

SECTION 3 PHYSICS OF RADIATION AND ION-PLASMA TECHNOLOGIES

<https://doi.org/10.46813/2023-147-111>

UDC 538.9:620.3:621.7

SYNTHESIS, STRUCTURE AND PROTECTIVE PROPERTIES OF PVD MAX PHASE COATINGS. A REVIEW. PART I. MAX PHASE COATINGS DEPOSITION

E.N. Reshetnyak¹, A.S. Kuprin¹, T.A. Prikhna², M.A. Bortnitskaya¹, V.A. Belous¹

¹*National Science Center “Kharkov Institute of Physics and Technology”, Kharkiv, Ukraine;*

²*V. Bakul Institute for Superhard Materials of the National Academy of Sciences of Ukraine,
Kyiv, Ukraine*

E-mail: reshetnyak@kipt.kharkov.ua

In recent decades, MAX phases have attracted considerable attention from the scientific community due to their unique combination of metallic and ceramic properties, which provide exceptional mechanical, thermal, electrical and chemical characteristics. The synthesis of MAX phases in the form of coatings is of increasing interest for many applications. The aim of this review is to summarize the progress made in the synthesis of coatings based on MAX phases using different methods. The advantages and characteristics of the implementation of ion-plasma physical vapor deposition methods are discussed. The use of ion-plasma methods allows to significantly reduce the synthesis temperature of MAX phases due to the high energy of the particles forming the coating. The effect of deposition parameters on the composition, structure and properties of the coatings is analyzed. Coatings with high protective properties and prospects for their application in industry are considered. This part of the review focuses on methods for depositing MAX phase based coatings.

INTRODUCTION

Materials with enhanced functional properties, both high-strength and lightweight, that are resistant to wear, pressure, temperature and various types of radiation are in demand in many industries. MAX phases have attracted considerable attention in recent years due to their distinctive nanolayered structure and properties, occupying a niche between ceramics and metals by merging different types of bonding. They form a significant group of oxygen-free ceramics, with over 150 different compositions. They are named according to their chemical formula as follows $M_{n+1}AX_n$ – where M is a transition metal; A is an element from the A group of the periodic table (mostly elements from groups 13 and 14); X is carbon or nitrogen, and $n = 1, 2, 3$ or more [1–5].

The history of the discovery and development of MAX phases can be divided into two stages. The first began in the early 1960-s, when the group of V.H. Nowotny's group in Vienna synthesized a series of new layered ternary carbides and nitrides. Among them were the so-called “H-phases” with M_2AX chemistry (i.e., $n = 1$) and their relatives Ti_3SiC_2 and Ti_3GeC_2 [6, 7]. For a long time, this topic did not arouse much interest until the mid-1990s. The second historical stage in the development of MAX phases began when in 1996 M.W. Barsoum and T. El-Raghy from Drexel University (USA) synthesized the first fully dense, phase-pure Ti_3SiC_2 and showed that this material combines the best properties of metals and technical ceramics [8]. The material was easy to machine due to its softness and possessed good electrical and thermal conductivity. It also demonstrated remarkable resistance to thermal shock and oxidation up to 1400 °C. Later, the discovery of the Ti_4AlN_3 compound by scientists of this

group showed that these phases have a common basic structure, and this similarity in properties led to the proposal of the name MAX phase and its subsequent classification [1, 9].

The excellent properties of MAX phases have led to a rapid growth in experimental and theoretical research, as well as attempts to commercialize the results, over the past 25 years on a global scale. The synthesis and properties of bulk MAX phases, as well as the crystal structure and history of research on multicomponent carbides and nitrides, are reviewed in detail in [1–4, 9–11].

To date, some of the most extensively studied bulk MAX phases are systems containing titanium ($Ti_{n+1}AlC_n$, $Ti_{n+1}AlN_n$, $Ti_{n+1}SiC_n$) or chromium ($Cr_{n+1}AlC_n$). These materials are typically synthesized by methods such as hot isostatic pressing, plasma discharge sintering, and high temperature self-propagating synthesis [2, 4, 12–14]. The methods currently available tend to be technologically complex and energy intensive. They sometimes require several lengthy additional steps, for example to increase the density of the initial porous materials or to ensure the required proportion of MAX phase in the final product. In this sense, the synthesis of MAX phases in the form of thin films and coatings appears to be more economical, since the condition and properties of the material surface layer largely determine the performance characteristics of the product as a whole.

The results of experimental and theoretical studies indicate a high potential for the use of coatings based on MAX phases [15–19]. Excellent mechanical properties, high electrical and thermal conductivity, damage resistance, self-healing ability, high thermal stability, and outstanding resistance to oxidation, corrosion, and

abrasion make such coatings useful for many applications. Especially for high-temperature electrical contacts, microelectronic coatings, magnetic and optical materials, thermal barriers, protection of structural materials for turbines, engines, pumps, bearings, accident resistant fuel cladding for nuclear power plants, protective coatings for aerospace, etc. Over the past few decades, many attempts have been made to grow high quality films with a variety of MAX phases by Thermal Spraying (TS), Chemical Vapor Deposition (CVD), and Physical Vapor Deposition (PVD) methods from the gas phase and plasma. TS and CVD methods require very high temperatures ($> 1000\text{ }^{\circ}\text{C}$) which are unsuitable for many substrate materials. The use of ion-plasma PVD methods can significantly reduce the synthesis temperature due to the high energy of the particles forming the coating [15, 16].

The purpose of this review is to analyze the current achievements in the field of ion-plasma synthesis of coatings based on MAX phases. The main focus is on the processes for the deposition of coatings with high protective properties, their strengths / weaknesses and prospects for industrial application.

1. COMPOSITION, STRUCTURE AND PROPERTIES OF MAX PHASES

Currently, about 85 triple MAX carbides and nitrides are known, with various elements in the M positions (Sc, Ti, V, Cr, Mn, Fe, Y, Zr, Nb, Mo, Hf, Ta, W, and most lanthanides) and A positions (Al, Si, P, S, Cu, Zn, Ga, Ge, As, Pd, Cd, In, Sn, Sb, Ir, Au, Tl, Pb, Bi) [5, 12]. Similar to MAX phases are nanolaminated borides, commonly referred to as MAB phases. It is believed that MAB phases contain fewer element combinations but have a greater number of structural variations. Since MAB phases and MAX phases share common structural features and properties, the possibility of extending $X = \text{C, N}$ by adding B to the list of MAX phases has recently been discussed [20–22]. Recently, another approach to increase the chemical diversity of MAX phases has emerged, which consists of forming a solid solution by doping the M, A, or X positions [3, 16, 23]. Solid solutions of elements with different atomic radii and electron valences in an identical crystal structure provide a variety of physical and chemical properties. Fig. 1 shows the different elements M, A, and X reported in the synthesized ternary and tetrahedral MAX phases. It illustrates the extremely wide range of variation in the composition of MAX phases.

Most MAX phases have a hexagonal crystal lattice belonging to the $P6_3/mmc$ space group. It consists of almost densely packed layers formed by ceramic octahedra $[\text{M}_6\text{X}]$ with common edges separated by metal-like layers of element A, as shown in Fig. 2. This type of lattice is called natural nanolaminates. The X-atoms are located in the octahedral positions between the M-layers. The octahedral part of the $[\text{M}_6\text{X}]$ unit cell is identical to the NaCl-type structures found in the corresponding MX carbides or nitrides. The A-element is located at the center of a trigonal prism formed by M-atoms. Thus, the amazing set of properties of MAX

phases (see Fig. 2) is due to the layered structure and the mixed nature of the bonds [2–4, 16].

Depending on the value of n , the M_2AX , M_3AX_2 , and M_4AX_3 phases are commonly referred to as 211, 312, and 413 phases, respectively. The main differences in the structures of 211, 312, and 413 phases lie in the number of M-layers between each pair of A-layers [3]. When $n = 1$, the A-layers are separated by two M-layers (see M_2AX in Fig. 2). When $n = 2$, they are separated by three layers (see M_3AX_2 in Fig. 2). When $n = 3$, they are separated by four layers (see M_4AX_3 in Fig. 2). Recently, some other phases with a higher value of n have been found in the MAX family, such as phase 523 ($\text{Ti}_5\text{Al}_2\text{C}_3$), phase 615 (Ta_6AlC_5), phase 725 ($\text{Ti}_7\text{Si}_2\text{C}_5$), etc.

The number of discovered MAX phase compositions is constantly increasing due to a combination of experimental work and theoretical calculations. However, not all possible combinations are thermodynamically stable. For example, in the Ti-Al-C system, the Ti_2AlC and Ti_3AlC_2 phases ($n = 1$ and 2, respectively) are stable over a wide temperature range, but in systems such as Cr-Al-C and Ti-Si-C there is only one stable phase each – Cr_2AlC and Ti_3SiC_2 . As for alloying, certain combinations have unlimited solubility of the components, for example, in the $\text{Ti}_3(\text{Al}_{1-x}\text{Si}_x)\text{C}_2$ system, the value of x varies from 0 to 1.11. Other combinations have low solubility, for example < 5 at.% Cr in Ti_2AlC . It is very useful that some solid solutions can be synthesized despite the fact that the initial MAX phases are unstable. In [15, 16], stable solid solutions of $(\text{Cr}_{2/3}\text{Ti}_{1/3})_3\text{AlC}_2$ and $(\text{Cr}_{5/8}\text{Ti}_{3/8})_4\text{AlC}_3$ were reported, although Cr_3AlC_2 , Cr_4AlC_3 and Ti_4AlC_3 are not thermodynamically stable. The stability of the solutions is explained by the formation and higher stability of the order of two elements M at two different positions [2].

The chemical diversity of MAX phases is key to optimizing their properties for potential applications. The presence of strong M-X bonds and weaker M-A bonds gives these compounds a unique combination of properties [3, 4, 14–17]:

- as metals are characterized by high thermal and electrical conductivity, resistance to thermal shock and fracture, ductile at high temperatures, and can be easily machined;

- as ceramic materials, they are resistant to oxidation, corrosion, and fatigue, are heat resistant, retain strength at high temperatures, have a low specific gravity, and are characterized by high moduli of elasticity and a low coefficient of friction;

- at the same time, they can have weak magnetic properties, high damping properties, radiation resistance, and self-healing ability.

MAX phase is a ceramic material with high resistance to mechanical damage, since the formation of microcracks, shear and kink bands, delamination and crushing, warping and microfractures of the layers act as effective energy absorption mechanisms during deformation and contribute to the dissipation of mechanical energy at the micro level. The localization of mechanical damage in a particular grain prevents macroscopic destruction of the material as a whole. This behavior was explained by the fact that the crystal

lattice of MAX phases allows dislocations to slide only in the base planes, which, together with weak bonds between atomic layers, leads to a strong anisotropy of the mechanical properties of MAX phases and the

realization of an unusual mechanism of plastic deformation – the formation of kink bands (Fig. 3) [2, 15, 16].

