DOI: https://doi.org/10.37434/tpwj2024.03.04

# THERMAL SPRAYING OF COATINGS, CONTAINING Cr,AIC MAX PHASE (REVIEW)

#### N.V. Vihilianska<sup>1</sup>, D.V. Filonenko<sup>1</sup>, A.O. Yushchenko<sup>1</sup>, C. Senderowski<sup>2</sup>, J.-C. Grivel<sup>3</sup>

<sup>1</sup>E.O. Paton Electric Welding Institute of the NASU
<sup>1</sup>I Kazymyr Malevych Str., 03150, Kyiv, Ukraine
<sup>2</sup>Warsaw Polytechnic University
<sup>1</sup> Polytechnic Sq., 00-661, Warsaw, Poland
<sup>3</sup>Technical University of Denmark
Anker Engelunds Vej, Building 301, Kongens Lyngby, Denmark, 2800

#### ABSTRACT

A review of research works is presented, devoted to formation of coatings, containing  $Cr_2AIC$  MAX-phase, under the conditions of the processes of thermal spraying. The main methods for producing coatings containing  $Cr_2AIC$  MAX-phase is plasma, high-velocity oxygen fuel and cold gas-dynamic spraying. As spraying materials, both powders with synthesized  $Cr_2AIC$  MAX-phase, obtained by the sintering method as well as powders of the mechanical mixture of initial components are used. To preserve the MAX-phase in a powder and prevent the oxidation of particles in the process of spraying, high-velocity spraying methods (high-velocity plasma, high-velocity oxygen fuel and cold gas-dynamic) are used. The velocity of particle flight during spraying by these methods is 500–900 m/s. Therefore, in these cases coatings are formed, the phase composition of which corresponds to the phase composition of sprayed powders, and the content of  $Cr_2AIC$  phase in such coatings amounts to 79–98 wt.%. In the case of using a mechanical mixture of components the plasma method is used in the spray process for running of synthesis of the MAX phase, resulting in the formation of coatings with MAX phase content of up to 42 wt.%. Studies of phase transformations in powder particles during spraying, mechanisms of decomposition and/or formation of the MAX phase, and the effects of spraying parameters on the structure and properties of coatings are shown. The prospect of further practical use of thermal coatings, containing  $Cr_2AIC$  MAX phase is described, which mainly consists in using them at elevated temperatures, in particular, in the structures of thermal barrier coatings.

KEYWORDS: Cr,AlC MAX phase, thermal coatings, microstructure, mechanical properties, heat protection properties

#### INTRODUCTION

MAX phases belong to the class of ternary carbide and nitride compounds, which are united by a common structural formula  $M_{n+1}AX_n$ , where M is the early transition metal, A is an element of A-group (predominantly groups 13 and 14), and X is C and/or N [1]. MAX phases can be additionally classified by their *n* value as "211" for M<sub>2</sub>AX (*n* = 1), "312" M<sub>3</sub>AX<sub>2</sub> (*n* = 2), "413" for M<sub>4</sub>AX<sub>3</sub> (*n* = 3), etc. They have a hexagonal crystalline structure, which consists of MX layers alternating with a layer of element A. M–X bonds are extremely strong due to mixed covalently ionic nature, whereas M–A metal bonds are relatively weak. This unique crystalline structure is responsible



Figure 1. Typical nanolaminated structure of MAX phases [2]

Copyright © The Author(s)

for the characteristic layered nanolaminated structure of MAX phases (Figure 1), and it ensures a unique set of properties, which consists in a combination of the properties of both ceramics and metal.

At present more than 150 MAX phases have been identified and their number grows regularly due to a combination of experimental studies and theoretical calculations. Nonetheless, not all the possible combinations are thermodynamically stable. For instance, in Ti–Al–C system Ti<sub>2</sub>AlC and Ti<sub>3</sub>AlC<sub>2</sub> phases (n = 1 and 2, respectively) are stable in a broad temperature range, while in Cr–Al–C system the only stable phase is Cr<sub>2</sub>AlC.

Ternary carbide  $Cr_2AIC$  is one of the most promising MAX phases for potential high-temperature application due to its resistance to high-temperature oxidation and hot corrosion [3]. At the same time, it demonstrates excellent mechanical properties, including relatively high hardness and Young's modulus, fracture resistance, bending strength and compressive strength, electric and heat conductivity properties.

Properties of ternary Cr,AlC carbide [4–7]

Density, g/cm <sup>3</sup>	5.21-5.24
Hardness, GPa	3.5–6.4
Modulus of elasticity, GPa	. 245–288
Shear modulus, GPa	. 102–116
Bending strength, GPa	. 305–513

Compressive strength, GPa	1159
Crack resistance characteristic, $MPa \cdot m^{1/2} \dots \dots \dots$	. 4.7–6.2
Heat conductivity, W/(m·K) (at 200 °C)	17.5
Coefficient of thermal expansion, K <sup>-1</sup>	1.33.10-5
Specific heat, J(kg·K)	590
Electric conductivity, S/m	1.4.106
Poisson's ratio	0.153

The traditional methods of producing samples of Cr<sub>2</sub>AlC ceramics are as follows: hot pressing [8, 9], hot isostatic pressing [10], high-temperature sintering [11–14], self-propagating high-temperature synthesis [15], spark plasma sintering [16, 17], and other technologies of mechanical alloying and sintering [18]. Used as raw materials are different mixtures of elements or compounds, including Cr/Al/graphite (or soot), CrC,/Al, AlCr,/graphite, Cr/Al,C,/graphite and Cr<sub>2</sub>O<sub>3</sub>/Al/Al<sub>4</sub>C<sub>3</sub>. However, a mandatory requirement for synthesis of Cr<sub>2</sub>AlC phase is conducting the above-listed processes at higher temperatures and high pressing pressures, that is why these processes are low-productive and energy consuming. These are exactly the factors limiting mass production of materials based on MAX phases.

