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DETONATION SPRAYING OF COATINGS CONTAINING Cr_2AlC MAX PHASE

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ABSTRACT

The paper investigates the process of forming coatings containing Cr_2AlC MAX phase by detonation spraying using powders produced by the mechanochemical synthesis. The powder mixtures of the Cr–Al–C and Cr_3C_2–Al systems were used as starting components. It has been found that no new phases are formed in the Cr–Al–C system as a result of mechanochemical synthesis within 1.5–5 h, while the synthesis of Cr_2AlC MAX phase occurs during the detonation spraying of the MChS powder of this mixture. In the Cr_3C_2–Al system, the formation of Cr_2AlC MAX phase is observed already at the processing stage after 1.5 h. Due to the interaction reaction of the components in the process of detonation spraying, the content of MAX phase grows in the coating relative to the MChS powder. Both types of coatings contain phases of chromium carbides and oxide components of chromium and aluminium. The produced coatings are characterized by high microhardness (about 5000 MPa), dense lamellar structure, and corrosion resistance in a 3 % NaCl solution.

KEYWORDS: MAX phase, detonation spraying, coating, microstructure, corrosion resistance

INTRODUCTION

In recent years, materials based on MAX phases have attracted increased interest for industrial use due to their unique combination of both metal and ceramic properties, which they owe to their typical nanolaminate structure [1, 2]. Among the currently known MAX phases, Cr_2AlC phase is of considerable interest due to its complex of physical and chemical properties, namely: low density, excellent mechanical properties, high rigidity, ease of processing, resistance to damage, corrosion resistance in many salt and acid solutions, electrical and thermal conductive properties [3–6]. Among the methods for producing Cr_2AlC MAX phase, the most common are sintering methods, including spark plasma sintering, hot pressing, methods of self-propagating high-temperature synthesis (SHS), and mechanochemical synthesis [7–11]. Powders of both simple elements as well as compounds of carbides, oxides, and intermetallics in various ratios are used as starting components. The produced materials have high strength, heat resistance and corrosion resistance.

Another method of using materials based on MAX phases is their depositing on the surface of parts in the form of coatings. Most of the available studies are devoted to the formation of coatings based on Cr_2AlC MAX phase in the form of thin films produced by magnetron sputtering of individual elements or segmented composite targets [12, 13]. Despite the high purity and density of magnetron coatings, they cannot be used in extreme conditions under high loads due to their small thickness, which is several microns.

To produce coatings based on MAX phases with a thickness of several hundred micrometers, thermal spraying methods such as plasma-arc, high-velocity oxygen fuel, and cold gas-dynamic spraying are used [14]. The raw materials used for spraying are powders with a synthesized Cr_2AlC MAX phase produced by sintering [15] and powders of mechanical mixtures of the starting components, such as Cr + Al + graphite [16], Cr_3C_2 + Al + Cr [17]. When using powders containing MAX phase for spraying, due to the oxidation of powder particles and decomposition reactions associated with incongruent melting of MAX phases, the content of Cr_2AlC MAX phase in the coatings is significantly reduced relative to the starting powder, which is one of the main problems when spraying this type of coatings. In the case of spraying powders of mechanical mixtures, the synthesis of MAX phase occurs during the spraying process and the formation of the coating layer at the interaction of starting components. The content of MAX phase in such coatings can be further increased by the following heat treatment [16].

THE AIM

of this work is to study the formation of coatings containing Cr_2AlC MAX phase under the conditions of the detonation spraying method using powders produced by the mechanochemical synthesis.

Table 1. Characteristics of starting powders of mechanical mixtures

Powder	Grade	Particle size, μm	Impurity content, wt.%
Cr	PKh1M	<20	0.009 N; 0.07 C; 0.20 Fe; 0.10 Ni; 0.10 Si; 0.10 Ca; 0.30 O; P i 0.032 O
Al	PA-4	40–50	<0.4 Si, <0.35 Fe, <0.02 Cu
Graphite	GL-1	<40	Ash content <13 %
Cr_3C_2	PKKh-1S	<40	–

MATERIALS AND RESEARCH PROCEDURES

Powders produced by the method of mechanochemical synthesis (MChS) of powder mixtures of 73Cr–19Al–8C and 91Cr_3C_2 + 9Al (wt.%) compositions were used as materials for spraying coatings by the detonation method. The characteristics of the starting powders used to produce the mechanical mixtures for the MChS process are given in Table 1.