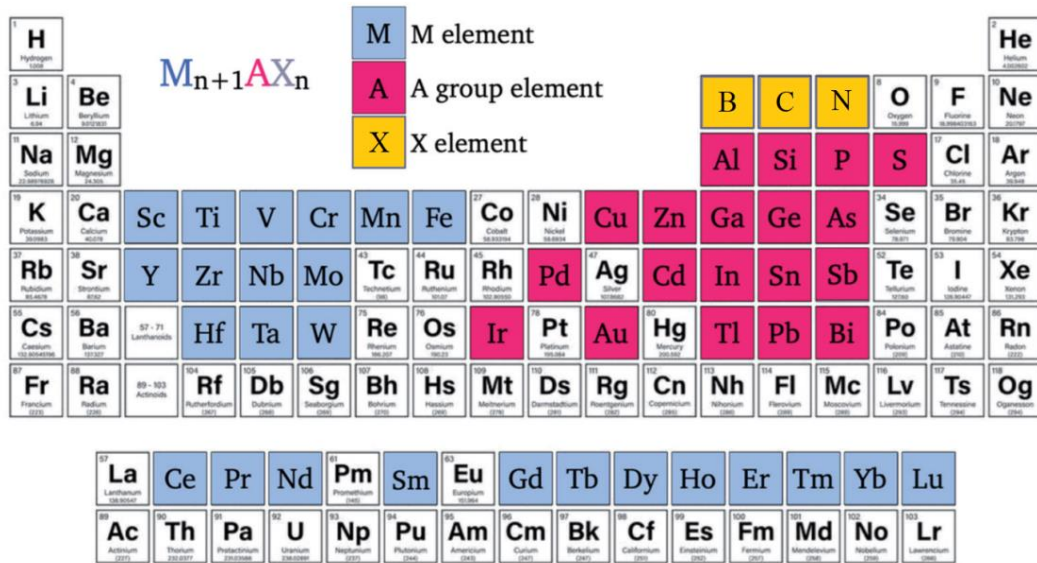


Fig. 1. Periodic table showing the location of M, A, and X elements in MAX phases [5, 12]

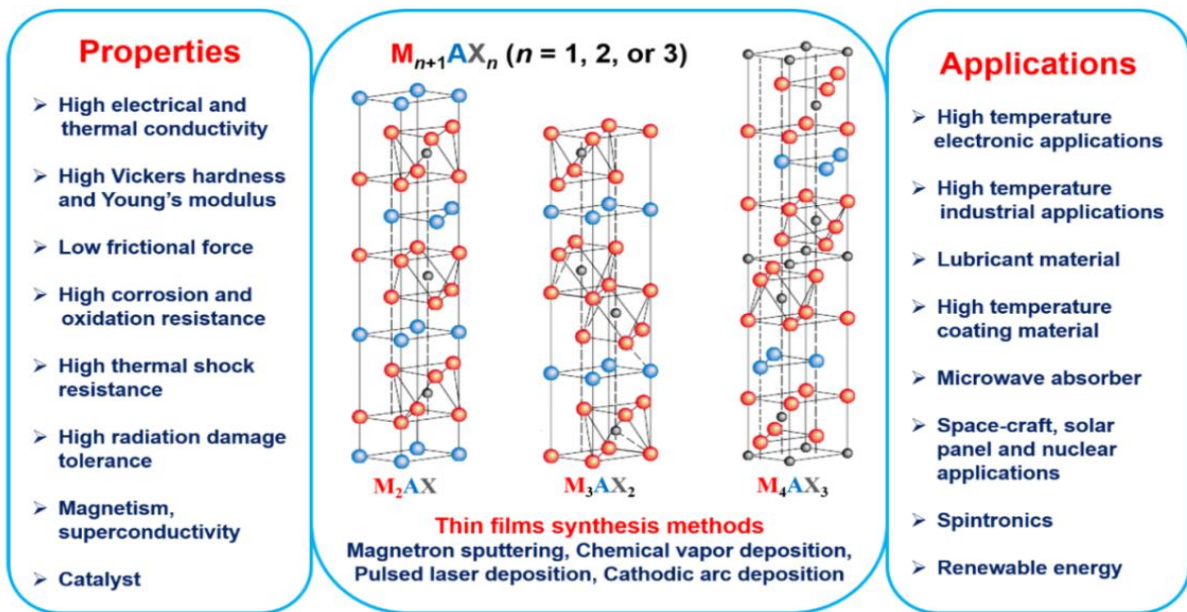


Fig. 2. Multilayer structure of ternary $M_{n+1}AX_n$ phases for n ranging from 1 to 3, including a brief overview of their typical properties and potential applications [19]

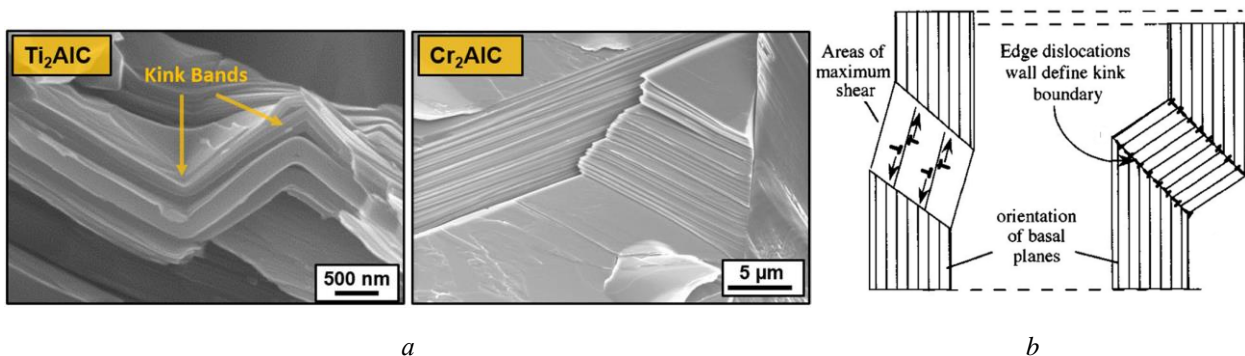


Fig. 3. SEM images of the characteristic layered structure and strain of the MAX phases (a) and the scheme of kink band formation limited by dislocation walls (b) [2, 16]

2. SYNTHESIS OF COATINGS BASED ON MAX PHASE

2.1. A GENERAL OVERVIEW OF THE DEPOSITION METHODS

The main difficulty in the synthesis of MAX phases is to ensure their high content in the obtained materials (≥ 95 wt.%), since MAX phases can coexist with other thermodynamically stable phases, such as carbides or nitrides and intermetallics [15, 16]. In addition, ensuring high functional properties of coatings requires the formation of a homogeneous, dense coating with a satisfactory level of adhesion. Fig. 4 shows a general classification of the main methods used to deposit MAX phase coatings.

For thicker coatings ($> 100 \mu\text{m}$), thermal spraying and cold spraying technologies are preferred, which are based on the application of powdered MAX phases to the surface to be treated using gas (plasma) streams [24–34]. In this way, coatings up to several millimeters thick can be applied to products of various sizes and geometries. Depending on the heat source used in the process, different methods of gas thermal spraying have been applied: plasma spraying [25, 26] and high velocity oxyfuel (HVOF) spraying [27–31]. However, thermal spraying technology requires the use of high temperatures ($>2000 \text{ }^\circ\text{C}$), which can cause oxidation and even decomposition of the MAX phases. This leads to a high content of undesirable phases in the coatings, which degrades their functional properties. In addition, tensile stresses are inevitable during thermal spraying causing cracking and even delamination of the coatings.

In cold spraying technology, particles are applied to the substrate at a lower temperature ($<1000 \text{ }^\circ\text{C}$), but at a very high velocity (up to 1200 m/s). With such coatings, it is sometimes difficult to ensure the strength of the bond to the surface of the metal substrate, which degrades under the influence of high-speed bombardment [32–34]. So far, only a few coating systems from the large family of MAX phases have been synthesized by the above methods (mainly Ti_3AlC_2 , Ti_3SiC_2 , Cr_2AlC , and Ti_2AlC), since there are currently very few commercial sources of powders [2].

Laser cladding is another option for obtaining thick MAX phase coatings. Its advantages include the ability

to form a metallurgical bond between dissimilar materials and a small heat affected zone. The deposition of coatings is realized both with the use of a powder of the MAX phase and with a mixture of elemental powders of the corresponding composition, which opens the possibility of reducing the cost of the process. Composite coatings containing Ti_3SiC_2 [35] or Ti_2AlC [36, 37] have been obtained, showing good adhesion to the substrate and no obvious defects such as pores and cracks, but an additional post-laser treatment was required to increase the content of the MAX phase [36]. Thus, the deposition of thick coatings with the composition and properties of MAX phases is still a challenging task.

Various CVD and PVD techniques are used to synthesize thin ($< 100 \mu\text{m}$) films of MAX phases. The use of CVD techniques started with Ti_3SiC_2 . Deposition was performed from a gas mixture of TiCl_4 , SiCl_4 , H_2 , and CCl_4 or CH_4 as carbon source [15]. CVD is based on processes close to thermodynamic equilibrium, so it is closer to the methods of synthesis of massive materials. Quite high temperatures ($1000 \dots 1300 \text{ }^\circ\text{C}$) are required for the formation of MAX phases. In addition, it is quite difficult to obtain single phase films. For example, in most synthesized CVD MAX films, the Ti_3SiC_2 phase coexists with other phases (TiC , TiSi_2 , SiC , and $\text{Ti}_5\text{Si}_3\text{C}_x$) [38–41].

High-quality, high-purity and dense thin films of MAX phases can be deposited by ion-plasma PVD methods at relatively low temperatures, which is certainly crucial for coatings on sensitive substrates such as certain types of steel [15, 16, 19]. The thickness of these films typically ranges from a few nm to $\sim 50 \mu\text{m}$. The first comprehensive review on the deposition of coatings based on MAX phases, nucleation and growth mechanisms, and resulting properties was published by P. Eklund et al. in 2010 [15]. Among the more recent reviews, it is worth mentioning the work of O. Berger in 2019, which focuses on analyzing the relationship between structure, properties, and applications of MAX phase coatings [16–18], as well as the review published by A. Biswas et al. in 2021, which summarizes the progress in epitaxial growth of coatings [19].

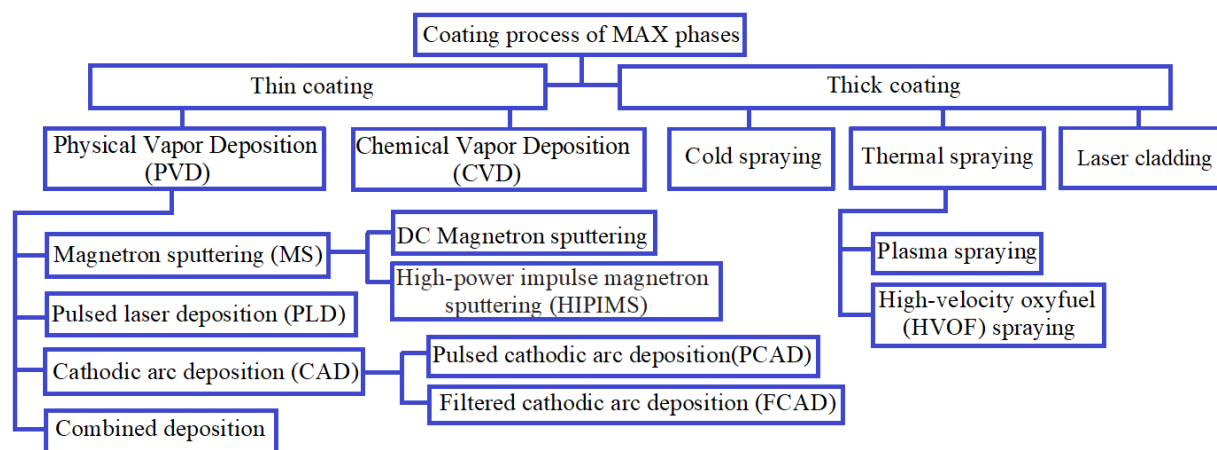


Fig. 4. Classification of methods used for deposition of MAX phase coatings

It should be noted that initially PVD deposition was performed at substrate temperatures between 800 and 1000 °C. Gradually, efforts were focused on lowering the deposition temperatures and significant progress was made.

2.2. FEATURES OF PVD SYNTHESIS METHODS

Ion-plasma physical vapor deposition methods are widely used to synthesize high quality coatings based on MAX phases of various compositions [2, 15, 16]. The peculiarity of ion-plasma PVD methods is that they operate under conditions far from thermodynamic equilibrium [42–46]. Energy is supplied to the system not so much by maintaining a high substrate temperature as by bombardment with energetic particles. In addition to thermal factors, other factors (degree of ionization, flux density, and particle energy) affect the kinetics of film formation and allow for the deposition of high-quality films of various compounds at much lower temperatures. As a result of bombardment, thermal energy is replaced by the kinetic energy of particles [47, 48], however, such bombardment is a non-equilibrium process that is not identical to conventional heating because the kinetic energy of the bombarding particles is transferred to the local region of nanometer size and is accompanied by excessively rapid cooling at a rate of about $10^{13} \dots 10^{14}$ K/s. In addition, the injection of reactive gases into the vacuum chamber has long been used for reactive ion plasma PVD synthesis of films of refractory compounds that are difficult to obtain by other methods [42, 45], so it can be effectively used to produce MAX phases.

