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ORIGINAL REPORT

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Low-temperature growth of epitaxial Ti_2AlC MAX phase thin films by low-rate layer-by-layer PVD

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ABSTRACT

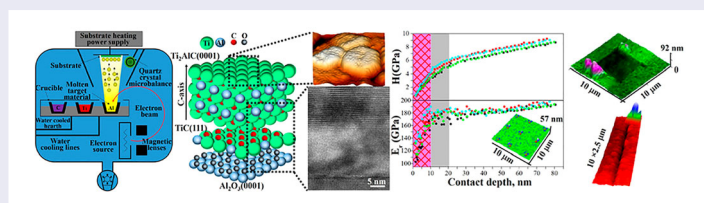
Here we report on the structural and tribo-mechanical characterization of epitaxial single-crystalline Ti_2AlC MAX phase thin films, grown by means of electron beam physical vapor deposition at relatively low temperature (700°C). The growth of phase pure Ti_2AlC at a relatively lower temperature when compared to other PVD methods was achieved utilizing a relatively low deposition rate and layer-by-layer deposition technique. The epitaxial growth is evidenced through the combination of XRD, HR-TEM and Raman spectroscopy measurements. The nanomechanical and micro-scale tribological properties of the Ti_2AlC thin films were studied by means of nanoindentation and nanoscratch tests.

ARTICLE HISTORY

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KEYWORDS

MAX phases; PVD; thin film growth; nanoindentation; low friction



IMPACT STATEMENT

The growth temperature of phase pure single-crystalline Ti_2AlC MAX phase thin films was reduced to 700°C utilizing the low-rate layer-by-layer PVD technique.

1. Introduction

$\text{M}_{n+1}\text{AX}_n$ ($n = 1, 2, 3$) phases are inherently lamellar ternary ceramic compounds (i.e. nitrides and carbides) with hexagonal structure with $\text{P6}_3/\text{mmc}$ symmetry, where M is an early transition group metal, A is an A-group element and X is carbon or nitrogen. Their inherently nanolaminated structure assumes different bonding between the layers of the constituent elements: the M–A are metallic, while the M–X are covalent. This combination of those bonding gives a unique combination of properties, typical for both metals (thermal and electrical conductivity) and ceramics (low coefficient of friction, high resistance to thermal shocks, high-temperature chemical stability). Such combination of properties makes them very promising functional materials for high-temperature structural applications, protective coatings, sensors, low friction surfaces,

electrical contacts, tunable damping films for micro-electromechanical systems, etc. [1]. Moreover, MAX phases are used as precursors for the synthesis of two-dimensional solids, MXenes, by etching of the A-element, which have recently shown promise as electrodes for supercapacitors, Li-S batteries and Li-, Na- and K-ion batteries [2,3].

The combination of metallic/covalent bonds and inherently laminated configuration makes the hexagonal crystal structure of MAX phases highly anisotropic that consequently promotes properties to be anisotropic. In this regard, the synthesis of MAX phases in thin films form via a controllable epitaxial growth, with desired crystallographic orientation on lattice matched substrates, makes possible the measurement of fundamental physical properties and their anisotropies. Moreover, continuous epitaxial MAX phase thin films are of

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special importance for the synthesis of large specific surface area MXenes [4]. Therefore, the growth of epitaxial and phase pure MAX phases are of tremendous scientific and technological importance.

Among the $Ti_{n+1}AlC_n$ MAX phase family, Ti_2AlC has gained a special interest of the research community due to a unique combination of excellent physical and functional properties [1,5]. The epitaxial Ti_2AlC MAX phases were grown by physical vapor deposition (PVD) methods at temperatures of order 900°C (see Supplementary note 2). However, the growth of pure single-crystal Ti_2AlC thin films by PVD at relatively lower temperatures remains challenging and limits the use of temperature sensitive substrates and thus hinder the applicability and studies on Ti_2AlC MAX phases and related composites. Recently, a rather innovative approach based on layer-by-layer deposition of MAX phase forming atomic species was reported by Vishnyakov et al. [6], which allowed to reduce the growth temperature of the polycrystalline Ti_3SiC_2 substantially from 900°C down to 650°C.