The ratio of the components of the Cr–Al–C powder mixture was calculated to produce Cr_2AlC MAX phase according to the reaction 2Cr + A1 + C = Cr_2AlC; the components of the Cr_3C_2–Al mixture were calculated on the basis of a thermodynamic assessment of the probability of reactions in the system with the formation of Cr_2AlC MAX phase and previous studies of the formation of Cr_2AlC MAX phase under plasma-arc spraying of Cr_3C_2–Al system powders [18].

The MChS process of powder mixtures was carried out in a high-energy planetary mill “Activator 2SL” at a drum rotation speed of 1000/1500 rpm, the processing time was 1.5 and 5 h.

For coating spraying, a detonation spraying unit “Perun-S” was used. A mixture of oxygen and propane-butane with the addition of air was used as a detonation mixture, the flow rate and ratio of oxygen to propane-butane was 3:1, the amount of powder per shot was ≈ 100 mg, and the number of shots was 100, the cycle frequency was 6.6 s^{-1}. The technological parameters of detonation spraying, such as propane-butane fuel gas flow rate ($Q_{C_3H_8}$), oxygen flow rate (Q_{O_2}), diluent gas flow rate (air) (Q_{air}), transport gas flow rate (air) Q_{tr}), and spraying distance (L), are given in Table 2. The technological parameters of detonation spraying were selected based on the calculation of obtaining a coating thickness of 4–6 μm for 1 cycle and minimizing the oxidation of the powder material during the spraying process.

A Neophot-32 optical microscope with a digital photography device was used to study the particle microstructure of MChS powders and sprayed coatings. The phase composition of the powder and coating particles was studied using a PANalytical X’Pert PRO diffractometer with CuK_αl-radiation (λ = 0.15406 nm). The voltage at the tube anode was 45 kV and the current was 40 mA. Diffraction patterns were taken in a step of 0.025° with a point accumulation time of 1 s. The diffractometric measurements data were processed using High Score Plus software. The microhardness *HV* of the coatings was measured using a PMT-3 microhardness tester at an indenter load of 50 g.

Table 2. Technological parameters of detonation spraying of coatings containing Cr_2AlC MAX phase

Gas flow rate, m³/h				L, mm
$Q_{C_3H_8}$	Q_{O_2}	Q_{air}	Q_{tr}	
0.5	1.55	0.4	0.5	110

The corrosion resistance of the coatings was studied using the potentiostatic method. The coatings with a thickness of 500 μm were deposited on the specimens of AISI 1017 steel with dimensions of 50×50×3 mm. Electrochemical studies were carried out in a P-5827M potentiostat with a scan rate of 2 mV/s at a temperature of 18–20 °C. The specimens under study were used as working electrodes, a chlorosilver electrode (Ag/AgCl) was used as a comparison electrode, and platinum was used as an auxiliary electrode. The study was carried out in a 3% NaCl solution. The current and corrosion potential were determined graphically from polarization curves.

RESEARCH RESULTS AND DISCUSSION

The analysis of the microstructure of the powders of Cr–Al–C and Cr_3C_2–Al systems (Figure 1) indicates the formation of conglomerate-type particles of irregular shape in the MChS process due to the repeated processes of refinement and “cold welding”: both after 1.5 h and after 5 h of processing. The size of the powders of MChS products after 1.5 h of processing is d_{10} = 9 μm, d_{50} = 21 μm, d_{90} = 43 μm for Cr–Al–C system and d_{10} = 8 μm, d_{50} = 17 μm, d_{90} = 45 μm for Cr_3C_2–Al system. When the processing time is increased to 5 hours, the size of the MChS products does not change significantly and is d_{10} = 10 μm, d_{50} = 21 μm, d_{90} = 41 μm for Cr–Al–C system and d_{10} = 8 μm, d_{50} = 16 μm, d_{90} = 40 μm for Cr_3C_2–Al system.