Another direction of MAX phase application is their forming as protective coatings on product surface. Coatings based on  $Cr_2AIC$  MAX phase are formed using the following methods of vacuum deposition (PVD-methods): cathode-arc deposition [19-21], pulsed-laser deposition [22, 23] and magnetron sputtering. The most widely accepted is the magnetron sputtering method, which allows producing dense homogeneous coatings [24–27]. For application of  $Cr_2AIC$  coatings by deposition methods individual element targets (for instance, Cr, Al and graphite) or composite targets (for instance, AlCr<sub>2</sub>, and Cr<sub>2</sub>AlC) are usually used.

Coatings produced by the methods of vacuum deposition, have the thickness of just several microns and do not meet the requirements to operation under extreme conditions. That is why the methods of thermal spraying are used for deposition of coatings based on  $Cr_2AIC$  MAX phase.

The objective of this work is analysis of literature data on the conditions of formation and properties of thermal coatings containing Cr<sub>2</sub>AlC MAX phase.

At present there exist just several dozens of works devoted to studying formation of coatings containing Cr<sub>2</sub>AlC MAX phase under the conditions of plasma [28–31], High Velocity Oxygen Fuel (HVOF)) [32, 33] and cold gas-dynamic spraying [34, 35]. This is, obviously related to difficulties of spraying materials manufacture in the form of powder with a high MAX phase content.

The methods of plasma, high-velocity oxygen fuel and cold spraying differ primarily by the jet temperature and particle flight velocity, which is one of the most important parameters of thermal spraying processes, influencing the coating structure and properties. In plasma spraying, the plasma jet temperature is equal to 10000-15000 °C (maximal particle flight velocity is 400 m/s), leading to powder particle oxidation and decomposition of MAX phases, as in the case of deposition of Ti<sub>2</sub>AlC powder [36]. MAX phase oxidation and degradation can be avoided using the methods of high-velocity oxygen fuel and cold spraying, where the jet temperature is equal to 2000–3000 °C and <1000 °C, respectively. Here, the particle flight velocity is equal to 500-900 m/s, which shortens time of particle interaction with oxygen and the high-temperature jet. At spraying of Ti<sub>2</sub>AlC MAX phase powders by high-velocity methods it is possible to minimize particle oxidation and development of phase transformations in them [37, 38].

## FORMATION OF COATINGS CONTAINING Cr<sub>2</sub>AIC MAX phase UNDER PLASMA SPRAYING CONDITIONS

The method of high-velocity plasma spraying was used to produce coatings of up to 100  $\mu$ m thickness from Cr<sub>2</sub>AlC powder, manufactured by sintering Cr, Al element powders and graphite (molar ratio of 2:1:1:1, respectively) and further grinding to particle size  $d_{10} = 5.5 \ \mu$ m,  $d_{50} = 10.4 \ \mu$ m,  $d_{90} = 18.3 \ \mu$ m [28]. Spraying was performed with TriplexProTM-210 plasmatron (Oerlicon Metco). Optimization of spraying parameters showed that the spraying distance has the greatest influence on coating thickness, reduction of which from 100 to 60 mm leads to coating thickness increase from 30 to 90  $\mu$ m. Formation of coatings of greater thickness at smaller spraying distances can

Table 1. Optimal modes of deposition of Cr,AIC powder by the method of high-velocity plasma spraying

Process parameters							Coatings characteristics	
$Q_1$ (Ar), l/min	), l/min I, A V, mm/s L, mm				$Q_2$ (He), l/min	Thickness, µm	Weight, mg	
				7.5	40	90	0.39	
170	450	500	60	8	40	100	0.34	
			7.5	20	70	0.36		
<i>Note.</i> Q <sub>1</sub> is the flow rate of primary plasma-forming gas; <i>I</i> is the current; <i>V</i> is the speed of plasmatron movement; <i>L</i> is the spraying distance;								
$Q_r$ is the transport gas flow rate; $Q_r$ is the flow rate of secondary plasma-forming gas. Deposition was performed in 5 passes.								



**Figure 2.** Microstructure of thermal barrier coating: I — Inconel 738 substrate; 2 — Cr<sub>2</sub>AlC coating; 3 — ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> coating

be associated with a higher velocity and temperature of particles. The results of the conducted optimization of plasma spraying parameters were used to establish the modes, which ensure formation of  $Cr_2AlC$  coatings with the best values of sprayed coating thickness and weight (Table 1).

The sprayed coatings have a homogeneous dense structure with pore content on the level of 7–8 %. The content of  $Cr_2AlC$  MAX phase somewhat decreases relative to that in the powder (from 98 to 93 %), and difficult to indentify secondary phases are recorded in the coatings. The secondary phases can be chromium carbides ( $Cr_2C$ ,  $Cr_{23}C_6$ ,  $Cr_7C_3$ ) and/or chromium aluminides ( $Al_3Cr_7$ ,  $Al_{84}Cr_{14}$ ,  $AlCr_2$ ). These phases form as a result of decomposition of  $Cr_2AlC$  MAX phase, because of the high temperature of plasma spraying process.