In general, three main ion-plasma PVD methods are used to synthesize MAX phase thin films: magnetron sputtering (MS) [49–111], cathodic arc deposition (CAD) [112–118], and pulsed laser deposition (PLD) [119–125]. Sometimes a combination of methods is used [126–132]. Each of these techniques has its own advantages and disadvantages, but they all have one thing in common: there is no need to maintain a high substrate temperature during the process because energetic particles (ions and neutrals) are involved in the deposition process.

The ion plasma synthesis of coatings is a complex multifactorial process that consists of several stages: generation of the particle stream, its transfer to the deposition surface, the interaction of the condensing particles with the gaseous medium and the deposition surface, and the formation of the coating. The chemical composition of the surface, structure, morphology and subsequently the properties of the growing film are affected at all stages of synthesis and are largely determined by the energy of the ions in the stream, which is controlled by a negative bias potential on the substrate. The higher the degree of ionization of the flow, the greater the number of particles with higher energy deposited on the substrate. However, excessive ion bombardment can have negative consequences, leading to atomization of the deposited material, decomposition of MAX phases, formation of defect structures, and amorphization of coatings [15, 16, 107].

Provided that the appropriate elemental composition of the coating on the substrate surface is maintained, there are two approaches to the synthesis of the MAX phase. First, the process can be performed in a single step, which requires a higher substrate temperature or energy of the particles forming the coating [49, 50, 60, 68–73, 91, 105, 109, 110, 112, 113]. A typical example of the development of a single-step process is the work of J. Frodelius et al. [49]. The joint magnetron sputtering of Ti_2AlC and Ti targets allowed the formation of epitaxial layers based on the MAX phase of Ti_2AlC on the Al_2O_3 (0001) substrate at a substrate temperature of 700 °C (power density ~ 3.2 W/cm², floating potential of the substrate -10 V). The TEM image of the cross section of the coating after deposition (Fig. 5,a-c) shows a columnar structure with two orientations of Ti_2AlC grains, which is confirmed by the results of X-ray diffraction analysis (see Fig. 5,d): Ti_2AlC with the base planes perpendicular to the growth direction, corresponding to the epitaxial ratio $Ti_2AlC(0001)//Al_2O_3(0001)$, and Ti_2AlC with the base planes inclined 37° from the growth direction, corresponding to the ratio $Ti_2AlC(10\bar{1}7)//Al_2O_3(0001)$. A small amount of cubic TiC carbide is also found in the coating.

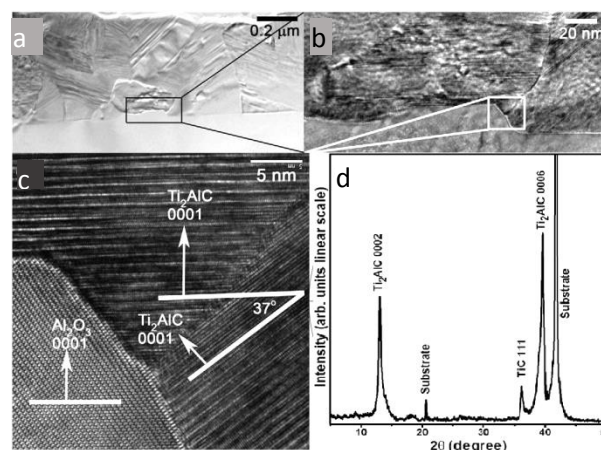


Fig. 5. Preparation of Ti_2AlC coatings by co-sputtering Ti_2AlC and Ti targets on Al_2O_3 (0001) substrate at 700 °C. TEM images of the cross-section of the coating (a-c): a – general view; b – enlarged area from (a); c – HREM image from (b).

X-ray diffractogram of the obtained coating (d) [49]

Another approach to synthesize the MAX phase in a coating is a multi-step process based on solid-state reactions. First, a film with the desired stoichiometry is deposited, and in the next step, annealing is performed to crystallize the MAX phase. The film must be in a metastable state, e.g. amorphous or multilayer. Annealing is performed at a temperature above the deposition temperature to initiate the transformation [51–53, 78–80, 84, 90, 94, 95, 106, 126–131].

In particular, good results are obtained by annealing multilayer coatings, and under certain conditions, such annealing does not require significant temperatures, and by changing the composition and thickness of the composition layers, the value of n in the formula $M_{n+1}AX_n$ can be controlled [51, 78, 80, 95, 126–131]. For example, Z. Wang et al. [126] successfully prepared

Ti₂AlC coatings by annealing multilayer TiC_{0.65}/Al coatings. The electron microscope images and X-ray energy dispersive spectroscopy data of the cross-section of one of the coatings show that after annealing at 550 °C for 100 h, the boundaries of the TiC_{0.65} and Al layers disappear (see Fig. 6,a–f). According to X-ray diffraction (Fig. 6,g), the coating forms the MAX phase of Ti₂AlC. A schematic representation of the diffusion formation process is shown in Fig. 6,h. It should be noted that prolonging the annealing time is no less effective than increasing the temperature. The sample annealed at 580 °C for 100 h has a significantly higher Ti₂AlC content than the sample annealed at 600 °C for 20 h (see Fig. 6,g).

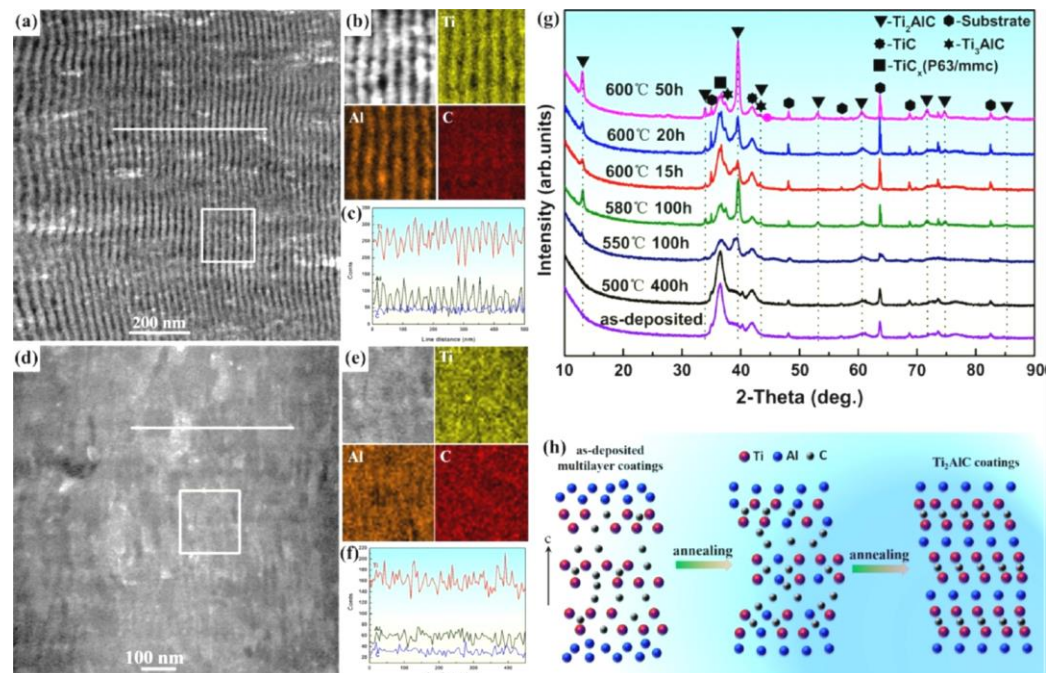


Fig. 6. Preparation of Ti₂AlC coatings by low-temperature long-term annealing of TiC_{0.65}/Al multilayer coating: a – STEM image of the cross-section of the synthesized coating; b, c – EDX results of the synthesized coating; d – STEM image of the coating annealed at 550 °C for 100 h; e, f – EDX results of the coating after annealing; g – XRD patterns of the coatings annealed at different temperatures for different times; h – schematic diagram of the MAX phase formation process [126]

2.2.1. Magnetron sputtering

Magnetron sputtering is the most commonly used method for MAX phase synthesis due to its relative ease of implementation, high process flexibility, and good control over phase purity and composition [15, 16, 19, 49–111]. The coatings obtained by this method are characterized by high homogeneity, low porosity, and satisfactory adhesion to the substrate and this method allows the deposition of coatings over a large area. MS method allows to obtain high ion current densities and consequently high sputtering rates at relatively low working gas pressures (usually Ar) of about 0.3 Pa and below [42, 43].

Synthesis of MAX phase coatings requires delivering a particle flux of appropriate elemental composition to the substrate. Fig. 7 shows three basic schemes of particle flux formation used to deposit MAX phase coatings by MS method. For MAX carbide coatings, magnetron sputtering deposition began with

The study of MAX phases in general has been accelerated by the introduction of PVD methods for the synthesis of thin films. Ion-plasma PVD technologies are used to synthesize single crystalline material by epitaxial growth, which allows us to study the fundamental properties of MAX phases. However, it should be noted that the properties of coatings and bulk MAX phases are not always completely identical, in particular, the decomposition of M_{n+1}AX_n thin films to form MX compounds occurs at temperatures of 1000...1100 °C, which is significantly lower than the decomposition temperatures usually reported for the corresponding bulk material [15, 19].

the simultaneous use of 3 direct current (DC) sources, each responsible for one element (see Fig. 7,a). The use of M, A, and a graphite target remains the most common method for laboratory synthesis, and has been used to deposit a wide range of MAX phases: Ti₂AlC, Ti₃AlC₂ [51, 52, 54, 58, 57], Ti₃SiC₂, Ti₄SiC₃ [60-63, 80, 81], Ti₂GeC, Ti₃GeC₂, Ti₄GeC₃ [81, 83], Ti₂SnC, Ti₃SnC₂ [67], V₂AlC [89], Nb₂AlC [92], Cr₂GeC [82], Cr₂AlC [58, 68, 70, 78, 80]. This approach allows individual and flexible control of the elemental content of coatings. The desired ratio of atoms of different elements in the coatings is achieved by applying the appropriate power to each target. Using targets of more complex composition, it is possible to form solid solutions in coatings based on MAX phases. In work [84], (Ti,Zr)₂AlC and (Ti,Zr)₃AlC₂ MAX phases were synthesized by sputtering elemental targets Al, C, and a Ti_{0.5}Zr_{0.5} alloy target.

On the other hand, a single alloy, powder sintered or combined target of M, A, and X elements, providing MAX phase stoichiometry, is considered desirable to simplify industrial processes (see Fig. 7,b). A common problem with sputtering a complex target is that the chemical composition of the resulting coating can be very different from the target. This problem is not specific to MAX phases, but is often observed for them [15, 16]. For example, sputtering targets from the MAX phases of Ti-Si-C or Ti-Al-C systems results in the formation of films with an increased C content, so that the formation of the MAX phase in the coating requires the addition of Ti to the deposition flux [49, 64]. In addition, there is a tendency for Al desorption at high deposition temperatures (above 700 °C). However, when a Cr₂AlC target is sputtered, the composition of the film is often close to the target [67, 75, 110].

The authors of [53] solve the problem of the mismatch between the composition of the target and the coating by optimizing the composition of the target. The Ti₂AlC and Ti₃AlC₂ coatings were deposited using cost-effective targets synthesized by hot pressing (800 °C) of elemental powders with Ti:Al:C molar ratios of 2:1.5:1 and 3:2:2, respectively. The MAX phases were formed by a two-step method with initial magnetron sputtering at ambient temperature followed by annealing at 800°C, but high stresses in the coatings caused them to crack after annealing.

