ($450 \pm 20^\circ C$). Prior to every deposition process, the chamber was evacuated to a high vacuum of $p_{base} \leq 5 \cdot 10^{-4}$ Pa. During all sputter deposition processes the total pressure, p_T , of 0.35 Pa and N_2 -to-total-pressure ratio, p_{N2}/p_T , of 0.32 were kept constant. Single-crystal silicon and austenite steel substrates were ultrasonically pre-cleaned in acetone and alcohol (for 5 min) and r.f. plasma etched (within the deposition chamber) using an Ar pressure of 2 Pa and a substrate potential of 350 V. After each deposition process, the substrates were cooled down to at least 90 – $100^\circ C$ before venting the deposition chamber, in order to minimise the surface chemistry alterations [8].

Phase analysis was carried out by means of X-ray diffraction (XRD) in Bragg-Brentano geometry using monochromised CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The chemical compositions of our coatings were evaluated based on energy dispersive X-ray spectroscopy (EDS) and Mo–N thin film standards that have been characterised with elastic recoil detection analyses [7,9]. Indentation hardness, H , and modulus, E , of our thin films were obtained by evaluating the load–displacement curves of nanoindentation tests (Berkovich diamond tip and a load range of 3 to 35 mN) after Oliver and Pharr [10], described in detail in Refs [7,11]. The instrument was calibrated using fused silica with an elastic modulus of 72.5 GPa [12]. To verify the accuracy of the measurements and indentation equipment, a few reference samples (listed in Table 1) were tested.

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Table 1Comparison of the measured indentation hardness, H , and modulus, E , with some references.

	Sapphire			Si-wafer			MgO		Fused silica	
	Exp.	Ref. [10]	Exp.	Ref. [12]	Exp.	Ref. [13,14]	Exp.	Ref. [10,12]		
H , GPa	(11–20) 30.7 ± 0.4	(1–102) 30.6 ± 0.6	$\sim 30^*$	13.2 ± 0.1	10–12	11.0 ± 0.2	~ 4 –10	10.5 ± 0.1	8–10	
E , GPa	483 ± 6	458 ± 5	404–499	185.0 ± 2.0	172	332 ± 14	248–349	72.5 ± 1.0	72.5	

According to the elemental composition analyses, our coatings show 5–7 at.% lower Al-contents than the respective target compositions ($\text{Cr}_{47}\text{Al}_{0.53}$, $\text{Cr}_{37}\text{Al}_{0.63}$, and $\text{Mo}_{0.45}\text{Al}_{0.55}$ in the films vs. $\text{Cr}_{0.40}\text{Al}_{0.60}$, $\text{Cr}_{0.30}\text{Al}_{0.70}$, and $\text{Mo}_{0.40}\text{Al}_{0.60}$ in the targets, respectively). This is basically due to the poisoning effect, resulting in the formation of the non-conductive AlN_x compounds on the target surfaces [15], and partly due to the different sputtering and scattering behaviour of the elements [16]. In order to simplify the investigations and discussions, we operate with the closest quasi-binary tie lines and describe the average chemical compositions of our Mo–Al–Cr–N thin films along the quasi-binary sections $\text{Cr}_{0.50}\text{Al}_{0.50}\text{N}$ – $\text{MoN}_{0.50}$ and $\text{Cr}_{0.40}\text{Al}_{0.60}\text{N}$ – $\text{MoN}_{0.50}$ when using $\text{Cr}_{0.40}\text{Al}_{0.60}$ - and $\text{Cr}_{0.30}\text{Al}_{0.70}$ -targets, respectively, see the corresponding dash-dotted lines in the $\text{MoN}_{0.50}$ – AlN – CrN ternary phase field, Fig. 1a.