In order to study the coating serviceability, a  $Cr_2AlC$  layer was deposited by the high-velocity plasma method on the high-temperature Inconel 738 nickel alloy as a bond coat in the system of thermal barrier coatings. A thermal barrier coating of zirconium dioxide, stabilized by yttrium oxide  $ZrO_2-8$  wt.%  $Y_2O_3$  was deposited over it by plasma spraying method. The thickness of  $Cr_2AlC$  bond coat was ~ 40 µm, that of the main  $ZrO_2-Y_2O_3$  thermal barrier layer was ~ 400 µm. Adhesion between Inconel 738 substrate

 Table 2. Phase composition of coatings of Cr-Al-C system at different heat treatment temperatures

HT temperature,	Phase content, wt.%				
°C	Al	Cr <sub>2</sub> AlC	Cr <sub>7</sub> C <sub>3</sub>		
Without HT	9.3	4.6	89.1		
400	6.7	2.7	90.6		
500	5.1	4.5	90.4		
600	_	8.2	91.8		
700	-	14.8	85.2		
800	_	23.7	76.3		

and Cr<sub>2</sub>AlC coating, as well as Cr<sub>2</sub>AlC coating and ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub> was visually dense without any cracks or delaminations on the interface (Figure 2). Coating resistance was studied under the conditions of thermal cycling at heating of the coating surface by the torch up to 1400 °C (of the base up to 1050 °C) and cooling to 70 °C. The coating fails after 745 cycles. The main causes for fracture are open porosity and presence of secondary phases in Cr<sub>2</sub>AlC bond coat, as well as interdiffusion between the bond coat and the substrate. Nonetheless, conducted investigations allow considering the possibility of application of coatings based on Cr<sub>2</sub>AlC MAX phase as a bond coat in systems of thermal barrier coatings.

A two-stage technology was proposed to produce coatings containing Cr<sub>2</sub>AlC MAX phase, which consists of coating deposition by the plasma method and further heat treatment (HT) [29]. A mechanical mixture of powders of chromium ( $d_p = 40-70 \mu m$ ), aluminium ( $d_p = 20-35 \mu m$ ) and graphite ( $d_p = 1-5 \mu m$ ) (2:1:1 molar ratio, respectively) produced by the method of mixing, conglomeration and spray-drying, was used for spraying. Heat treatment of the coated samples was conducted in an argon atmosphere at the temperature of 400, 500, 600, 700 and 800 °C for 1 h.

Sprayed coating (without HT) consists predominantly of  $Cr_7C_3$  phase with residual Al; MAX phase content is equal to only 1.6 wt.% (Table 2). Heat treat-



Figure 3. Schematic explanation of the influence of HT temperature on deposited coating of Cr–Al–C system: a — without HT; b — HT at the temperature of <660 °C; c — HT at the temperature of >660 °C

ment at the temperature of <600 °C does not lead to any significant changes in the phase composition of the coatings, but it changes considerably at the temperature of >600 °C. Aluminium disappears from the coatings and weight fraction of Cr<sub>2</sub>AlC MAX phase increases up to 8.2 % after HT at 600 °C, up to 14.8 % after HT at 700 °C and up to 23.7 % after HT at 800 °C. It means that liquid Al promotes atom diffusion, thus accelerating nucleation and increase of the content of Cr<sub>2</sub>AlC phase. Since Cr and C are homogeneously dispersed at the molar level in Cr–C carbides (Cr<sub>7</sub>C<sub>3</sub> or Cr<sub>23</sub>C<sub>6</sub>), they can thus react with residual Al with Cr<sub>2</sub>AlC formation. Influence of HT temperature on formation of composite coatings based on Cr<sub>2</sub>AlC is schematically shown in Figure 3.

After spraying the coating has a dense lamellar structure, after heat treatment the coating structure does not essentially change and the structure lamellarity is preserved (Figure 4).

Figure 5 gives the microhardness and crack resistance values of coatings of Cr–Al–C system, produced by plasma spraying with subsequent HT.

Hardness of the produced coatings is equal from 544 up to 857 HV, and it mainly depends on chromium carbide content. The coating hardness is somewhat lower than that of chromium carbides, because of the presence of residual aluminium and porosity in them. At coating heat treatment the quantity of soft Al metal decreases, and that of the newly-formed Cr<sub>2</sub>AlC phase increases, leading to an increase of hardness, which reaches the maximal value after HT at the temperature of 600 °C. After HT at 700 and 800 °C, the coating hardness somewhat decreases, because of an increase of the content of Cr<sub>2</sub>AlC MAX phase, the hardness of which is equal to 350–640 HV.

Crack resistance value for a sprayed Cr<sub>2</sub>AlC coating (without HT) is equal to 1.29 MPa·m<sup>1/2</sup>, while after HT performance the crack resistance value increases, and it reaches the maximal value (2.02 MPa·m<sup>1/2</sup>) after conducting HT at 700 °C. Increase of coating crack resistance after HT is attributable to formation of a more homogeneous microstructure and more uniform phase distribution in the coatings.

Possibility of producing plasma coatings with a higher content of  $Cr_2AlC$  MAX phase (up to ~ 43 %) without additional HT performance is demonstrated **Table 3.** Phase content in plasma coatings of  $Cr_3C_2$ -Al-Cr system

Al content in the	Phase content in the coating, wt.%				
powder, mol.%	Cr <sub>2</sub> AlC	Cr–C			
0,5	22.41	77.59			
1	28.02	71.98			
2	42.78	57.22			
3	30.25	69.75			



**Figure 4.** Microstructure of plasma coating of Cr–Al–C system: a — without HT; b — after HT at 800 °C

in the case of  $Cr_3C_2$  chromium carbide application as a carbon source, instead of graphite [30]. The spraying powder was manufactured by the method of conglomeration with subsequent spray-drying in the mixture of initial powders of  $Cr_3C_2$ , Al and Cr in the molar ratio of 1:*x*:1, where x = 0.5, 1, 2, 3.

Investigations of the phase composition showed that all the coatings contain  $Cr_2AlC$ ,  $Cr_7C_3$  and  $Cr_{23}C_6$  MAX phases, which is indicative of running of the process of interaction of the powder initial components during spraying with new phase formation. The content of the carbide component and MAX phase in the coatings is given in Table 3.