The composition of M-Al-C (M = Cr, Zr and Hf) films deposited by magnetron sputtering from stoichiometric M₂AlC composite targets was investigated in [111]. It was found that the composition of the Cr-Al-C film is close to the stoichiometric one, while the Al content in the Zr-Al-C and Hf-Al-C films is significantly reduced compared to the target. Thus, the composition of the film is strongly dependent on the atomic weight of the transition metal. Zr and Hf atoms are 1.8 and 3.4 times heavier than Cr, respectively. Based on the modeling, the authors conclude that the re-sputtering of Al in the deposited film by energetic Ar neutrals formed as a result of the reflection of sputtering argon ions from the target is significant. Both the energy and flux of Ar reflected from the target increase with increasing mass of the transition metal in the target.

In addition to the bombardment of the surface of the growing coating with Ar neutrals, several other factors cause differences in the composition of the films and coatings: selective sputtering of the target, scattering of the sputtered particle stream in the gas phase, evaporation of the A element, differences in the angular and energy distribution for different elements, etc. The composition of films depends largely on the pressure of the working gas (Ar) during deposition. At high pressure, sputtered atoms reflected from the target collide with the working gas on their way to the substrate. In this case, their energy distribution shifts to lower values [15, 16], which can affect not only the elemental composition of the coatings, but also the substrate temperature required for the formation of the MAX phase.

The results of numerous studies show that the temperatures required for the synthesis of most MAX phases in ion plasma coatings are in the range of

500...900 °C and are always lower than for bulk synthesis. The order of the MAX phase (211, 312, or 413) is important in determining the growth temperature. Larger unit cells require a higher growth temperature due to the longer diffusion length. In addition, the bond energy affects the temperature. For example, for MAX carbides, the M-C bond energy decreases as one moves from group 4 to 6 (e.g., Ti to Cr), resulting in a decrease in temperature [15]. Record low formation temperatures of 370...450 °C have been demonstrated for the MAX phase of Cr₂AlC [67, 71], which is much lower than that of Ti₂AlC, Ti₃SiC₂, and Nb₂AlC coatings [52, 59, 88]. Together with the high resistance to oxidation and hot corrosion due to the formation of a continuous, well-adhered and inert protective Al₂O₃ layer [68, 74], this has led to a significant increase in interest in the synthesis of Cr₂AlC-based coatings by various methods [67–79, 107–111, 120, 125, 129–131].

Reactive deposition is commonly used to deposit MAX nitrides (see Fig. 7,c) using N₂ as the nitrogen source in the coating [96–103]. For example, reactive deposition of Ti₂AlN is achieved by sputtering a 2Ti:Al target in an Ar/N₂ mixture [97, 98] or from single-component Ti and Al targets [96, 99–101]. There have been other attempts at reactive deposition of MAX phase nitrides, particularly in the Sc-Al-N system [102, 103]. This can be explained by the extremely narrow process window in terms of the partial pressure of N₂ for depositing the monophase coating [96, 98]. An attempt at reactive deposition of MAX carbonitride coatings was made in [86]. The deposition was performed by sputtering targets of the MAX phases Ti_{2-x}Cr_xAlC (where x = 0, 0.5, 1.5, and 2) in an Ar atmosphere or in a gas mixture of Ar+N₂, which allowed comparative studies of the structure and properties of TiAlC(N), TiCrAlC(N), and CrAlC(N) coatings. The coatings had a lower Al content than the targets, which prevented the formation of MAX phases. The exception is the Cr₂AlC MAX phase, which crystallizes in the TiCrAlC coating (x = 1.5) deposited at a substrate temperature of 300 °C under conditions of a relatively high bias potential of -250 V.

Reactive deposition of carbides typically uses acetylene or methane as the carbon source [15]. For example, in [77] Cr₂AlC-based coatings were deposited by co-sputtering Cr₂Al and Al targets in a CH₄/Ar atmosphere followed by annealing at 750 °C. The atomic content of Al was controlled by changing the current of the Al target. However, due to the relative ease with which MAX carbides can be grown using other deposition schemes, there is not much interest in using the reactive method for the synthesis of magnetron MAX carbides [55, 56, 85].

It should be noted that the deposition of high quality magnetron coatings requires careful attention to purity. Imperfect vacuum conditions or insufficient purity of the working gas can lead to contamination of the coatings with unwanted impurities. In particular, J.J. Li et al. [71] reported that DC magnetron coatings of Cr₂AlC had an oxide sublayer on the substrate due to water desorption in the chamber at the beginning of deposition.

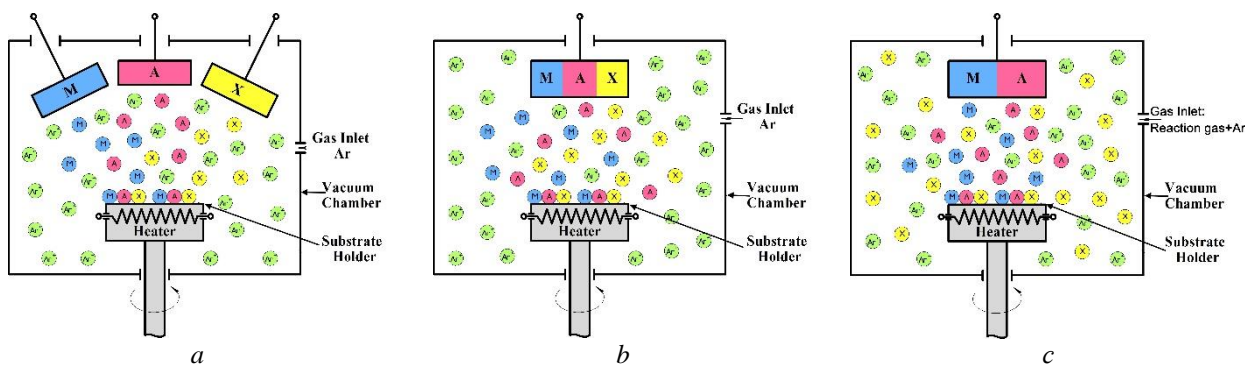


Fig. 7. Typical schemes for the deposition of coatings of MAX phases by magnetron and cathodic arc methods: a – each element M, A, X has its own cathode (target); b – a composite cathode (target) containing all the necessary components is used; c – reactive deposition, when the source of X is a reaction gas, and a cathode (target) is used for M and A

The possibility of a one-step synthesis of MAX phases at a reduced deposition temperature is primarily determined by the high energy of the particles that form the coating. The low degree of ionization of the flow of film-forming particles in DC magnetron sputtering does not allow for the effective implementation of the energy control mechanism using a negative bias potential on the substrate. An innovative approach is to apply high-power pulses to the target rather than DC [43]. This technique is called high-power pulsed magnetron sputtering (HIPIMS) and somewhat imitates cathodic arc deposition, but without the corresponding disadvantages [44]. Powerful pulses applied to the target create a highly ionized deposition stream, allowing the composition of the stream and the distribution of ion energy to be controlled by applied electric and magnetic fields. The deposition rate of coatings is typically 2...3 $\mu\text{m/h}$. HIPIMS facilitates the production of denser, smoother coatings with a specific texture and morphology compared to the DC method [43, 44, 48]. Using the Ti-Si-C system as an example, it has been shown that for HIPIMS deposition from a complex target, the degree of ionization is a particularly important parameter, which differs between elements (e.g. several percent for C and up to 90% for Ti). This means that controlling the structure and composition of the film requires careful selection of process parameters such as pressure, substrate angle and bias potential. In addition, the C content is strongly influenced by the gas phase, which is similar to the results for DC magnetron sputtering [104].

At certain deposition parameters, the problem of composition mismatch between the film and the target can be aggravated by the HIPIMS method [110, 111]. The Cr-Al-C composite target was sputtered using direct current magnetron sputtering (DCMS, 2.3 W/cm^2) and high power pulsed magnetron sputtering (HPPMS, 373 W/cm^2). At floating potential, Cr-Al-C thin films had the same composition regardless of the power density applied. However, when the substrate bias potential was increased to -400 V, an aluminum deficit of 1.6 times for DCMS and 4.1 times for HPPMS was obtained. When the substrate temperature was increased to 560 $^{\circ}\text{C}$, the Al concentration decreased by a factor of 1.9 compared to room temperature deposition. This additional decrease can be explained by the fact that

thermally induced desorption is active in addition to re-sputtering [110]. Nevertheless, in [107] the MAX phase Cr_2AlC was successfully synthesized using a split $\text{Cr}_{0.46}\text{-Al}_{0.25}\text{-C}_{0.29}/\text{Cr}_{0.15}\text{-Al}_{0.75}\text{-C}_{0.10}$ composite target, which compensates for the lack of Al. The authors note that it is inappropriate to reduce the substrate bias potential to -200 and -100 V when using DCMS and HPPMS, respectively. There is an optimal moderate ion energy for the formation of dense Cr_2AlC films. Too low energy will result in insufficiently dense coatings. Too high energy results in the formation of $(\text{Cr, Al})_2\text{C}_x$ carbide in addition to Cr_2AlC .

In a number of studies, during the synthesis of Ti_2AlN , Ti_2AlC , and Cr_2AlC , it was possible to prevent a significant difference between the elemental composition of the targets and the HIPIMS films [105, 106, 108, 109]. Under these conditions, the mechanism of MAX phase formation in the films was determined by the deposition temperature. At room temperature, the films had an amorphous structure and annealing was required for the formation of MAX phases. Increasing the temperature promoted the formation of MAX phases directly during deposition, but they coexisted with other phases [105, 109].

2.2.2. Cathodic arc deposition

Cathodic arc deposition has not been as widely used as magnetron sputtering for the synthesis of MAX phases due to the higher complexity of the process and equipment [112–118]. The process is based on the generation of highly ionized plasma fluxes by an arc discharge. An electrically conductive material is used as a cathode. In particular, cathodes based on MAX phases show good performance and high deposition rates, in particular for the Ti_2AlC cathode, the rate is about 5 $\mu\text{m/h}$ [117]. In contrast to the magnetron method, the cathodic arc process does not require the use of an inert gas, thus avoiding the introduction of undesirable gas impurities into the coating. The high degree of ionization of the cathodic arc plasma (70...90%), including for all elements of complex cathodes, and the ability to adjust the synthesis process parameters in a wide range allow flexible and targeted influence on the structural properties of coatings. The cathodic arc method allows better control of the ion energy to reduce

the deposition temperature compared to magnetron sputtering [44, 45].

The peculiarity and disadvantage of arc discharge is the presence of cathode material droplets in the plasma flow – macroparticles, which, when they enter the coating, disrupt its homogeneity and lead to an increase in surface roughness, deterioration of adhesion, which can adversely affect the performance of coatings. Typically, the size of macroparticles in coatings is in the range of 0.1...10 μm [45]. The presence of macroparticles is acceptable for many industrial applications of cathodic arc technology, however, when synthesizing MAX phases, it is advisable to prevent the ingress of macroparticles into the coating. This can be achieved by using a pulsed discharge current mode [112, 113] or by using magnetoelectric filters [115], although the presence of filters reduces the performance of the process.

For the synthesis of cathodic arc coatings, the same schemes for the deposition of MAX phase coatings as for magnetron sputtering can be used: from one or more cathodes, as well as reactive deposition (see Fig. 7). In [112, 113] the synthesis of epitaxial Ti_2AlC was reported using a pulsed cathodic arc setup from elemental Ti, Al and C cathodes at a substrate temperature of 900 °C. However, initial attempts at cathodic arc deposition of the MAX phase from a single Ti_2AlC cathode were not successful [117]. Similar to magnetron deposition, the synthesis of Ti-Al-C coatings faces the problem of mismatch between the composition of the cathodes based on the MAX phase and the coatings [117, 118]. In particular, when using a Ti_2AlC cathode and a bias potential of -100 V on the substrate, a significant decrease in the aluminum content in vacuum arc coatings is observed. The atomic ratio of the components in the coating is Ti:Al:C = 9:1:4 and the MAX phase is not formed [117].