The Cr/Al-ratios within the coatings remain at ~ 0.6 and ~ 0.9 , respectively, depending on the target composition used. Similarly, when using $\text{Mo}_{0.40}\text{Al}_{0.60}$ -target and placing Cr-cubes onto the racetrack, the composition follows the quasi-binary section $\text{Mo}_{0.45}\text{Al}_{0.55}\text{N}$ – CrN , see the corresponding dash-dotted line in Fig. 1a. Again, the Mo/Al-ratio remains at ~ 0.8 . When adding the cubes of $\text{Cr}_{0.15}\text{Al}_{0.85}$, or $\text{Cr}_{0.40}\text{Al}_{0.60}$ onto $\text{Mo}_{0.45}\text{Al}_{0.55}$ -target during deposition, Al-contents, x , of our quaternary $\text{Mo}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}_z$ coatings are even above 0.6 (these quasi-binary sections are not marked in Fig. 1a).

The nitrogen content (Fig. 1b) increases nearly linearly from ~ 35 at.% (for $\text{MoN}_{0.53}$) to over 50 at.% (for Cr–Al–N) with decreasing Mo-content. However, coatings produced from $\text{Mo}_{0.40}\text{Al}_{0.60}$ -target exhibit a slight deviation from this tendency, showing a Me:N stoichiometry of nearly 1:1 with ~ 49 –50 at.% nitrogen, especially for low Cr-contents. The nearly linear decreasing N-content with increasing Mo-content excellently agrees with our earlier studies on the ternary material systems Mo–Cr–N [7] and Mo–Al–N [6], and suggests for N-vacancy formation with increasing Mo-content (according to $\text{MoN}_{0.50}$).

XRD investigations reveal a polycrystalline single-phase cubic structure for all coatings prepared from $\text{Cr}_{0.40}\text{Al}_{0.60}$ - and $\text{Cr}_{0.30}\text{Al}_{0.70}$ -targets

with the addition of Mo-cubes (Fig. 2a and b, respectively) as well as for all coatings prepared from $\text{Mo}_{0.40}\text{Al}_{0.60}$ -target with the addition of Cr-cubes (Fig. 2c). Consequently, single-phase cubic-structured $\text{Mo}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}_z$ coatings are obtained, as long as their chemical composition follows the three quasi-binary tie lines: $\text{Cr}_{0.50}\text{Al}_{0.50}\text{N}$ – $\text{MoN}_{0.50}$, $\text{Cr}_{0.40}\text{Al}_{0.60}\text{N}$ – $\text{MoN}_{0.50}$, and $\text{Mo}_{0.45}\text{Al}_{0.55}\text{N}$ – CrN , compare Figs. 1 and 2. When adding $\text{Cr}_{0.15}\text{Al}_{0.85}$ - or $\text{Cr}_{0.40}\text{Al}_{0.60}$ -cubes onto $\text{Mo}_{0.40}\text{Al}_{0.60}$ -target, all quaternary coatings also contain hexagonal phases, because their Al-content, x , is always above 0.6 (see e.g. Fig. 2c, representing the coatings prepared by alloying with $\text{Cr}_{0.15}\text{Al}_{0.85}$).

All single-phase cubic-structured quaternary $\text{Mo}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}_z$ coatings exhibit indentation hardnesses, H , above 30 GPa (Fig. 3a). The lower values belong to the coatings synthesised from $\text{Cr}_{0.40}\text{Al}_{0.60}$ -target, hence, coatings with lower Al-contents, x , between 0.24 and 0.53 along the $\text{Cr}_{0.50}\text{Al}_{0.50}\text{N}$ – $\text{MoN}_{0.50}$ tie line. Higher Al-contents in the target ($\text{Cr}_{0.30}\text{Al}_{0.70}$) and thus higher Al-contents in the coatings ($x = 0.31$ –0.61) lead to significantly higher indentation hardnesses of our single-phase cubic-structured quaternaries of ~ 34 –37 GPa, see Fig. 3a. When using $\text{Mo}_{0.40}\text{Al}_{0.60}$ -target and adding Cr-cubes, the hardness increases even to 41.2 ± 2.9 GPa for $\text{Mo}_{0.39}\text{Al}_{0.52}\text{Cr}_{0.09}\text{N}_{0.98}$. But also for the other compositions along this $\text{Mo}_{0.45}\text{Al}_{0.55}\text{N}$ – CrN tie line, the hardnesses are around 40 GPa, Fig. 3b. Consequently, super-hard nitride coatings are accessible even without the formation of nanocomposites. The quaternary coatings prepared from $\text{Mo}_{0.40}\text{Al}_{0.60}$ -target with the addition of Al-containing cubes have only hardnesses between 18 and 21 GPa, because they also contain the hexagonal Al-rich phase as their Al-contents, x , is always above 0.6.