At deposition of powders with Al content of 0.5 and 1 %, initial  $Cr_3C_2$  phase is recorded in the coatings, whereas at increase of Al content in the powders up to 2 and 3 % this phase disappears, which is indicative of a complete interaction of powder components. Formation of substable (Cr, Al)C<sub>x</sub> carbide was also noted in the coatings, which arises as a result of Al



**Figure 5.** Microhardness (1) and crack resistance (2) of plasma coatings of Cr–Al–C system



Figure 6. Scheme of phase transformations at plasma deposition of powder of Cr<sub>3</sub>C<sub>2</sub>-Al-Cr system

substitution in Cr–C lattice. At 2 % Al concentration in the powder, a more intensive interaction of liquid aluminium with  $Cr_3C_2$  and Cr with formation of (Cr, Al) $C_x$  and  $Cr_2AlC$  is in place, which results in MAX phase content in the coating reaching 42.78 %. At the same time, increase of Al content in the powder up to 3 % leads to increase of (Cr, Al) $C_x$  phase content and decrease of the quantity of  $Cr_2AlC$  phase to 30.25 % in the coating. The mechanism of phase transformations at plasma deposition of powder of  $Cr_3C_2$ –Al–Cr system is shown in Figure 6.

Coating microhardness is equal to 11.33, 10.64, 10.27 and 10.1 GPa at Al content of 0.5, 1, 2, 3 % in the powder, respectively. Coating hardness somewhat decreases with increase of Al powder content in the coating, which is attributable to phase composition of the coatings, as phase hardness is of the following order:  $Cr-C > (Cr, Al)C_{v} > Cr_{v}AlC$ .

The coefficient of coating crack resistance is equal to 2.37, 2.5, 2.6 and 2.4 MPa·m<sup>1/2</sup> at Al content in the powder of 0.5, 1, 2 and 3 %, respectively. Coating strength is ensured by microlamellarity of the structure (Figure 7) which consists of alternating layers of carbides and MAX phase. As MAX phase proper has a nanolayered structure, its presence in the coatings prevents crack propagation, leading to increase of the coating strength as a whole.



Figure 7. Microstructure of plasma coating of Cr<sub>3</sub>C<sub>2</sub>-Al-Cr system

## FORMATION OF COATINGS CONTAINING Cr,AIC MAX PHASE, UNDER THE CONDITIONS OF HIGH-VELOCITY OXY-FUEL SPRAYING (HVOF)

The influence of addition of  $Cr_2AIC$  MAX phase powder on formation and properties of NiMoAl based coatings produced by HVOF-spraying method was studied [32]. A mechanical mixture of Ni–Mo–Al powder with addition of  $Cr_2AIC$  MAX phase powder in the amount of 10, 20 and 50 wt.% was used for spraying.  $Cr_2AIC$  powder was produced in several stages: sintering of chromium and graphite powders (Cr:C = 2:1at 1550 °C for 1 h in argon atmosphere), grinding of  $CrC_x$  powder (x = 0.5) for 15 h and subsequent sintering of  $CrC_x$  and Al powders ( $CrC_x:AI = 2:1.4$ ) at 800 °C for 2 h in argon atmosphere) [39]. The powder consists of >99 %  $Cr_2AIC$  phase with a small additive of chromium carbide (<1 %). Characteristics of spraying powder are given in Table 4.

It is shown that no decomposition or oxidation of powders takes place as a result of HVOF-spraving, and the coating phase composition corresponds to phase composition of the powders. At the same time, at deposition of the same compositions by plasma spraying method [31] Cr<sub>2</sub>AlC MAX phase is absent in the coatings, and oxides  $(Al_2O_3 \text{ and } Cr_2O_3)$  and carbides (Cr<sub>7</sub>C<sub>3</sub> and Cr<sub>3</sub>C<sub>2</sub>) form as a result of decomposition and oxidation. This is associated with a higher temperature of the jet at plasma spraying than at HVOF-process. In other works [33] it is reported that during HVOF-spraying partial decomposition of Cr,AlC MAX phase takes place with formation of  $Cr_7C_3$  chromium carbide. In this study it was possible to minimize the process of oxidation and ensure preservation of MAX phase in the coating by conducting the process of HVOF-spraying at lower oxygen flow rate (250 l/min) and 0.24 ratio of propane/oxygen flow rates.

Produced composite coatings of NiMoAl– $Cr_2AlC$  system have a dense layered structure; coating porosity decreases compared to NiMoAl coatings from 4.6 to 3.6, 2.13 and 1.95 % when using powders with addition of 10, 20 and 50 wt.% of Cr<sub>2</sub>AlC powder, respectively.

Dovudon nomo	Element composition, wt.%						A
Powder name	Ni	Мо	Cr	Al	С	Phase composition	Average particle size, µm
NiMoAl	54	44	-	2	-	Ni, Mo	70.98 ± 1.5
NiMoAl-10 wt.% Cr <sub>2</sub> AlC	48.3	39.3	5.43	5.54	1.43	Ni, Mo, Cr <sub>2</sub> AlC	69.54 ± 3.5
NiMoAl-20 wt.% Cr <sub>2</sub> AlC	43.2	35.2	11.2	7.5	2.9	Ni, Mo, Cr <sub>2</sub> AlC	68.12 ± 4.0
NiMoAl–50 wt.% Cr <sub>2</sub> AlC	27	22	27.96	15.99	7.05	Ni, Mo, Cr <sub>2</sub> AlC	79.38 ± 5.0
Cr <sub>2</sub> AlC	-	-	55.99	29.98	14.03	Cr <sub>2</sub> AlC	66.34 ± 1.5

Table 4. Characteristics of powders of NiMoAl-Cr,AlC system for HVOF-deposition

Formation of a denser microstructure can be the consequence of addition of fine  $Cr_2AIC$  particles to NiMoA1 matrix and their uniform distribution in the coating structure, which leads to their densification.