The cathodic arc method is traditionally used for the reactive deposition of protective coatings based on nitrides, oxides, and carbides of transition metals. The advantages of reactive deposition are that complex refractory compounds can be formed using easily fabricated metal targets. Therefore, reactive deposition looks quite attractive for cathodic arc synthesis of MAX phases. The review [15] reports on the reactive cathodic arc deposition of Ti_2AlN coatings from a 2Ti:Al cathode. It is noteworthy that in this way it was possible to deposit Ti_2AlN on a substrate at a temperature of 500 °C, which is ~ 200 °C lower than reported for sputtering.

In [114–116], the formation of the MAX phases Ti_2AlC and Ti_3AlC_2 was observed by a two-stage reactive cathodic arc deposition from Ti-Al alloy cathodes in a $\text{C}_2\text{H}_2/\text{Ar}$ gas mixture followed by vacuum annealing. The study revealed that the MAX phase formation in the annealed coating is contingent upon the C_2H_2 flow rate during deposition, cathode composition, and annealing temperature. It appears that the optimal conditions for the process are an annealing temperature of 800 °C and a $\text{C}_2\text{H}_2/\text{Ar}$ ratio of 1/4. When annealed at 800 °C, only the MAX phase Ti_2AlC was formed from the 1Ti-2Al target, whereas annealing of the 1Ti-1Al

target produced three carbides, including the MAX phases Ti_2AlC and Ti_3AlC_2 [114].

The cathodic arc deposition method of MAX phases shows potential and warrants further investigation. It is especially interesting to conduct an extensive examination of the impact of substrate bias potential on the composition and structure of coatings during the formation process.

2.2.3. Pulsed laser deposition

PLD is less studied than other PVD methods, despite the possibility of depositing some MAX phases at substrate temperatures below even 300 °C [119]. The method produces materials with much higher energy than sputtering. A high power pulsed laser beam evaporates a single target of a suitable composition in a high vacuum chamber and has the ability to reproduce the elemental composition well and provide high purity, but in the case of MAX phases, some carbides between nanometer grains are usually detected, amorphous structures are formed, or concentration gradients are found within the films [120]. There have been several unconvincing attempts to synthesize Ti_3SiC_2 at low temperatures [121–123]. However, 80 nm thick Ti_3SiC_2 films have recently been synthesized at a substrate temperature of Al_2O_3 (0001) close to 700 °C [124]. It has also been possible to grow thin (up to 50 nm) epitaxial films of the MAX phase of Cr_2AlC on $\text{MgO}(111)$ and Al_2O_3 (0001) substrates at 600 °C [125]. So far, no clear growth models for such films have been presented, but the high potential of PLDs calls for further research.

2.2.4. Combined methods

The original deposition method, combining magnetron and cathodic arc deposition, was used by the authors of [126–131] to synthesize MAX coatings of Ti_2AlN , Ti_2AlC , V_2AlC , and Cr_2AlC phases. A schematic diagram of the coating synthesis equipment is shown in Fig. 8,a. An Al target was used for magnetron sputtering, and Ti, V, and Cr cathodes were used as the arc source. The reactive gases N_2 and CH_4 were used as nitrogen and carbon sources, respectively. This approach combines the advantages of both methods and provides flexible control of the elemental composition at a high deposition rate and a reduced content of macroparticles that would be generated by a cathode containing low-melting Al. In the first step, amorphous coatings were deposited at a low substrate temperature of 200 °C, and the synthesis of MAX phases took place in the second step, which was the vacuum annealing of the samples. Thanks to in-situ X-ray diffraction analysis, the authors were able to thoroughly investigate the effect of annealing temperature on the phase composition of M-Al-C coatings. Fig. 8,b shows the details of the sequential formation and decomposition of the MAX phases in the coatings as a function of the annealing temperature, which increases from room temperature (RT, ~ 25 °C) to 900 °C [131]. The results show that the formation and decomposition temperatures of Ti_2AlC were higher than those of V_2AlC and Cr_2AlC coatings, which is in good agreement with the results of theoretical calculations

based on density functional theory (DFT). In addition, there were no intermediate phases before the appearance of the Ti_2AlC MAX phase, unlike V_2AlC and Cr_2AlC , whose appearance was preceded by the formation of V_2C and Cr_2C , respectively.

Among the combined ion-plasma deposition methods is the approach used by the authors of [132]. The coating was deposited by sputtering a target based on the MAX phase of Ti_2AlC using a gas plasma source operating on the basis of a low-pressure arc discharge with a hot cathode. Target sputtering was performed by gas ions extracted from the discharge plasma when a

negative bias potential was applied to the target. Ar was used as the working gas. It was found that Ti_2AlC is a relatively difficult material to sputter, with a sputtering coefficient 1.5 times lower than that of Ti. In addition, as a result of ion sputtering, phase transformations occur on the target surface associated with the decay of the MAX phase and the selective sputtering of light elements, which makes it difficult to control the elemental composition of the coatings. It has been found that the composition of deposited coatings is significantly influenced by the value of the negative bias potential on the substrate.

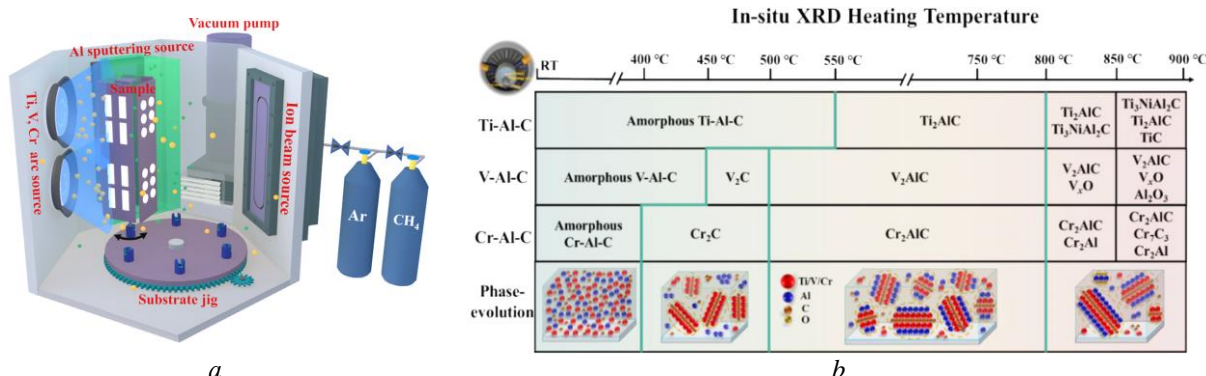


Fig. 8. Schematic diagram of the combined cathodic arc / magnetron deposition scheme (a), phase composition and schematic diagram of M-Al-C coatings formation as a function of annealing temperature according to the results of in-situ X-ray diffraction analysis (b) [131]

CONCLUSIONS

Advanced methods in surface modification technologies that enable the creation of new coatings with multifunctional properties are in demand for the advancement of future engineering applications. In recent decades, materials with $M_{n+1}AX_n$ (MAX) phases, which have a nanolaminate hexagonal crystal structure with mixed bonding, have attracted considerable attention from the scientific community due to their unique and unusual combination of metallic and ceramic properties. Another advantage of MAX phases is the ease with which their chemical composition can be modified and customized, including the formation of solid solutions, while maintaining their original structure. New compounds and possible elements of MAX phases are still being discovered, so this family of materials is expanding every month, revealing interesting hybrid properties. However, the high synthesis temperatures are a major obstacle to the widespread use of MAX phase coatings.

High-quality, high-purity and dense MAX phase thin films can be deposited by ion-plasma PVD methods at relatively low temperatures, which is certainly critical for coatings on sensitive substrates. The reduction of the synthesis temperature is due to the additional energy flow resulting from the bombardment of the growth surface with energetic particles. The most widely studied method is magnetron sputtering. Cathodic arc and laser deposition are less studied, although they have great potential for further reducing the synthesis temperature of coatings.

Several schemes have been developed for the deposition of coatings based on MAX phases: from a multicomponent cathode (target), from several different

cathodes (targets), and by reactive deposition. Provided that the appropriate elemental composition of the coating on the substrate surface is maintained, there are two approaches to the synthesis of the MAX phase. First, the process can be performed in a single step, which requires a higher substrate temperature or energy of the particles forming the coating. Second, a stepwise process can be used, in which films of the desired stoichiometry are deposited at low temperature followed by heat treatment.

Despite significant progress in the development of methods for depositing MAX phase coatings, further work is necessary to transfer technologies to the market. Successful production of MAX phases requires systematic research to clearly define the relationship between energy, thermodynamic synthesis parameters, and the structure and properties of coatings from different systems.

ACKNOWLEDGEMENTS

The work was financially supported by The European Federation of Academies of Sciences and Humanities (ALLEA), within the framework the “European Fund for Displaced Scientists”, Grant EFDS-FL2-04 and by the National Academy of Science of Ukraine (program “Support of the development of main lines of scientific investigations” (KPKVK 6541230)).

REFERENCES

1. M.W. Barsoum. The $M_{n+1}AX_n$: a new class of solids; thermodynamically stable nanolaminates // *Prog. Solid St. Chem.* 2000, v. 28, p. 201-281.
2. J. Gonzalez-Julian. Processing of MAX phases: From synthesis to applications // *J. Am. Ceram. Soc.* 2021, v. 104, p. 659-690.