In this work, we utilize the layer-by-layer approach and additionally reduce the deposition rate for the growth of epitaxial Ti_2AlC MAX phase thin films by electron beam physical vapor deposition at 700°C. The nanomechanical and micro-scale tribological characterization of the Ti_2AlC thin films are also reported.

2. Methods

2.1. Materials and deposition

The growth of the films was carried out in cryopumped ultra-high vacuum (UHV) environment (with a base pressure of 6.7×10^{-10} Torr) by means of electron-beam physical vapor deposition (Figure S1). The evaporation materials were Al (99.96% pure), Ti (99.99% pure) pellets and C pieces (99.99% pure) placed into water-cooled intermetallic (BN-TiB₂), TiC and graphite crucibles, respectively. The MAX phase thin film was deposited with a deposition rate of approximately 0.3, 0.4, and 0.1 Å/s for Ti, Al and C, respectively. The Ti_2AlC film was grown by sequential layer-by-layer deposition 120 Å of Ti, 60 Å of C and 72 Å of Al up to the total thickness of 1200 Å. The 200 Å-thick TiC seed layer was grown by sequential deposition 60 Å of Ti and 40 Å of C. Due to the exchange of the crucibles and the heating of the materials up to evaporation (sublimation of C) and subsequent cooling before the exchange, the overall deposition time was 8 h.

The substrate was a polished 10 × 10 mm single-crystal Al_2O_3 (0001) wafer. The substrate temperature

during the deposition was kept at 700°C. See Supplementary materials for details on the deposition.

2.2. Structural characterization

Structural characterization of the thin film was performed by means of X-ray diffraction (XRD) by Θ -2 Θ , ψ , and *pole-figure* (ψ - χ - ϕ) scans. High-resolution transmission electron microscopy (HR-TEM) with energy dispersive analysis (EDS), atomic force microscopy (AFM) and Raman spectroscopy. The cross-section for TEM studies was prepared by means of a focused ion beam system (FIB) with Ga ions.

2.3. Nanomechanical testing

The nanoindentation, nanoscratch and nanowear tests were performed at room temperature using Hysitron TriboIndenter TI 950 equipped with a Berkovich diamond tip (see Supplementary materials for the details).

3. Results and discussions

The XRD analysis allowed to reveal Ti_2AlC and TiC phases together with peaks from Al_2O_3 substrate (Figure 1(a)). Moreover, the peak around 36° (and the 222 peak at 76°, not shown) is an indication of TiC (111), originating from the seed layer, which is slightly shifted to higher angles compared to stoichiometric TiC. The peak shift is associated with reduced cubic unit cell due to the substitution of Ti atoms to smaller Al atoms as a result of inward diffusion of the latter from the substrate or/and Ti_2AlC layer, as was revealed by the TEM-EDS mapping (see Figure S2). This is an important process for initial reactions at the surface during nucleation and growth of Ti_2AlC [7]. Only the (000 l) type peaks from the MAX phase Ti_2AlC and (111) TiC are observed that is typical for epitaxial growth of the MAX-phase film with out-of-plane orientation (0001) Ti_2AlC || (111)TiC|| (0001) Al_2O_3 . In such growth configuration (Figure 1(a), inset), (111) TiC layer acts as a template for nucleation and epitaxy of (000 l) Ti_2AlC MAX phase because the (111) TiC and (000 l) surfaces are isomorphous due to relatively similar structure and orientation of (111) TiC to TiC slabs in Ti_2AlC MAX phase structure and forms the first basal plane of the MAX phase. The epitaxial growth is additionally confirmed by the XRD pole figure measurements of the (11 $\bar{2}$ 3) Al_2O_3 substrate, (002) TiC and (10 $\bar{1}$ 3), (10 $\bar{1}$ 6), (0002) Ti_2AlC MAX phase reflections (Figure 1(b-f)). The {002} TiC pole figure displays a six-peak pattern at $\psi = 54.7^\circ$ originating from {111} planes due to the growth of TiC(111) in two different stacking sequences,