It was found by X-ray diffraction analysis (XRD) that during the MChS process for 1.5 and 5 h of Cr–Al–C system powder, no new phases were synthesized, and only the peaks of the chromium and aluminium phases were present on the XRD patterns of the produced powders (Figure 2, *a*, *b*). The graphite phase

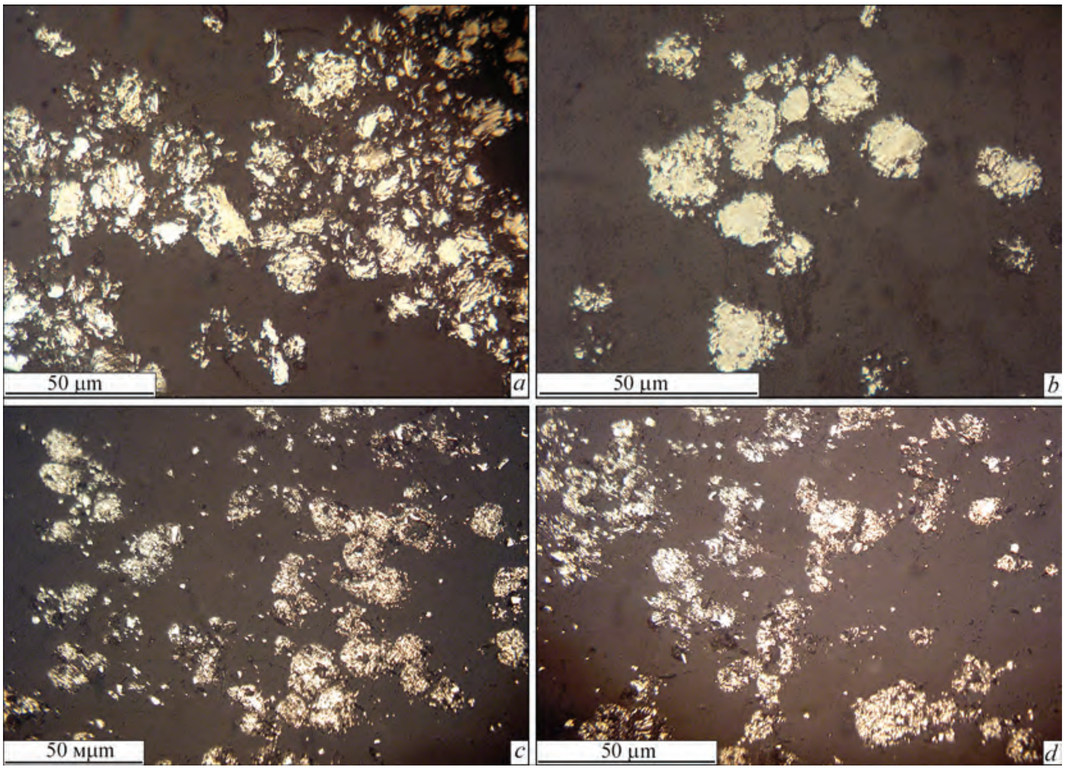

Figure 1. Microstructure of powders of Cr–Al–C (*a*, *b*) and Cr_3C_2–Al (*c*, *d*) systems produced by the MChS method for 1.5 (*a*, *c*) and 5 (*b*, *d*) h

was not revealed in the XRD patterns, which may be the result of its transition to an amorphous state or refinement in the mill during processing to a nanosize. With an increase in the processing time to 5 h, a slight shift towards lower angles of the chromium lines is observed, which may indicate the dissolution of aluminium in chromium to form a solid solution.

In the case of Cr_3C_2–Al system powder, during the MChS process, both at 1.5 and 5 h of processing, the starting components of the mixture of chromium and aluminium carbide interact with the formation of Cr_2AlC MAX phase and a small amount of the intermetallic Cr_5Al_8 compound in the final product of the MChS phase (Figure 2, *c*, *d*). In addition to the start-