3. Z. Zhang, X. Duan, D. Jia, Y. Zhou, S. Van Der Zwaag. On the formation mechanisms and properties of MAX phases: A review // *J. Eur. Ceram. Soc.* 2021, v. 41, p. 3851-3878.
4. N. Goossens, B. Tunca, T. Lapauw, K. Lambri-nou, J. Vleugels. *MAX Phases, Structure, Processing, and Properties: Encyclopedia of Materials: Technical Ceramics and Glasses* / Ed. M. Pomeroy. Oxford: Elsevier, 2021, p. 182-199.
5. M. Sokol, V. Natu, S. Kota, M.W. Barsoum. On the Chemical Diversity of the MAX Phases // *Trends in Chemistry.* 2019, v. 1, N 2, p. 210-223.
6. W. Jeitschko, H. Nowotny, F. Benesovsky. Kohlenstoffhaltige ternäre Verbindungen (H-Phase) // *Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.* 1963, v. 94, p. 672-676.
7. H. Nowotny, J.C. Schuster, P. Rogl. Structural chemistry of complex carbides and related compounds // *J. Solid State Chem.* 1982, v. 44, p. 126-133.
8. M.W. Barsoum, T. El-Raghy. Synthesis and characterization of a remarkable ceramic: Ti_3SiC_2 // *J. Am. Ceram. Soc.* 1996, v. 79, p. 1953-1956.
9. M.W. Barsoum, T. El-Raghy. The MAX phases: unique new carbide and nitride materials: ternary ceramics turn out to be surprisingly soft and machinable, yet also heat-tolerant, strong and lightweight // *American Scientist.* 2001, v. 89, N4, p. 334-343.
10. M.W. Barsoum, *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides.* Weinheim: Wiley-VCH, 2013, 436 p.
11. M.W. Barsoum, M. Radovic. Elastic and Mechanical Properties of the MAX Phases // *Annu. Rev. Mater. Res.* 2011, v. 41, p. 195-227.
12. J. Lyu, E.B. Kashkarov, N. Travitzky, M.S. Syrtanov, A.M. Lider. Sintering of MAX-phase materials by spark plasma and other methods // *J. Materials Science.* 2021, v. 56, p. 1980-2015.
13. A.V. Starostina, T.A. Prikhna, M.V. Karpets, S.N. Dub, P. Chartier, T. Cabiosh, V.B. Sverdun, V.E. Moshchil, A.V. Kozyrev. Synthesis of ternary compound of the Ti-Al-C system at high pressures and temperatures // *J. Superhard Mater.* 2011, v. 33, p. 307-314.
14. T.A. Prikhna, S.N. Dub, A.V. Starostina, M.V. Karpets, T. Cabiosh, P. Chartier. Mechanical properties of materials based on MAX phases of the Ti-Al-C system // *J. Superhard Mater.* 2012, v. 34, p. 102-109.
15. P. Eklund, M. Beckers, U. Jansson, H. Högberg, L. Hultman. The $M_{n+1}AX_n$ phases: Materials science and thin-film processing // *Thin Solid Films.* 2010, 518, v. 8, p. 1851-1878.
16. O. Berger. The correlation between structure, multifunctional properties and application of PVD MAX phase coatings. Part I. Texture and room temperature properties // *Surface Engineering.* 2020, v. 36, N 3, p. 225-267.
17. O. Berger. The correlation between structure, multifunctional properties and applications of PVD MAX phase coatings. Part II. Texture and high-temperature properties // *Surface Engineering.* 2020, v. 36, N 3, p. 268-302.
18. O. Berger. The correlation between structure, multifunctional properties and application of PVD MAX phase coatings. Part III. Multifunctional applications. *Surface Engineering // Surface Engineering.* 2020, v. 36, N 3, p. 303-325.
19. A. Biswas, V. Natu, A. B. Puthirath. Thin film growth of MAX phases as functional materials // *Oxford Open Materials Science.* 2021, v. 1, N1, itab020.
20. T. Rackl, D. Johrendt. The MAX phase borides Zr_2SB and Hf_2SB // *Solid State Sci.* 2020, v. 106, p. 106316.
21. Q. Zhang, Y. Zhou, X. San, W. Li, Y. Bao, Q. Feng, S. Grasso, C. Hu. Zr_2SeB and Hf_2SeB : Two new MAB phase compounds with the Cr_2AlC -type MAX phase (211 phase) crystal structures // *J. Advanced Ceramics.* 2022, v. 11, N11, p. 1764-1776.
22. A. Carlsson, J. Rosen, M. Dahlqvist. Theoretical predictions of phase stability for orthorhombic and hexagonal ternary MAB phases // *Phys. Chem. Chem. Phys.* 2022, v. 24, N18, p. 11249-11258.
23. C. Hu, H. Zhang, F. Li, Q. Huang, Y. Bao. New phases' discovery in MAX family // *Int. J. Refract. Met. Hard Mater.* 2013, v. 36, p. 300-312.
24. N. Markocsan, D. Manitsas, J. Jiang, S. Björklund. MAX phase Coatings Produced by Thermal Spraying // *J. Superhard Mater.* 2017, v. 39, N5, p. 355-364.
25. V. Pasumarthi, Y. Chen, S.R. Bakshi, A. Agarwal. Reaction synthesis of Ti_3SiC_2 phase in plasma sprayed coating // *J Alloy Compd.* 2009, v. 484, N1-2, p. 113-117.
26. F. Zhang, S. Yan, C. Li, Y. Ding, J. He, F. Yin. Synthesis and characterization of MAX phase Cr_2AlC based composite coatings by plasma spraying and post annealing // *J. Eur. Ceram. Soc.* 2019, v. 39, N16, p. 5132-5139.
27. J. Frodelius, M. Sonestedt, S. Björklund, J.P. Palmquist, K. Stiller, H. Hogberg, L. Hultman. Ti_2AlC coatings deposited by high velocity oxy-fuel spraying // *Surf. Coat. Technol.* 2008, v. 202, N24, p. 5976-5981.
28. Y. Chen, M. Chu, L. Wang, Z. Shi, X. Wang, B. Zhang. Microstructure and performance of Cr_2AlC coatings deposited by HVOF spraying // *Chin. J. Rare Met.* 2012, v. 36, p. 568-573.
29. J. Jiang, A. Fasth, P. Nylen, W.B. Choi. Microindentation and inverse analysis to characterize elastic-plastic properties for thermal sprayed Ti_2AlC and $NiCoCrAlY$ // *J. Therm. Spray Technol.* 2009, v. 18, N2, p. 194-200.
30. M. Sonestedt, J. Frodelius, J.P. Palmquist, H. Hogberg, L. Hultman, K. Stiller. Microstructure of high velocity oxy-fuel sprayed Ti_2AlC coatings // *J. Mater. Sci.* 2010, v. 45, N10, p. 2760-2769.
31. Z. Zhang, S.H. Lim, J. Chai, D.M.Y. Lai, P.C. Lim, A.K.H. Cheong, S. Wang, H. Jin, J. Pan. Kerosene-fuelled high velocity oxy-fuel (HVOF) spray of Ti_2AlC MAX phase powders // *J. Alloy. Compd.* 2018, v. 735, p. 377-385.
32. W. Zhang, S. Li, X. Zhang, X. Chen. Research and Development on Cold-Sprayed MAX Phase Coatings // *Coatings.* 2023, v. 13, N5, p. 869 (15).

33. T. Go, Y.J. Sohn, G. Mauer, R. Vaßen, J. Gonzalez-Julian. Cold spray deposition of Cr₂AlC MAX phase for coatings and bond-coat layers // *J. Eur. Ceram. Soc.* 2019, v. 39, N4, p. 860-867.
34. A. Elsenberg, M. Busato, F. Gartner, A. List, A. Bruera, G. Bolelli, L. Lusvardi. Influence of MAX-Phase Deformability on Coating Formation by Cold Spraying // *J. Thermal Spray Technology*. 2021, v. 30, p. 617-642.
35. X. Li, C.H. Zhang, S. Zhang, C.L. Wu, Y. Liu, J.B. Zhang, M.B. Shahzad. Manufacturing of Ti₃SiC₂ lubricated Co-based alloy coatings using laser cladding technology // *Optics and Laser Technology*. 2019, v. 114, p. 209-215.
36. Y. Tian, H. Xiao, L. Ren, J. Feng, Y. Xiao, N. Chen, X. Zhou. A new strategy to fabricate Ti₂AlC MAX coatings by the two-step laser method // *Surf. Coat. Technol.* 2022, v. 448, p. 128944.
37. P. Richardson, D. Cuskelly, M. Brandt, E. Kisi. Microstructural analysis of in-situ reacted Ti₂AlC MAX phase composite coating by laser cladding // *Surf. Coat. Technol.* 2020, v. 385, p. 125360.
38. T. Goto, T. Hirai. Chemically vapor deposited Ti₃SiC₂. // *Mater Res Bull.* 1987, v. 22, p. 1195-1201.
39. C. Racault, F. Langlais, R. Naslain, Y. Kihn. On the chemical vapour deposition of Ti₃SiC₂ from TiCl₄-SiCl₄-CH₄-H₂ gas mixtures. Part II. An experimental approach // *J. Mater. Sci.* 1994, v. 29, p. 3941-3948.
40. H. Fakih, S. Jacques, M.-P. Berthet, F. Bosselet, O. Dezellus, J.-C. Viala. The growth of Ti₃SiC₂ coatings onto SiC by reactive chemical vapor deposition using H₂ and TiCl₄ // *Surf. Coat. Technol.* 2006, v. 201, p. 3748-3755.
41. J.S. Espinoza, F. Trabelsi, C. Escape, L. Charpentier, M. Fivel, E. Blanquet, F. Mercier. Ti₃SiC₂-SiC multilayer thin films deposited by high temperature reactive chemical vapor deposition // *Surf. Coat. Technol.* 2022, v. 447, p. 128815.
42. D.M. Mattox. *Handbook of Physical Vapor Deposition (PVD) Processing: Film Formation, Adhesion, Surface Preparation and Contamination Control*. Westwood, N.J.: Noyes Publications, 1998, 945 p.
43. G. Greczynski, I. Petrov, J.E. Greene, L. Hultman. Paradigm shift in thin-film growth by magnetron sputtering: From gas-ion to metal-ion irradiation of the growing film // *J. Vac. Sc. Technol. A*. 2019, v. 37, N2, p. 060801.
44. A. Anders. A review comparing cathodic arcs and high power impulse magnetron sputtering (HiPIMS) // *Surf. Coat. Technol.* 2014, v. 257, p. 308-325.
45. A. Anders. *Cathodic Arcs: From Fractal Spots to Energetic Condensation*. New York: Springer Inc., 2008, 540 p.
46. B. Subedi, V.S. Puli, I.W. Boyd, D.B. Chrisey. Pulsed Laser Deposition of Thin Films // *Handbook of Laser Technology and Applications* / Eds C. Guo, S.C. Sing. Boca Raton, FL: CRC Press, 2021, p. 111124.
47. A. Anders. A structure zone diagram including plasma-based deposition and ion etching // *Thin Solid Films*. 2010, v. 518, p. 4087-4090.
48. D. Manova, J.W. Gerlach, S. Mandl. Thin Film Deposition Using Energetic Ions // *Materials*. 2010, v. 3, p. 4109-4141.
49. J. Frodelius, P. Eklund, M. Beckers, P.O.Å. Persson, H. Högberg, L. Hultman. Sputter deposition from a Ti₂AlC target: Process characterization and conditions for growth of Ti₂AlC // *Thin Solid Films*. 2010, v. 518, p. 1621-1626.
50. R.R. Su, H.L. Zhang, D.J. O'Connor, L.Q. Shi, X.P. Meng, H.B. Zhang. Deposition and characterization of Ti₂AlC MAX phase and Ti₃AlC thin films by magnetron sputtering // *Mater. Lett.* 2016, v. 179, p. 194-197.
51. A. Abdulkadhim, T. Takahashi, D. Music, F. Munnik, J.M. Schneider. MAX phase formation by intercalation upon annealing of Ti_{C_x}/Al (0.4 ≤ x ≤ 1) bilayer thin films // *Acta Mater.* 2011, v. 59, p. 6168-6175.
52. C. Tang, M. Klimenkov, U. Jaentsch, H. Leiste, M. Rinke, S. Ulrich, M. Steinbrück, H.J. Seifert, M. Stueber. Synthesis and characterization of Ti₂AlC coatings by magnetron sputtering from three elemental targets and ex-situ annealing // *Surf. Coat. Technol.* 2017, v. 309, p. 445-455.
53. Y. Li, G. Zhao, Y. Qian, J. Xu, M. Li. Deposition and characterization of phase-pure Ti₂AlC and Ti₃AlC₂ coatings by DC magnetron sputtering with cost-effective targets // *Vacuum*. 2018, v. 153, p. 62-69.
54. O. Wilhelmsson, J.P. Palmquist, E. Lewin, J. Emmerlich, P. Eklund, P.O.Å. Persson, H. Högberg, S. Li, R. Ahuja, O. Eriksson, L. Hultman, U. Jansson. Deposition and characterization of ternary thin films within the Ti-Al-C system by DC magnetron sputtering // *J. Cryst. Growth*. 2006, v. 291, p. 290.
55. Z. Feng, P. Ke, A. Wang. Preparation of Ti₂AlC MAX Phase Coating by DC Magnetron Sputtering Deposition and Vacuum Heat Treatment // *J. Mater. Sci. Technol.* 2015, v. 31, p. 1193-1197.
56. Z. Feng, P. Ke, Q. Huang, A. Wang. The scaling behavior and mechanism of Ti₂AlC MAX phase coatings in air and pure water vapor // *Surf. Coat. Technol.* 2015, v. 272, p. 380-386.
57. O. Wilhelmsson, J.P. Palmquist, T. Nyberg, U. Jansson. Deposition of Ti₂AlC and Ti₃AlC₂ epitaxial films by magnetron sputtering // *Appl. Phys. Lett.* 2004, v. 85, p. 1066.
58. N. Laska, P. Bauer, O. Helle, F. Kreps. Sputtering and Characterization of MAX-Phase Forming Cr-Al-C and Ti-Al-C Coatings and Their Application on γ-Based Titanium Aluminides // *Adv. Eng. Mater.* 2022, v. 24, p. 2100722.
59. T. Sonoda, S. Nakao, M. Ikeyama. Deposition and characterization of MAX-phase containing Ti-Si-C thin films by sputtering using elemental targets // *Vacuum*. 2013, v. 92, p. 95-99.
60. J. Emmerlich, H. Högberg, S. Sasvári, P.O.Å. Persson, L. Hultman, J.-P. Palmquist, U. Jansson, J.M. Molina-Aldareguia, Z. Czígány. Growth of Ti₃SiC₂ thin films by elemental target magnetron sputtering // *J. Appl. Phys.* 2004, v. 96, N9, p. 4817-4826.
61. J.-P. Palmquist, S. Li, P.O.Å. Persson, J. Emmerlich, O. Wilhelmsson, H. Högberg,