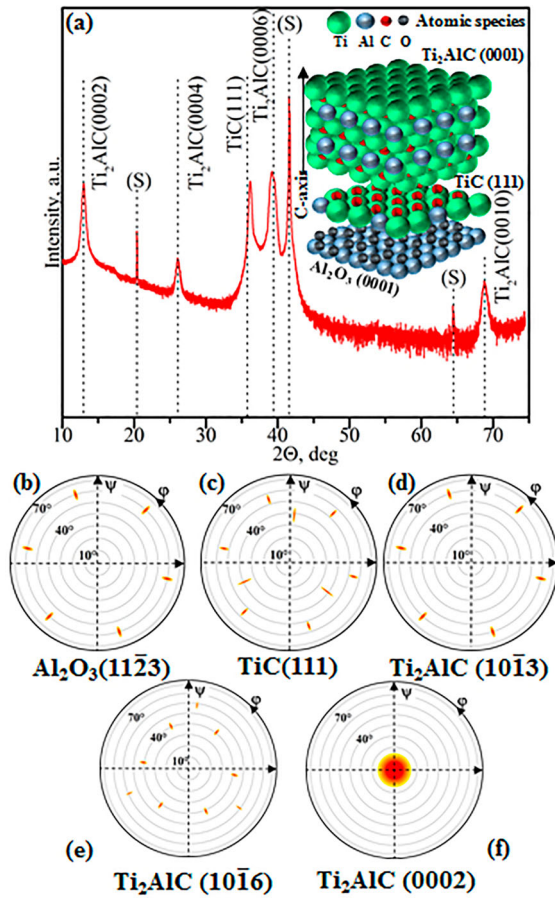


Figure 1. (a) Θ - 2Θ XRD pattern of the Ti_2AlC (000 l) thin film grown on TiC (111) pre-seeded Al_2O_3 (0001) substrate at 700°C. XRD pole figures of the (1123) Al_2O_3 substrate (b), (111) TiC (c), (1013) Ti_2AlC (d), (1016) (e) and (0002) (f) MAX phase (d) reflections. (S) denotes Al_2O_3 substrate.

ABC and BCA. (1123) Al_2O_3 pole figure (Figure 1(b)) exhibit six-peak pattern, which is positioned at identical ψ as the six-peak patterns of (1013) and (1016) MAX phase and (111) TiC. The three-peak patterns at $\psi = 38^\circ$ and 68° from the Al_2O_3 substrate were also detected at (111) TiC and (1016) MAX phase pole figures, respectively. The (0002) MAX phase pole figures contain one peak at the surface normal ($\psi = 0^\circ$). Thus, the growth is indeed epitaxial (000 l) $\text{Ti}_2\text{AlC} \parallel (111)\text{TiC} \parallel (000l)\text{Al}_2\text{O}_3$ yielding an in-plane epitaxial relation of $[10\bar{1}0]\text{Ti}_2\text{AlC} \parallel [1\bar{1}0]\text{TiC} \parallel [10\bar{1}0]\text{Al}_2\text{O}_3$ and $[10\bar{1}0]\text{Ti}_2\text{AlC} \parallel [\bar{1}10]\text{TiC} \parallel [10\bar{1}0]\text{Al}_2\text{O}_3$.

Figure 2(a) shows an overview TEM image from the Ti_2AlC (000 l) thin film grown on TiC (111) pre-seeded Al_2O_3 (0001) substrate. The TEM image clearly shows two different structures on Al_2O_3 substrate with sharp interfaces perpendicular to the growth direction. No secondary phases or grain boundaries within each layer were detected (Figure 2(b)). The upper part of Figure 2(b)