Addition of Cr<sub>2</sub>AlC powder to NiMoAl alloy powder leads to increase of both the coating hardness and modulus of elasticity. Average nanohardness of NiMoAl, NiMoAl–10 % Cr<sub>2</sub>AlC, NiMoAl–20 % Cr<sub>2</sub>AlC, NiMoAl–50 % Cr<sub>2</sub>AlC and Cr<sub>2</sub>AlC coatings is equal to 390  $\pm$  20, 446  $\pm$  20, 501  $\pm$  20, 637  $\pm$  20 and 663  $\pm$  20 VHN<sub>0.001</sub>, respectively; modulus of elasticity is 193  $\pm$  4.201, 201  $\pm$  5, 209  $\pm$  3, 221  $\pm$  6 and 264  $\pm$  5 GPa, respectively.

Among the studied composite coatings Ni-MoAl-20 wt.%  $Cr_2AlC$  coating has the lowest friction coefficient and highest wear resistance under the conditions of sliding friction, which was determined by pin-on-disk procedure. Increase of the strengthening phase amount to 50 wt.%  $Cr_2AlC$  leads to lowering of the tribological properties, because of poor cohesion strength of the coating.

## FORMATION OF COATINGS CONTAINING Cr<sub>2</sub>AIC MAX PHASE UNDER THE CONDITIONS OF COLD GAS-DYNAMIC SPRAYING

Investigations of formation of coatings containing Cr<sub>2</sub>AlC MAX phase under the conditions of cold gas-dynamic spraying were conducted in work [34]. Spraying was performed using powder of Sandvik

Company (Sweden), which was ground prior to that to particle size  $d_{10} = 2 \ \mu m$ ,  $d_{50} = 9 \ \mu m$ ,  $d_{90} = 23 \ \mu m$ . Spraying was conducted using Impact 5/11 System of Impact Innovations Company (Rattenkirchen, Germany). Nitrogen at the pressure of 50 bar and 1000 °C temperature was used as the carrier and working gas.

In the produced coating, similar to the powder, the main phase is  $Cr_2AlC$  MAX phase (approximately 68 % in the powder and 79 % in the coating); secondary phases are chromium carbides, such as  $Cr_7C_3$  (approximately 17 % in the powder and 10 % in the coating) and  $Cr_3C_2$  (approximately 16 % in the powder and 12 % in the coating). It is noted that as the phase content in the coatings and powder was determined by comparing the peak height on the roentgenograms, the obtained data on their amount are of a tentative nature.

It is shown that at collision of  $Cr_2AlC$  MAX phase particles with the substrate, their plastic deformation and spreading take place, resulting in formation of a dense microstructure of the coating (porosity <3 %) and an interface with the steel base (Figure 8, *a*). Coating thickness is nonuniform and varies from 200 to 320 µm. Coatings are characterized by local heterogeneity of the microstructure and presence of cracks and delaminations (Figure 8, *b*), which is caused by insufficient strength of cohesion between the particles. Availability of such coating defects is attributable to nonuniform powder feeding, because of its low flowability and vibration mode of operation of the



Figure 8.  $Cr_2AIC$  coating produced by the method of cold gas-dynamic spraying: a — microstructure; b — appearance of coating cracking

Gas pressure $(N_2)$ , bar	Spraying dis- tance, mm	Number of passes	Gas temperature $(N_2)$ , °C
			650
40	60	10	750
			950

**Table 5.** Technological parameters of cold gas-dynamic deposition of powder based on MAX phase Cr2AlC

powder feeder, which may lead to power fraction separation into particles of different size. It is noted that increasing the coating quality required performance of further investigations on improvement of technological properties of the powders and optimization of cold spraying parameters.

Coating microhardness is equal to  $585 \pm 63 \ HV_{0.1}$ , nanohardness is  $1153 \pm 321 \ HV_{0.001}$ . The difference in micro- and nanohardness values is attributable to the difference in measurement procedures. Loading at nanoindentation is much smaller, and, thus the indentations are limited to the plane of one deformed coating particle and reflect its properties. Results of microindentation reflect the averaged value of microhardness of the entire coating and they largely depend on cohesion between the particles and presence of pores in the coatings. Proceeding from photos of indentations from nanoindenter, the measured nanohardness corresponds to hardness of chromium carbide and hardness of the interface between the carbide particles and Cr<sub>2</sub>AlC inclusions.

In work [35] the method of cold gas-dynamic spraying was used to produce relatively dense (9 % porosity) of the coating with up to 98 % MAX phase content. Powder produced by sintering a mixture of  $Cr_3C_2$ , Cr, Al powders (in the ratio of 1:1:2.05) at 1300 °C in argon atmosphere for 2 h with subsequent grinding in a planetary mill for 2 h was used as the spraying material. The produced powder has high purity, its main phase (>98 %) being  $Cr_2AIC$  MAX phase with admixtures of  $Cr_7C_3$  carbide,  $Cr_2AI$  aluminide and  $Al_2O_3$  oxide. Particle size is equal to:  $d_{10} = 4.1 \mu m$ ,  $d_{50} = 7.6 \mu m$ ,  $d_{90} = 13.2 \mu m$ .

Spraying was conducted onto a stainless steel substrate using Kinetiks 8000 system (Oerlikon Metco, Switzerland) with application of technological parameters, shown in Table 5.

Coatings of 40–100  $\mu$ m thickness were formed as a result of spraying. The coating phase composition corresponds to that of the powder, which is indicative of absence of particle oxidation during spraying and degradation of Cr<sub>2</sub>AIC MAX phase.