- M.I. Katsnelson, B. Johansson, R. Ahuja, O. Eriksson, L. Hultman, U. Jansson. $M_{n+1}AX_n$ phases in the Ti-Si-C system studied by thin-film synthesis and ab initio calculations // *Phys. Rev. B*. 2004, v. 70, N6, p. 165401.
62. P. Eklund, A. Murugaiah, J. Emmerlich, Z. Czigany, J. Frodelius, M.W. Barsoum, H. Högborg, L. Hultman. Homoepitaxial growth of Ti-Si-C MAX-phase thin films on bulk Ti_3SiC_2 substrates // *J. Cryst. Growth*, 2007, v. 304, N1, p. 264-269.
63. M. Magnuson, M. Mattesini, O. Wilhelmsson, J. Emmerlich, J.-P. Palmquist, S. Li, R. Ahuja, L. Hultman, O. Eriksson, U. Jansson. Electronic structure and chemical bonding in Ti_4SiC_3 investigated by soft X-ray emission spectroscopy and first-principles theory // *Phys. Rev. B*. 2006, v. 74, p. 205102.
64. P. Eklund, M. Beckers, J. Frodelius, H. Högborg, L. Hultman. Magnetron sputtering of Ti_3SiC_2 thin films from a compound target // *J. Vac. Sci. Technol. A*. 2007, v. 25, p. 1381-1388.
65. Z. Sun, J. Zhou, D. Music, R. Ahuja, J.M. Schneider. Phase stability of Ti_3SiC_2 at elevated temperatures // *Scripta Mater.* 2006, v. 54, N1, p. 105-107.
66. M. Magnuson, L. Tengdelius, G. Greczynski, F. Eriksson, J. Jensen, J. Lu, M. Samuelsson, P. Eklund, L. Hultman, H. Högborg. Compositional dependence of epitaxial $Ti_{n+1}SiC_n$ MAX-phase thin films grown from a Ti_3SiC_2 compound target // *J. Vac. Sci. Technol. A*. 2019, v. 37, p. 021506.
67. C. Walter, D.P. Sigumonrong, T. El-Raghy, J.M. Schneider. Towards large area deposition of Cr_2AlC on steel // *Thin Solid Films*. 2006, v. 515, N2, p. 389-393.
68. Q.M. Wang, A. Flores Renteria, O. Schroeter, R. Mykhalonka, C. Leyens, W. Garkas, M. to Baben. Fabrication and oxidation behavior of Cr_2AlC coating on Ti6242 alloy // *Surf. Coat. Technol.* 2010, v. 204, N15, p. 2343-2352.
69. S. Mraz, M. Tyra, M. to Baben, M. Hans, X. Chen, F. Herrig, K. Lambrinou, J.M. Schneider. Thermal stability enhancement of Cr_2AlC coatings on Zr by utilizing a double layer diffusion barrier // *J. Eur. Ceram. Soc.* 2020, v. 40, N4, p. 1119-1124.
70. M. Imtyazuddin, A.H. Mir, M.A. Tunes, V.M. Vishnyakov. Radiation resistance and mechanical properties of magnetron-sputtered Cr_2AlC thin films // *J. Nucl. Mater.* 2019, v. 526, p. 151742.
71. J.J. Li, L.F. Hu, F.Z. Li, M.S. Li, Y.C. Zhou. Variation of microstructure and composition of the Cr_2AlC coating prepared by sputtering at 370 and 500°C // *Surf. Coat. Technol.* 2010, v. 204, p. 3838-3845.
72. M. Naveed, A. Obrosov, A. Zak, W. Dudzinski, A.A. Volinsky, Sabine Weiß. Sputtering Power Effects on Growth and Mechanical Properties of Cr_2AlC MAX Phase Coatings // *Metals*. 2016, v. 6, N11, p. 265 (11).
73. A. Obrosov, R. Gulyaev, A. Zak, M. Ratzke, M. Naveed, W. Dudzinski, S. Weiß. Chemical and Morphological Characterization of Magnetron Sputtered at Different Bias Voltages Cr-Al-C Coatings // *Materials*. 2017, v. 10, N2, p. 156 (16).
74. D.E. Hajas, M.T. Baben, B. Hallstedt, R. Iskandar, J. Mayer, J. Schneider. Oxidation of Cr_2AlC coatings in the temperature range of 1230 to 1410°C // *Surf. Coatings Technol.* 2011, v. 206, N4, p. 591-598.
75. J.M. Schneider, D.P. Sigumonrong, D. Music, C. Walter, J. Emmerlich, R. Iskandar, J. Mayer. Elastic properties of Cr_2AlC thin films probed by nanoindentation and ab initio molecular dynamics // *Scripta Mater.* 2007, v. 57, N12, p. 1137-1140.
76. X. Chen, B. Stelzer, M. Hans, R. Iskandar, J. Mayer, J. M. Schneidera. Enhancing the high temperature oxidation behavior of Cr_2AlC coatings by reducing grain boundary nanoporosity // *Mater. Res. Lett.* 2020, v. 9, N3, p. 127-133.
77. J. Liu, X. Zuo, Z. Wang, L. Wang, X. Wu, P. Ke, A. Wang. Fabrication and mechanical properties of high purity of Cr_2AlC coatings by adjustable Al contents // *J. Alloys and Compounds*. 2018, v. 753, p. 11-17.
78. R. Grieseler, B. Hähnlein, M. Stubenrauch, T. Kups, M. Wilke, M. Hopfeld, J. Pezoldt, P. Schaaf. Nanostructured plasma etched, magnetron sputtered nanolaminar Cr_2AlC MAX phase thin films // *Applied Surface Science*. 2014, v. 292, p. 997-1001.
79. Z. Zhang, Y. Qian, J. Xu, J. Zuo, M. Li. Effect of annealing on microstructure evolution and corrosion resistance of an amorphous Cr-Al-C coating // *Corrosion Science*. 2021, v. 178, p. 10906.
80. M. Hopfeld, R. Grieseler, A. Vogel, H. Romanus, P. Schaaf. Tribological behavior of selected $M_{n+1}AX_n$ phase thin films on silicon substrates // *Surf. Coatings Technol.* 2014, v. 257, p. 286-297.
81. H. Hfgberg, L. Hultman, J. Emmerlich, T. Joelsson, P. Eklund, J.M. Molina-Aldareguia, J.-P. Palmquist, O. Wilhelmsson, U. Jansson. Growth and characterization of MAX-phase thin films // *Surf. Coatings Technol.* 2005, v. 193, N1-3, p. 6-10.
82. P. Eklund, M. Bugnet, V. Mauchamp, S. Dubois, T. Tromas, J. Jensen, L. Piraux, L. Gence, M. Jaouen, T. Cabioc'h. Epitaxial growth and electrical transport properties of Cr_2GeC thin films // *Phys Rev B*. 2011, v. 84, p. 075424.
83. H. Högborg, P. Eklund, J. Emmerlich, J. Birch, L. Hultman. Epitaxial Ti_2GeC , Ti_3GeC_2 , and Ti_4GeC_3 MAX-phase thin films grown by magnetron sputtering // *J. Mater. Res.* 2005, v. 20, p. 779.
84. C. Azina, P. Eklund. Effects of temperature and target power on the sputter-deposition of $(Ti,Zr)_{n+1}AlC_n$ MAX-phase thin films // *Results in Materials*. 2021, v. 9, p. 100159.
85. Z. Wang, J. Sun, B. Xu, Y. Liu, P. Ke, A. Wang. Reducing the self-healing temperature of Ti_2AlC MAX phase coating by substituting Al with Sn // *J. Eur. Ceram. Soc.* 2020, v. 40, p. 197-201.
86. D.V. Shtansky, Ph.V. Kiryukhantsev-Korneev, A.N. Sheveyko, B.N. Mavrin, C. Rojas, A. Fernandez, E.A. Levashov. Comparative investigation of $TiAlC(N)$, $TiCrAlC(N)$, and $CrAlC(N)$ coatings deposited by sputtering of MAX-phase $Ti_{2-x}Cr_xAlC$ targets // *Surf. Coatings Technol.* 2009, v. 203, N23, p. 3595-3609.
87. H. Högborg, J. Emmerlich, P. Eklund, O. Wilhelmsson, J.-P. Palmquist, U. Jansson, L. Hultman. Growth and Property Characterization of Epitaxial MAX-Phase Thin Films from the $Ti_{n+1}(Si, Ge, Sn)C_n$ // *Systems Adv. Sci. Technol.* 2006, v. 45, p. 2648-2655.