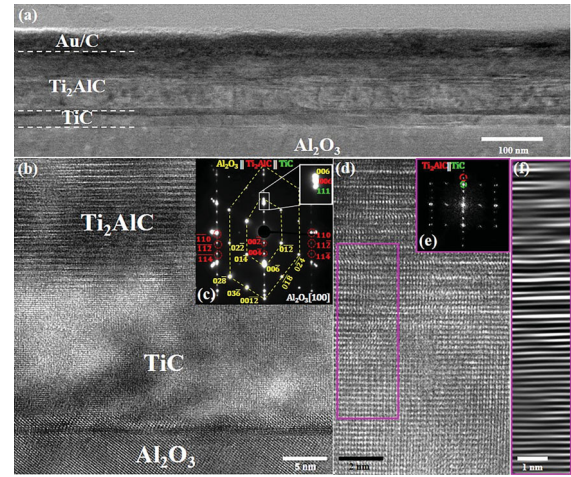


Figure 2. TEM analysis of the Ti_2AlC (000 l) thin film grown on TiC (111) pre-seeded Al_2O_3 (0001) substrate at 700°C: an overview bright field TEM image (a), cross-sectional bright field image (b), SAED pattern taken from the area of Ø220 nm of the sample with the electron beam parallel to the $[10\bar{1}0]$ Al_2O_3 zone axis (c), HR-TEM image taken at the $\text{Ti}_2\text{AlC}/\text{TiC}$ interface (d), fast-Fourier transform pattern of the area marked with purple square (e) and the filtered image of the reciprocal-lattice spots on the FFT pattern corresponding to (111) TiC planes and (0008) Ti_2AlC planes (f).

demonstrates bright and dark stripes typical for MAX phases.

The SAED pattern in Figure 2(c) obtained from the area of Ø220 nm of the sample together with a part of the substrate recorded with the electron beam parallel to the $[10\bar{1}0]$ Al_2O_3 zone axis. The indexation of the SAED pattern reveals symmetric reflections from the (111) TiC, (000 l) MAX phase and (000 l) Al_2O_3 sequentially arranged along the growth direction (see Figure 2(c), inset) and are slightly superimposed due to a small difference in the corresponding interplanar distances.

Figure 2(d) shows a high-resolution image of the TiC/ Ti_2AlC interface recorded along Al_2O_3 $[10\bar{1}0]$ zone axis. The typical stacking sequence of the dark bands separated by thin bright lines can be seen. Such a contrast is characteristic for the Ti_2AlC phase with TiC slabs interleaved with a square-planar Al-layers. The filtered image of the reciprocal-lattice spots on the FFT pattern (Figure 2(e)) corresponding to (111) TiC planes and (0008) Ti_2AlC planes visualize the epitaxial growth and sharp interface between the MAX phase and the seed layer. Hence, these results give much stronger support to the XRD measurements thus giving sufficient evidence to conclude that the phase pure (000 l) Ti_2AlC MAX phases grow epitaxially on (111) TiC seed layer.

The presence of ω_1 , ω_2/ω_3 and ω_4 Raman-active modes of Ti_2AlC (Figure 3) additionally confirms and support the XRD and HR-TEM measurements that the grown thin film is truly Ti_2AlC MAX phase with TiC seed

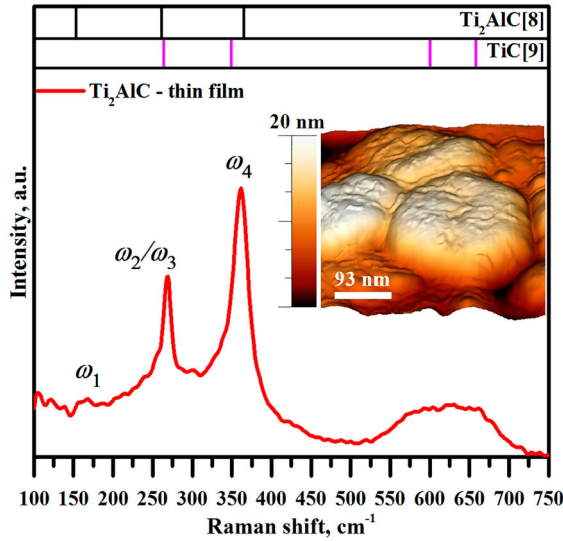


Figure 3. Raman spectra of Ti_2AlC thin film with Raman-active modes reported in the literature for single-crystal Ti_2AlC and TiC [8,9]. The inset is an AFM image showing the surface of Ti_2AlC MAX phase film.

layer. The growth of Ti_2AlC is additionally evidenced by hexagonally shaped crystals with low-energy faces (0001) and $\{10\bar{1}0\}$ revealed at the surface by means of AFM (Figure 3, inset), which are commonly observed on the surface of MAX phases [1].