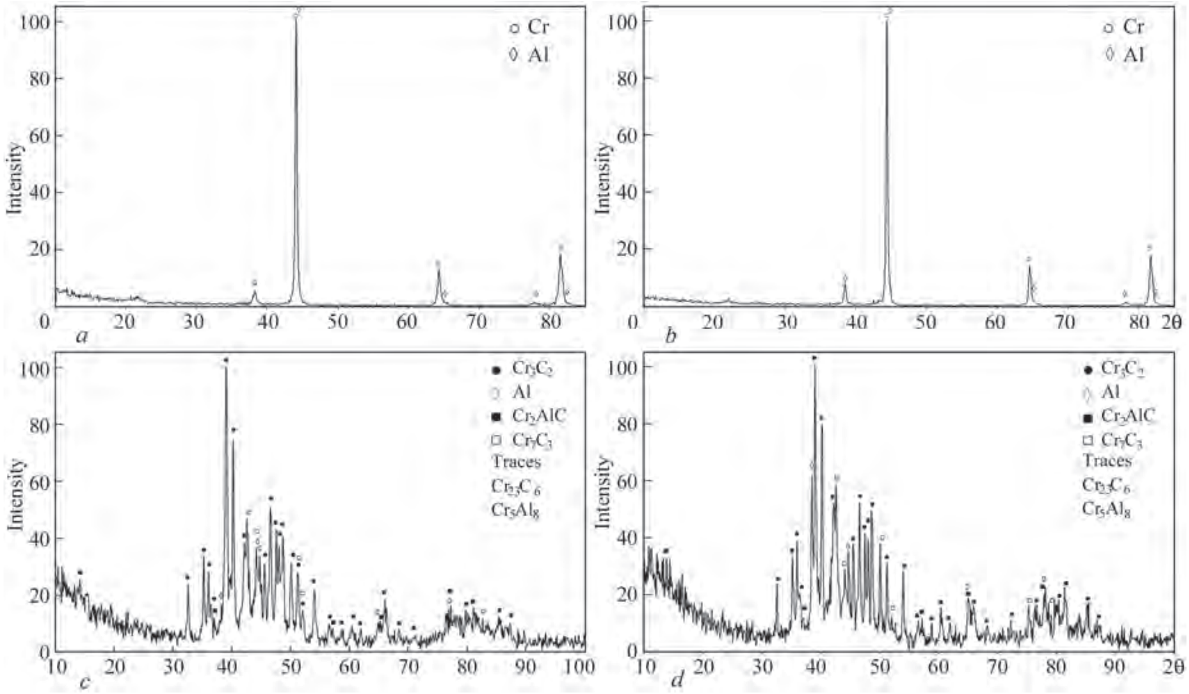

Figure 2. X-ray diffraction patterns of powders of Cr–Al–C (*a*, *b*) and Cr_3C_2–Al (*c*, *d*) systems produced by the MChS method for 1.5 (*a*, *c*) and 5 (*b*, *d*) h