It is shown that at increase of gas temperature from  $650 \text{ to } 950 \text{ }^{\circ}\text{C}$  denser coatings are formed (porosity decreases from 12.4 to 9.1 %, respectively) and the number of cracklike defects is reduced. This is attributable

to increase of temperature and velocity of the sprayed particles and degree of their deformation at collision with the base. It results in greater cohesion between the particles and formation of coatings with a smaller number of defects. No cracks or delaminations were observed on the interface of the coating–steel substrate, which is indicative of a good strength of cohesion with the substrate. At the same time, it is noted that at increase of working gas temperature from 650 to 950 °C the value of residual stresses in the coatings increases from 200 up to 310 MPa, respectively, and it may lead to coating delamination during operation.

The possibility of using a coating with  $Cr_2AlC$  MAX phase as a bond coat in the thermal barrier coating system of a bond coat-main thermal barrier layer of  $ZrO_2-Y_2O_3$  was considered. A  $Cr_2AlC$  bond coat was deposited on the steel substrate by cold spraying and a  $ZrO_2-Y_2O_3$  coating was applied over it by the plasma method. No spallations, delaminations or secondary phase formation as a result of the reaction on the bond coat-main layer interface are observed. This is indicative of the potential for application of  $Cr_2AlC$  coating produced by the method of cold gas-dynamic spraying, as a bond coat in thermal barrier coating systems.

### CONCLUSIONS

Based on the conducted analysis of the specialized scientific literature, the possibility was shown of producing coatings, containing  $Cr_2AIC$  MAX phase, by the methods of thermal spraying, using both synthesized powders with a high content of the MAX phase, and a mechanical mixture of individual elements.

One of the most critical aspects during the process of thermal spraying of coatings containing  $Cr_2AIC$ MAX phase, is particle oxidation and running of undesirable reactions with MAX phase decomposition and reduction of its amount in the coatings. These decompositions are caused by noncongruent melting of MAX phases, which, certainly, is one of the main difficulties of their spray deposition.

When deposition is performed using powders, where the main phase is  $Cr_2AlC$  MAX phase, it is rational to apply high-velocity thermal spraying methods, such as high-velocity plasma, high-velocity flame and cold gas-dynamic spraying. Owing to high velocities of particle flight, the time of interaction with oxygen and high-temperature jet is reduced, which allows producing coatings, where the phase composition corresponds to that of the deposited powder. However, coatings based on  $Cr_2AlC$  MAX phase produced by the method of cold gas-dynamic spraying, are characterized by presence of cracks and inner delaminations, considering their low cohesive strength.

Powders of a mechanical mixture of  $(Cr + Al + graphite, Cr_3C_2 + Al + Cr)$  initial components are used in plasma spraying. In this case,  $Cr_2AlC$  MAX phase synthesis occurs directly during deposition and formation of the coating layer at interaction of the initial components. Increase of MAX phase content in these coatings can be achieved through their further heat treatment.

Under the conditions of the above-mentioned deposition methods dense coatings with <9 % porosity and dense interface with the steel substrates are formed. Coating hardness depends mainly on their phase composition, and it varies from 5 to 11 GPa.

On the whole, the need for further development of materials for deposition and optimisation of the processes of producing the coatings is stated in the works devoted to investigations of formation of thermal coatings containing Cr,AIC MAX phase.

### REFERENCES

- Sokol, M., Natu, V., Kota, S., Barsoum, M.W. (2019) On the chemical diversity of the MAX phases. *Trends in Chemistry*, 1(2), 210–223. DOI: https://doi.org/10.1016/j.trechm.2019.02.016
- Gonzalez□Julian, J. (2021). Processing of MAX phases: From synthesis to applications. J. of the American Ceramic Society, 104(2), 659–690. DOI: https://doi.org/10.1111/jace.17544
- Lin, Z.J., Li, M.S., Wang, J.Y., Zhou, Y.C. (2007) High-temperature oxidation and hot corrosion of Cr<sub>2</sub>AlC. *Acta Materialia*, 55(18), 6182–6191. DOI: https://doi.org/10.1016/j. actamat.2007.07.024
- Barsoum, M.W., Radovic, M. (2011) Elastic and mechanical properties of the MAX phases. *Annual Review of Materials Research*, **41**, 195–227. DOI: https://doi.org/10.1146/annurev-matsci-062910-100448
- Tian, W., Wang, P., Zhang, G. et al. (2006) Synthesis and thermal and electrical properties of bulk Cr<sub>2</sub>AlC. *Scripta Materialia*, 54(5), 841–846. DOI: https://doi.org/10.1016/j.scriptamat.2005.11.009
- Tian, W.B., Wang, P.L., Zhang, G.J. et al. (2007) Mechanical properties of Cr<sub>2</sub>AlC ceramics. *J. of the American Ceramic Society*, 90(5), 1663–1666. DOI: https://doi.org/10.1111/ j.1551-2916.2007.01634.x
- Li, S.B., Yu, W B., Zhai, H.X. et al. (2011) Mechanical properties of low temperature synthesized dense and fine-grained Cr<sub>2</sub>AlC ceramics. *J. of the European Ceramic Society*, 31(1–2), 217–224. DOI: https://doi.org/10.1016/j.jeurceramsoc.2010.08.014
- Tian, W., Wang, P., Zhang, G. et al. (2007) Effect of composition and processing on phase assembly and mechanical property of Cr<sub>2</sub>AlC ceramics. *Materials Sci. and Eng.: A*, 454, 132–138. DOI: https://doi.org/10.1016/j.msea.2006.11.032
- Ying, G., He, X., Li, M. et al. (2011) Synthesis and mechanical properties of high-purity Cr<sub>2</sub>AlC ceramic. *Materials Sci. and Eng.: A*, 528(6), 2635–2640. DOI: https://doi.org/10.1016/j. msea.2010.12.039
- Manoun, B., Gulve, R.P., Saxena, S.K. et al. (2006) Compression behavior of M<sub>2</sub>AlC (M = Ti, V, Cr, Nb, and Ta) phases to above 50 GPa. *Physical Review B*, 73(2), 024110. DOI: https://doi.org/10.1103/physrevb.73.024110
- 11. Tian, W., Sun, Z., Du, Y., Hashimoto, H. (2009) Mechanical properties of pulse discharge sintered Cr,AlC at 25-