Consequently, the single-crystal phase pure epitaxial Ti_2AlC MAX phase is grown at a relatively lower temperature of 700°C compared to simultaneous deposition by means of magnetron sputtering and pulsed cathodic arc deposition at 900°C (see Supplementary note 2). Generally, Ti_2AlC starts to nucleate already at 700°C while phase pure Ti_2AlC has been grown only at 900°C (see Supplementary note 2). Typically, in order to promote the formation of a large unit cell of MAX phases, the nucleation dynamics and growth conditions should fulfill long adatom diffusion length. Since the mean diffusion distance per adatom on the surface is proportional to the surface diffusion coefficient and inversely proportional to the deposition rate (Equation (1)), desired mobility of adatoms can be tuned by properly adjusting growth temperature and growth rate, as follows from the equation [10]:

$$\bar{x} = \sqrt{2D_s t} = \sqrt{\frac{2\nu a}{R}} \cdot a \cdot \exp\left(-\frac{E_D}{2kT}\right) \quad (1)$$

where D_s is the surface diffusion coefficient, ν is the vibrational frequency of surface atoms, a is the individual jump distance, $t \sim a/R$, where R is the deposition rate, E_D is the activation energy for surface diffusion, k is Boltzmann's constant and T is the substrate temperature. It is clear that the mean diffusion distance can be less than

one interatomic spacing below a critical temperature or above a critical deposition rate. Therefore, it is reasonable to suggest that in our approach a relatively low deposition temperature was compensated by low deposition rate during layer-by-layer growth that facilitates sufficient adatom diffusion length and growth of single-crystalline Ti_2AlC MAX phase.

Moreover, the sublimation of Al is a limiting factor for nucleation and growth dynamics of MAX phases during low-rate deposition at high temperatures [7]. Although an excess of Al with respect to 2:1:1 stoichiometry was supplied during the deposition in our experiment, a slight outward diffusion of Al was observed (see Figure S2). The driving forces for Al release from the crystal are the low diffusion barrier for Al atom self-diffusion along the (0001) plane [11], lower energy for vacancy formation [12] and higher isotropic thermal motion of Al [13] in comparison to Ti and C. However, defective Ti_2AlC may sustain phase stability down to an Al sub-stoichiometry of $\text{Ti}_2\text{Al}_{0.5}\text{C}$ [11]. Importantly, O inward diffusion from the substrate is less pronounced than Al (see Figure S2) that is of considerable importance for the synthesis of phase pure MAX phases, since O tends to substitute C atoms in the hexagonal lattice [7]. The more pronounced Al inward diffusion from the sapphire substrate can be assigned to lower activation energy for diffusion of Al than of O in sapphire [14].

It is well-known that the thin film growth kinetics can additionally be affected by the energy delivered to the growing film by the species impinging on the growing films (i.e. ions and neutrals). Considering that the vapor flux energy is significantly different between magnetron sputtering, cathodic arc deposition and electron beam evaporation, it is impossible to critically compare our results with those reported before. However, the outcomes of the present study can be an excellent starting point for further optimization and understanding of MAX phase thin film grown by both magnetron sputtering and cathodic arc deposition.

Figure 4 shows the extracted values of hardness and Young's modulus from load-displacement curves (Figure S4) for $1200 \text{ \AA}$ -thick Ti_2AlC thin film. The substrate independent hardness and reduced elastic modulus values of 4.8 ± 2 and $182.5 \pm 10 \text{ GPa}$, respectively, were obtained for the Ti_2AlC thin film. These hardness values are in a good agreement with those for bulk Ti_2AlC reported by Barsoum et al. [15], while the elastic modulus of $280.4 \pm 10 \text{ GPa}$ (calculated taking Poisson's ratio of 0.19) is slightly lower than theoretical and experimental values (see Table S1). The hardness and modulus values increase with increasing indentation depth approaching much harder TiC layer and the substrate. Figure 4(a), inset shows the residual impression after