The mechanism of hardness enhancement within our single-phase cubic-structured $\text{Mo}_{1-x-y}\text{Al}_x\text{Cr}_y\text{N}_z$ coatings can be understood by the impact of the valence electron concentration on the shear modulus [17,18]. Here, we obtained the highest hardnesses for the VEC-values (per unit cell) close to 8.4 (cf. Fig. 3c), which indicates the fully occupied non-metal–metal bonding states (i.e., shear-resistive) while partially vacant

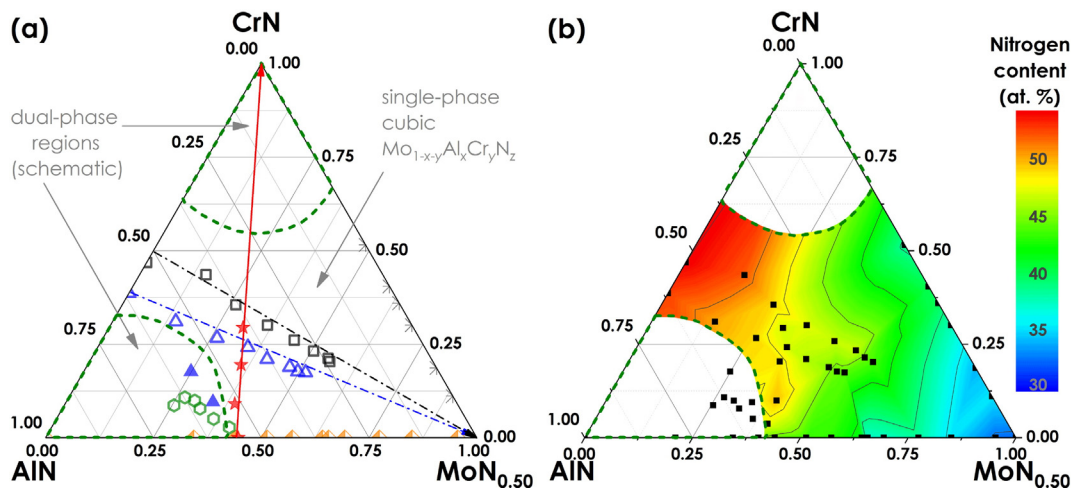


Fig. 1. Development of the elemental composition within the Mo–Al–Cr–N system: metal fraction (a) and nitrogen content (b). Evolution of the metal fraction along the intermetallic tie lines $\text{Cr}_{0.50}\text{Al}_{0.50}\text{N}$ – $\text{MoN}_{0.50}$ (black line and empty squares), $\text{Cr}_{0.40}\text{Al}_{0.60}\text{N}$ – $\text{MoN}_{0.50}$ (blue line and empty triangles) $\text{Mo}_{0.45}\text{Al}_{0.55}\text{N}$ – CrN (red line and stars), as well as Al-containing cubes $\text{Cr}_{0.15}\text{Al}_{0.85}$ (green filled hexagons) or $\text{Cr}_{0.40}\text{Al}_{0.60}$ (blue filled triangles) at the $\text{Mo}_{0.45}\text{Al}_{0.55}$ -target. The grey and orange symbols on the quasi-binary tie lines $\text{MoN}_{0.50}$ – CrN and $\text{MoN}_{0.50}$ – AlN represent the results of our recent investigations. The green dotted lines separate the region of single-phase cubic-structured quaternary nitrides from the dual-phase coatings with hexagonal structures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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