1000 °C. *Materials Letters*, 63(8), 670–672. DOI: https://doi. org/10.1016/j.matlet.2008.12.024

- Panigrahi, B.B., Chu, M.C., Kim, Y.I. et al. (2010) Reaction synthesis and pressureless sintering of Cr<sub>2</sub>AlC powder. *J.* of the American Ceramic Society, 93(6), 1530–1533. DOI: https://doi.org/10.1111/j.1551-2916.2009.03560.x
- Xiao, L.O., Li, S.B., Song, G., Sloof, W.G. (2011) Synthesis and thermal stability of Cr<sub>2</sub>AlC. *J. of the European Ceramic Society*, 31(8), 1497–1502. DOI: https://doi.org/10.1016/j. jeurceramsoc.2011.01.009
- Tian, W., Sun, Z., Du, Y., Hashimoto, H. (2008) Synthesis reactions of Cr<sub>2</sub>AlC from Cr–Al<sub>4</sub>C<sub>3</sub>–C by pulse discharge sintering. *Materials Letters*, 62(23), 3852–3855. DOI: https://doi. org/10.1016/j.matlet.2008.05.001
- Yeh, C.L., Kuo, C.W. (2011) Effects of Al and Al<sub>4</sub>C<sub>3</sub> contents on combustion synthesis of Cr<sub>2</sub>AlC from Cr<sub>2</sub>O<sub>3</sub>–Al–Al<sub>4</sub>C<sub>3</sub> powder compacts. *J. of Alloys and Compounds*, 509(3), 651– 655. DOI: https://doi.org/10.1016/j.jallcom.2010.09.169
- 16. Duan, X., Shen, L., Jia, D. et al. (2015) Synthesis of high-purity, isotropic or textured Cr<sub>2</sub>AlC bulk ceramics by spark plasma sintering of pressure-less sintered powders. *J. of the European Ceramic Society*, 35(5), 1393–1400. DOI: https://doi.org/10.1016/j.jeurceramsoc.2014.11.008
- Yeh, C.L., Yang, W.J. (2013) Formation of MAX solid solutions (Ti, V)<sub>2</sub>AlC and (Cr, V)<sub>2</sub>AlC with Al<sub>2</sub>O<sub>3</sub> addition by SHS involving aluminothermic reduction. *Ceramics Inter.*, 39(7), 7537–7544. DOI: https://doi.org/10.1016/j.ceramint.2013.03.005
- Yembadi, R., Panigrahi, B.B. (2017) Thermodynamic Assessments and mechanically activated synthesis of ultrafine Cr<sub>2</sub>AlC MAX phase powders. *Advanced Powder Technology*, 28(3), 732–739. DOI: https://doi.org/10.1016/j. apt.2016.11.020
- Li, J.J., Qian, Y.H., Niu, D. et al. (2012) Phase formation and microstructure evolution of arc ion deposited Cr<sub>2</sub>AlC coating after heat treatment. *Applied Surface Sci.*, 263, 457–464. DOI: https://doi.org/10.1016/j.apsusc.2012.09.082
- Mockute, A., Persson, P.O., Magnus, F. et al. (2014) Synthesis and characterization of arc deposited magnetic (Cr, Mn)<sub>2</sub>AlC MAX phase films. *Physica Status Solidi (RRL)–Rapid Research Letters*, 8(5), 420–423. DOI: https://doi.org/10.1002/ pssr.201409087
- Wang, Z., Ma, G., Liu, L. et al. (2020) High-performance Cr<sub>2</sub>AlC MAX phase coatings: Oxidation mechanisms in the 900–1100 °C temperature range. *Corrosion Sci.*, **167**, 108492. DOI: https://doi.org/10.1016/j.corsci.2020.108492
- Stevens, M., Pazniak, H., Jemiola, A. et al. (2021) Pulsed laser deposition of epitaxial Cr<sub>2</sub>AlC MAX phase thin films on MgO (111) and Al<sub>2</sub>O<sub>3</sub> (0001). *Materials Research Letters*, 9(8), 343–349. DOI: https://doi.org/10.1080/21663831.2021. 1920510
- Lange, C., Hopfeld, M., Wilke, M. et al. (2012) Pulsed laser deposition from a pre-synthesized Cr<sub>2</sub>AlC MAX phase target with and without ion-beam assistance. *Physica Status Solidi (A)*, 209(3), 545–552. DOI: https://doi.org/10.1002/pssa.201127537
- 24. Li, Y., Zhao, G., Qian, Y. et al. (2018) Deposition of phasepure Cr<sub>2</sub>AlC coating by DC magnetron sputtering and post annealing using Cr–Al–C targets with controlled elemental composition but different phase compositions. *J. Mater. Sci. & Technol.*, 34(3), 466–471. DOI: https://doi.org/10.1016/j. jmst.2017.01.029
- Qureshi, M.W., Ma, X., Tang, G. et al. (2021) Fabrication and mechanical properties of Cr<sub>2</sub>AlC MAX phase coatings on TiBw/Ti6Al4V composite prepared by HiPIMS. *Materials*, 14(4), 826. DOI: https://doi.org/10.3390/ma14040826