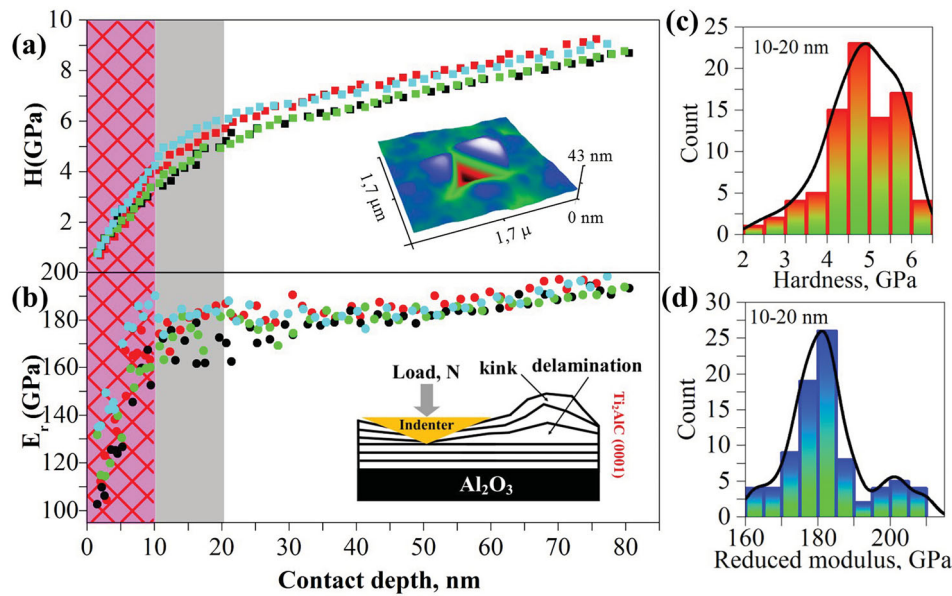


Figure 4. Hardness (a) and elastic modulus (b) vs contact depth for 1200 Å thick Ti_2AlC (0001) thin films grown on Al_2O_3 with SPM image of the residual impression after nanoindentation with 10 mN, corresponding to indentation depth of 85 nm (inset a) and schematic representation of delamination and kink band formation during nanoindentation of epitaxial (0001) Ti_2AlC thin films (inset b). Histograms with kernel fitting for the hardness (c) and elastic modulus (d) values in the range 10–20 nm of the Ti_2AlC film.