88. Y. Li, Y. Qian, G. Zhao, J. Xu, M. Li. Preparation of Nb₂AlC coating by DC magnetron sputtering and subsequent annealing // *Ceram. Int.* 2017, v. 43, N8, p. 6622-6625.
89. J.M. Schneider, R. Mertens, D. Music. Structure of V₂AlC Studied by Theory and Experiment // *J. Appl. Phys.* 2006, v. 99, N1, p. 013501.
90. Z. Wang, X. Li, J. Zhou, P. Liu, Q. Huang, P. Ke, A. Wang. Microstructure evolution of V-Al-C coatings synthesized from a V₂AlC compound target after vacuum annealing treatment // *J. Alloys and Compounds.* 2015, v. 661, p. 476-482.
91. R. Shu, F.F. Ge, F.P. Meng, P. Li, J. Wang, Q. Huang, P. Eklund, F. Huang. One-step synthesis of polycrystalline V₂AlC thin films on amorphous substrates by magnetron co-sputtering // *Vacuum.* 2017, v. 146, p. 106-110.
92. T.H. Scabarozzi, J. Roche, A. Rosenfeld, S.H. Lim, L. Salamanca-Riba, G. Yong, I. Takeuchi, M.W. Barsoum, J.D. Hettinger, S.E. Lofland. Synthesis and characterization of Nb₂AlC thin films // *Thin Solid Films.* 2009, v. 517, N9, p. 2920-2923.
93. T.F. Zhang, Q. Xia, Z. Wan, Q.M. Wang, K.H. Kim. Microstructures and properties of amorphous, polycrystalline, and M_{n+1}AX_n-phase Ti-Al-N films synthesized from an M_{n+1}AX_n-phase Ti₂AlN compound target // *Ceramics International.* 2019, v. 45, N 3, p. 3940-3947.
94. T. Zhanga, H. Myounga, D. Shinc, K.H. Kim. Syntheses and properties of Ti₂AlN MAX-phase films // *J. Ceram. Process. Res.* 2012, v. 13, NS1, p. 149-153.
95. C. Höglund, M. Beckers, N. Schell, J.V. Borany, J. Birch, L. Hultman. Topotaxial growth of Ti₂AlN by solid state reaction in AlN/Ti(0001) multilayer thin films // *Appl. Phys. Lett.* 2007, v. 90, p. 174106.
96. P.O.Å. Persson, S. Kodambaka, I. Petrov, L. Hultman. Epitaxial Ti₂AlN(0001) thin film deposition by dual-target reactive magnetron sputtering // *Acta Mater.* 2007, v. 55, N13, p. 4401-4407.
97. T. Joelsson, A. Hörling, J. Birch, L. Hultman. Single-crystal Ti₂AlN thin films // *Appl. Phys. Lett.* 2006, v. 86, p. 111913.
98. T. Joelsson, A. Flink, J. Birch, L. Hultman. Deposition of single-crystal Ti₂AlN thin films by reactive magnetron sputtering from a 2Ti:Al compound target // *J. Appl. Phys.* 2007, v. 102, p. 074918.
99. M. Beckers, N. Schell, R.M.S. Martins, A. Mücklich, W. Möller. Phase stability of epitaxially grown Ti₂AlN thin films // *Appl. Phys. Lett.* 2006, v. 89, p. 074101.
100. M. Beckers, N. Schell, R.M.S. Martins, A. Mücklich, W. Möller, L. Hultman. Nucleation and growth of Ti₂AlN thin films deposited by reactive magnetron sputtering onto MgO(111) // *J. Appl. Phys.* 2007, v. 102, p. 074916.
101. M. Magnuson, M. Mattesini, S. Li, C. Höglund, M. Beckers, L. Hultman, O. Eriksson. Bonding mechanism in the nitrides Ti₂AlN and TiN: An experimental and theoretical investigation // *Phys. Rev. B.* 2007, v. 76, p. 195127.
102. C. Höglund, J. Birch, M. Beckers, B. Alling, Z. Czigány, A. Mücklich, L. Hultman. Sc₃AlN – A New Perovskite // *Eur. J. Inorg. Chem.* 2008, v. 8, p. 1193-1195.
103. M. Magnuson, M. Mattesini, C. Höglund, I.A. Abrikosov, J. Birch, L. Hultman. Electronic structure investigation of the cubic inverse perovskite Sc₃AlN // *Phys. Rev. B.* 2008, v. 78, p. 235102.
104. J. Alami, P. Eklund, J. Emmerlich, O. Wilhelms-son, U. Jansson, H. Högberg, L. Hultman, U. Helmers-son. High-power impulse magnetron sputtering of Ti-Si-C thin films from a Ti₃SiC₂ compound target // *Thin Solid Films.* 2006, v. 515, p. 1731.
105. T.F. Zhang, Q.M. Wang, J. Lee, P. Ke, R. Nowak, K.H. Kim. Nanocrystalline thin films synthesized from a Ti₂AlN compound target by high power impulse magnetron sputtering technique // *Surf. Coatings Technol.* 2012, v. 212, p. 199-206.
106. J. Fu, T.F. Zhang, Q. Xia, S-H. Lim, Z. Wan, T.-W. Lee, K.H. Kim. Oxidation and Corrosion Behavior of Nanolaminated MAX-Phase Ti₂AlC Film Synthesized by High-Power Impulse Magnetron Sputtering and Annealing // *Journal of Nanomaterials.* 2015, v. 2015, Article ID 213128, 12 p.
107. H. Rueß, J. Werner, Y. Unutulmazsoy, J.W. Gerlach, X. Chen, B. Stelzer, D. Music, S. Kolozsvari, P. Polcik, T.E. Weirich, J.M. Schneider. Effect of target peak power density on the phase formation, microstructure evolution, and mechanical properties of Cr₂AlC MAX-phase coatings // *J. Eur. Ceram. Soc.* 2021, v. 41, p. 1841-1847.
108. D. Eichner, A. Schlieter, C. Leyens, L. Shang, S. Shayestehaminzadeh, J.M. Schneider. Solid particle erosion behavior of nanolaminated Cr₂AlC films // *Wear.* 2018, v. 402-403, p. 187-195.
109. O. Berger, C. Leyens, S. Heinze, R. Boucher, M. Ruhnaw. Characterization of Cr-Al-C and Cr-Al-C-Y films synthesized by High Power Impulse Magnetron Sputtering at a low deposition temperature // *Thin Solid Films.* 2015, v. 580, p. 6-11.
110. H. Rueß, M. to Baben, S. Mraz, L. Shang, P. Polcik, S. Kolozsvari, M. Hans, D. Primetzhofer, J.M. Schneider. HPPMS deposition from composite targets: Effect of two orders of magnitude target power density changes on the composition of sputtered Cr-Al-C thin films // *Vacuum*, 2017, v. 145, p. 285-289.
111. Y.-P. Chien, S. Mraz, M. Fekete, M. Hans, D. Primetzhofer, S. Kolozsvari, P. Polcik, J.M. Schneider. Deviations between film and target compositions induced by backscattered Ar during sputtering from M₂-Al-C (M=Cr, Zr, and Hf) composite targets // *Surf. Coatings Technol.* 2022, v. 446, p. 128764.
112. J. Rosén, L. Ryves, P.O.Å. Persson, M.M.M. Bilek. Deposition of epitaxial Ti₂AlC thin films by pulsed cathodic arc // *J. Appl. Phys.* 2007, v. 101, p. 56101.
113. M.C. Guenette, M.D. Tucker, M. Ionescu, M. Bilek, D.R. McKenzie. Cathodic arc co-deposition of highly oriented hexagonal Ti and Ti₂AlC MAX phase thin films // *Thin Solid Films.* 2010, v. 519, N2, p. 766-769.
114. Z. Mahmoudi, S.H. Tabaian, H.R. Rezaie, F. Mahboubi, M.J. Ghazali. Synthesis of Ti₂AlC and Ti₃AlC₂ MAX phases by arc-PVD using Ti-Al target in

- C₂H₂/Ar gas mixture and subsequent annealing // *Ceram. Int.* 2020, v. 46, N4, p. 4968-4975.
115. H. Li, H. Cao, J. Yang, Y. Li, F. Qi, N. Zhao, X. Ouyang. Influence of annealing temperature on the structure and properties of Ti₃AlC₂ coatings by FCVA method // *Materials Characterization.* 2022, v. 194, p. 112421.
116. H. Li, H. Cao, F. Liu, Y. Li, F. Qi, X. Ouyang, N. Zhao. Microstructure, mechanical and electrochemical properties of Ti₃AlC₂ coatings prepared by filtered cathode vacuum arc technology // *J. Eur. Ceram. Soc.* 2022, v. 42, N5, p. 2073-2083.
117. M.A. Bortnitskaya, E.N. Reshetnyak, A.S. Kuprin, T.A. Prikhna, V.B. Sverdun, I.V. Kolodiy, V.A. Belous, V.G. Marinin, T.B. Serbenyuk. Structure and Mechanical Characteristics of Ti₂AlC MAX phase cathodes and cepsited ion-plasma coatings // *J. Nano- and Electronic Physics.* 2021, v. 13, N5, p. 05031 (7).
118. T.A. Prikhna, O.P. Ostash, A.S. Kuprin, V.Ya. Podhurska, T.B. Serbenyuk, E. S. Gevorkyan, M. Rucki, W. Zurowski, W. Kucharczyk, V.B. Sverdun, M.V. Karpets, S.S. Ponomaryov, B.D. Vasylyv, V.E. Moshchil, M.A. Bortnitskaya. A new MAX phases-based electroconductive coating for high-temperature oxidizing environment // *Composite Structures.* 2021, v. 277, p. 114649.
119. J.J. Hu, J.E. Bultman, S. Patton, J.S. Zabinski, T. Ti. Pulsed laser deposition and properties of M_{n+1}AX_n phase formulated Ti₃SiC₂ thin films // *Tribol Lett.* 2004, v. 16, N1-2, p. 113-22.
120. C. Lange, M. Hopfeld, M. Wilke, J. Schawohl, T. Kups, M.W. Barsoum. Pulsed laser deposition from a pre-synthesized Cr₂AlC MAX phase target with and without ion-beam assistance // *Physica Status Solidi (A).* 2012, v. 209, N3, p. 545-552.
121. J.J. Hu, J.S. Zabinski. Reply to the comment on 'Pulsed laser deposition and properties of M_{n+1}AX_n phase formulated Ti₃SiC₂ thin films' // *Tribol Lett.* 2004, v. 17, p. 979-982.
122. P. Eklund, J.P. Palmquist, O. Wilhelmsson, U. Jansson, J. Emmerlich, H. Högberg, L. Hultman. Comment on 'Pulsed laser deposition and properties of M_{n+1}AX_n phase formulated Ti₃SiC₂ thin films' // *Tribol Lett.* 2004, v. 17, p. 977-978.
123. C. Lange, M.W. Barsoum, P. Schaaf. Towards the synthesis of MAX-phase functional coatings by pulsed laser deposition // *Appl. Surf. Sci.* 2007, v. 254, N4, p. 1232-1235.
124. A. Biswas, A. Sengupta, U. Rajput, S.K. Singh, V. Antad, Sk.M. Hossain, S. Parmar, D. Rout, A. Deshpande, S. Nair, S. Ogale. Growth, properties, and applications of pulsed laser deposited nanolaminate Ti₃AlC₂ thin films // *Phys. Rev. Appl.* 2020, v. 13, p. 044075.
125. M. Stevens, H. Pazniak, A. Jemiola, M. Felek, M. Farle, U. Wiedwald. Pulsed laser deposition of epitaxial Cr₂AlC MAX phase thin films on MgO(111) and Al₂O₃(0001) // *Mater. Res. Lett.* 2021, v. 9, N8, p. 343-349.
126. Z. Wang, W. Li, Y. Liu, J. Shuai, P. Ke, A. Wang. Diffusion-controlled intercalation approach to synthesize the Ti₂AlC MAX phase coatings at low temperature of 550 °C // *Appl. Surf. Sci.* 2020, v. 502, p. 144130.
127. Z.Y. Wang, J.Z. Liu, L. Wang, X.W. Li, P.L. Ke, A.Y. Wang. Dense and high-stability Ti₂AlN MAX phase coatings prepared by the combined cathodic arc/sputter technique // *Appl. Surf. Sci.* 2017, v. 396, p. 1435-1442.
128. Z.Y. Wang, X.W. Li, J. Zhou, P. Liu, Q. Huang, P.L. Ke, A.Y. Wang. Microstructure evolution of V-Al-C coatings synthesized from a V₂AlC compound target after vacuum annealing treatment // *J. Alloys Compd.* 2016, v. 661, p. 476-482.
129. G. Ma, D. Zhang, P. Guo, H. Li, Y. Xin, Z. Wang, A. Wang. Phase orientation improved the corrosion resistance and conductivity of Cr₂AlC coatings for metal bipolar plates // *J. Mater. Sci. Technol.* 2022, v. 105, p. 36-44.
130. Z. Wang, G. Ma, L. Liu, L. Wang, P. Ke, Q. Xue, A. Wang. High-performance Cr₂AlC MAX phase coatings: Oxidation mechanisms in the 900–1100 °C temperature range // *Corrosion Science.* 2020, v. 167, p. 108492.
131. J. Yuan, Z. Wang, G. Ma, X. Bai, Y. Li, X. Cheng, P. Ke, A. Wang. MAX phase forming mechanism of M-Al-C (M = Ti, V, Cr) coatings: In-situ X-ray diffraction and first-principle calculations // *J. Mater. Sci. Technol.* 2023, v. 143, p. 140-152.
132. A.S. Kuprin, T.A. Prikhna, E.N. Reshetnyak, M.A. Bortnitskaya, I.V. Kolodiy, V.A. Belous, S.N. Dub, A.V. Ilchenko, V.B. Sverdun. Coating Deposition by Ion-plasma Sputtering of MAX Phase Ti₂AlC Target // *J. Nano- and Electronic Physics.* 2020, v. 12, N5, p. 05011(6).

Article received 25.08.2023

СИНТЕЗ, СТРУКТУРА ТА МЕХАНІЧНІ ВЛАСТИВОСТІ PVD-ПОКРИТТІВ МАХ-ФАЗ. ОГЛЯД. ЧАСТИНА І. ОСАДЖЕННЯ ПОКРИТТІВ МАХ-ФАЗ

О.М. Решетняк, О.С. Купрін, Т.О. Пріхна, М.О. Бортницька, В.А. Білоус

В останні десятиліття МАХ-фази привернули значну увагу наукової спільноти завдяки унікальному поєднанню металевих і керамічних властивостей, які забезпечують виняткові механічні, термічні, електричні та хімічні характеристики. Синтез фаз МАХ у формі покриттів викликає все більший інтерес для багатьох застосувань. Метою цього огляду є узагальнення прогресу, досягнутого у синтезі покриттів на основі МАХ-фаз різними методами. Обговорено переваги та особливості використання іонно-плазмових методів фізичного осадження з газової фази. Застосування іонно-плазмових методів дозволяє значно знизити температуру синтезу МАХ-фаз за рахунок високої енергії частинок, що утворюють покриття. Проаналізовано вплив параметрів осадження на склад, структуру та властивості покриттів. Розглянуто покриття з високими захисними властивостями та перспективи їх застосування в промисловості. Ця частина огляду присвячена методам нанесення покриттів на основі МАХ-фаз.