- 26. Naveed, M., Obrosov, A., Zak, A. et al. (2016) Sputtering power effects on growth and mechanical properties of Cr<sub>2</sub>AlC MAX phase coatings. *Metals*, 6(11), 265. DOI: https://doi. org/10.3390/met6110265
- Liu, J., Zuo, X., Wang, Z. et al. (2018) Fabrication and mechanical properties of high purity of Cr<sub>2</sub>AlC coatings by adjustable Al contents. *J. of Alloys and Compounds*, **753**, 11–17. Doi: 10.1016/j.jallcom.2018.04.100.
- Gonzalez Julian, J., Mauer, G., Sebold, D. et al. (2020) Cr<sub>2</sub>AlC MAX phase as bond coat for thermal barrier coatings: Processing, testing under thermal gradient loading, and future challenges. *J. of the American Ceramic Society*, 103(4), 2362–2375. DOI: https://doi.org/10.1111/jace.16935
- Zhang, F., Yan, S., Li, C. et al. (2019) Synthesis and characterization of MAX phase Cr<sub>2</sub>AlC based composite coatings by plasma spraying and post annealing. *J. of the European Ceramic Society*, 39(16), 5132–5139. DOI: https://doi.org/10.1016/j.jeurceramsoc.2019.08.039
- Zhang, F., Yu, G., Yan, S. et al. (2023) Characterization and reaction mechanism of in-situ micro-laminated Cr<sub>2</sub>AlC coatings by plasma spraying Cr<sub>3</sub>C<sub>2</sub>/Al/Cr powder mixtures. *Surf. and Coat. Technol.*, **456**, 129271. DOI: https://doi.org/10.1016/j. surfcoat.2023.129271
- 31. Davis, D., Srivastava, M., Malathi, M. et al. (2018) Effect of Cr<sub>2</sub>AlC MAX phase addition on strengthening of Ni–Mo–Al alloy coating on piston ring: Tribological and twist-fatigue life assessment. *Applied Surface Sci.*, **449**, 295–303. DOI: https://doi.org/10.1016/j.apsusc.2018.01.146
- Davis, D., Singh, S., Chakradhar, R.P.S., Srivastava, M. (2020). Tribo-mechanical properties of HVOF-sprayed Ni-MoAl-Cr<sub>2</sub>AlC composite coatings. *J. Thermal Spray Technol.*, **29**, 1763–1783. DOI: https://doi.org/10.1007/s11666-020-01069-8
- Chen, Y., Chu, M., Wang, L. et al. (2012) Microstructure and performance of Cr(2)AlC coatings deposited by HVOF spraying. *Chinese J. of Rare Metals*, 36(4), 568–573. DOI: https:// doi.org/10.3969/j.issn.0258-7076.2012.04.011
- Elsenberg, A., Busato, M., Gärtner, F. et al. (2021) Influence of MAX phase deformability on coating formation by cold spraying. *J. Thermal Spray Technol.*, **30**, 617–642. DOI: https://doi.org/10.1007/s11666-020-01110-w
- 35. Go, T., Sohn, Y.J., Mauer, G. et al. (2019) Cold spray deposition of Cr<sub>2</sub>AlC MAX phase for coatings and bond-coat layers. *J. of the European Ceramic Society*, 39(4), 860–867. DOI: https://doi.org/10.1016/j.jeurceramsoc.2018.11.035

- 36. Zhang, Z., Lim, S.H., Chai, J. et al. (2017) Plasma spray of Ti<sub>2</sub>AlC MAX phase powders: Effects of process parameters on coatings' properties. *Surf. and Coat. Technol.*, **325**, 429– 436. DOI: https://doi.org/10.1016/j.surfcoat.2017.07.006
- 37. Zhang, Z., Lai, D.M.Y., Lim, S.H. et al. (2018) Isothermal oxidation of the Ti,AlC MAX phase coatings deposited by kerosene-fuelled HVOF spray. *Corrosion Sci.*, **138**, 266–274. DOI: https://doi.org/10.1016/j.corsci.2018.04.022
- Gutzmann, H., Gärtner, F., Höche, D. et al. (2013) Cold spraying of Ti<sub>2</sub>AlC MAX phase coatings. *J. Thermal Spray Technol.*, 22, 406–412. DOI: https://doi.org/10.1007/s11666-012-9843-1
- Rajkumar, Y., Rahul, B.M., Ananth Akash, P., Panigrahi, B.B. (2017) Nonisothermal sintering of Cr<sub>2</sub>AlC powder. *Inter. J. of Applied Ceramic Technology*, 14(1), 63–67. DOI: https://doi. org/10.1111/ijac.12617

## ORCID

N.V. Vihilianska: 0000-0001-8576-2095,| D.V. Filonenko: 0009-0004-9021-2425,

- A.O. Yushchenko: 0009-0005-6636-8275,
- C. Senderowski: 0000-0002-0331-3702,
- J.-C. Grivel: 0000-0001-7835-9054

## **CONFLICT OF INTEREST**

The Authors declare no conflict of interest

## **CORRESPONDING AUTHOR**

N.V. Vihilianska

E.O. Paton Electric Welding Institute of the NASU 11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine. E-mail: pewinataliya@gmail.com

## SUGGESTED CITATION

N.V. Vihilianska, D.V. Filonenko,

A.O. Yushchenko, C. Senderowski, J.-C. Grivel (2024) Thermal spraying of coatings, containing  $Cr_2AIC$  MAX phase (Review). *The Paton Welding J.*, **3**, 24–32.

## JOURNAL HOME PAGE

https://patonpublishinghouse.com/eng/journals/tpwj

Received: 16.11.2023