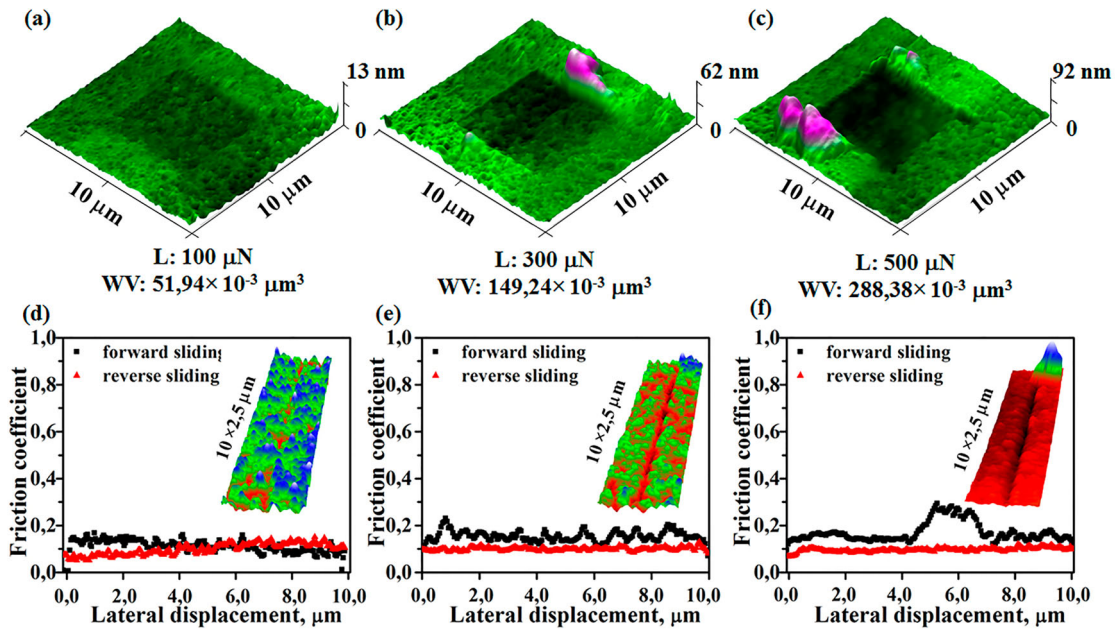


Figure 5. Tribological characterization of the Ti_2AlC thin films: 3D scanning probe microscopy images after nanowear tests of the Ti_2AlC thin film at load 100 μN (a), 300 μN (b) and 500 μN (c). Coefficient of friction as a function of lateral displacement of the indenter under constant load mode at 100 μN (d), 300 μN (e) and 500 μN (f) load with corresponding 3D scanning probe microscopy images of the scratch as insets. Normal load (L) and wear volume (WV) are indicated.

nanoindentation under maximum load, revealing a pile-up around the indent, which forms due to typical deformation mechanism for MAX phases proceeding through cohesive delamination of the basal planes and kink band formation (Figure 4(b), inset). The averaged hardness (Figure 4(c)) and reduced elastic modulus (Figure 4(d))

for depth 10–20 nm are presented as histograms with kernel fitting [16].

The nanowear test was performed over the area of $5 \times 5 \mu\text{m}$ of the Ti_2AlC thin film (Figure 5(a–c)). The nanowear volume increases with the applied load from for the Ti_2AlC thin film. The same trend was observed

for the wear depth from ~ 2 nm at 100 μ N load to about 15 nm at 500 μ N. The removed surface parts (debris) due to delamination and kinking are well-visible at the edges of the wear track after tests at higher loads. This process in MAX phases, according to Emmerlich et al. [17], associated with basal plane gliding and slipping when the load exceeds the deformation energies. The nanowear volume and wear depth of the Ti_2AlC thin film are in the range of the values reported for ultra-low nanowear nanocomposite films and much harder thin films (see Table S5).

The low nanowear of the film can be associated with a low coefficient of friction of the Ti_2AlC (Figure 5(d–f)) due to the layered structure with relatively weak metallic bonding. An abrupt increase of the coefficient of friction to about 0.3 at 500 μ N can be due to the pushing of the debris along the scratch and their subsequent penetration beneath the indenter, which are well-visible at the top end of the scratch. Importantly, as most functional properties, tribological properties of MAX phases are known to be anisotropic [18], and therefore the measured friction coefficient at micro-scale is related to the c -plane oriented Ti_2AlC . These outcomes point on the outstanding micro-scale tribological properties of the Ti_2AlC film at micro-Newton loads.

4. Conclusions

In summary, herein we demonstrated that low-rate layer-by-layer electron-beam physical vapor deposition method is suitable for the growth of epitaxial single-crystalline Ti_2AlC MAX phase thin films. Utilizing three independent sources, epitaxial Ti_2AlC thin films were deposited at a relatively low temperature of 700°C in comparison to other PVD methods due to properly adjusting deposition rate and layer-by-layer deposition. The reported approach offers prospects for epitaxial growth of other MAX phases and $\text{Ti}_{n+1}\text{AlC}_n$ MAX phases with higher stoichiometry and related composites by PVD methods. The micro-scale tribological characterization revealed ultra-low nanowear of the MAX phases due to low friction coefficient that can ultimately contribute to improved performance in a wide range of applications where low friction coefficient and good wear resistance is required at micro-Newton loads.

Author contributions

Film deposition: AVP, MK, Raman Experiments and Analysis: AVP, BS, HR-TEM experiment and Analysis: AVP, EC, X-ray experiments and analysis: AVP, EC, AFM

experiments and Analysis: AVP, Nanomechanical experiments and Analysis: AVP, Manuscript Preparation: AVP, Critical reading of the manuscript: EC, SJ.

Disclosure statement

No potential conflict of interest was reported by the authors.

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