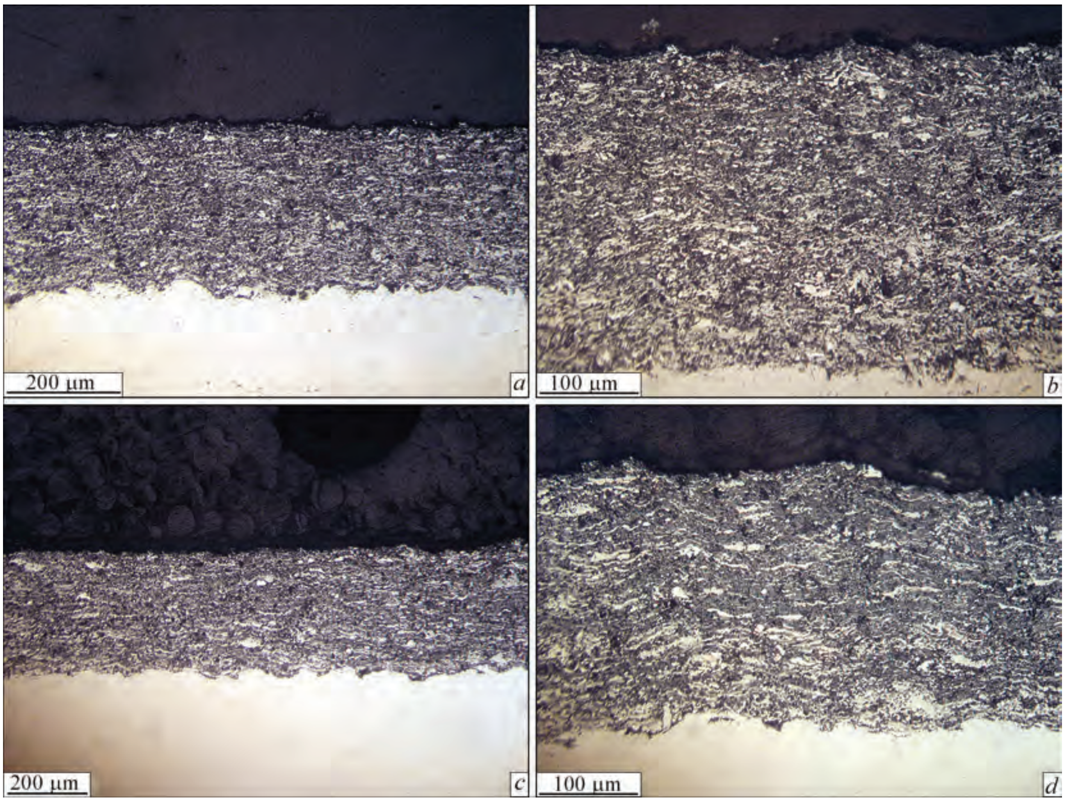

Figure 3. Microstructure of detonation spray coatings produced from MChS powders: *a*, *b* — Cr–Al–C; *c*, *d* — Cr_3C_2–Al

ing components Cr_3C_2 and A1, as well as Cr_7C_3 and $Cr_{23}C_6$ carbides are present in the powders.

Since the phase composition of the produced MChS powders does not differ significantly during processing for 1.5 and 5 h, further MChS powders of Cr–Al–C and Cr_3C_2–Al systems produced within 1.5 h of processing were used to study the formation of coatings under detonation spraying conditions.

As a result of the detonation spraying of the produced MChS powders, dense coatings with a thin-lamellar structure are formed consisting of alternating light and dark grey oxide lamellae (Figure 3). The amount of the oxide component in Cr–Al–C coating is ~35 %, the porosity is ~7 %: in Cr_3C_2–Al coating — ~30 % and 4 %, respectively. The microhardness of Cr–Al–C and Cr_3C_2–Al coatings is 4910±1150 and 5030±1015 MPa, respectively. The presence of a large discrepancy of microhardness values in the range of 3000–10000 MPa is associated with the presence of heterogeneous phases in the coating.

The main phases in the sprayed coatings of Cr–Al–C and Cr_3C_2–Al systems are chromium carbide phases in the quantitative ratio according to the intensity of the peaks: $Cr_7C_3 > C_3C_2 > Cr_{23}C_6$ (Figure 4). In the case of spraying a coating of Cr–Al–C system, the appearance of chromium carbides is predetermined by the interaction of the starting components of chromium powder and graphite during the spraying process. In the case of spraying Cr_3C_2–Al coating, the appearance of a significant amount of Cr_7C_3 carbide is predetermined by the partial transformation of Cr_3C_2 carbide during the spraying process under the influence of temperature and the interaction of powder particles with ambient oxygen. The coatings contain a significant amount of chromium oxide Cr_2O_3 and a small amount of aluminium oxide Al_2O_3 of the co-

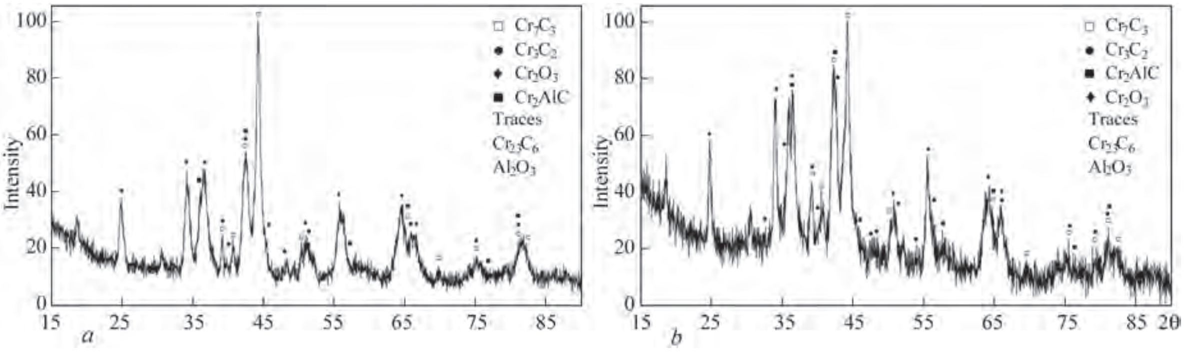

Figure 4. X-ray diffraction patterns of detonation spray coatings of Cr–Al–C (*a*) and Cr_3C_2–Al (*b*) systems

Table 3. Electrochemical characteristics of Cr–Al–C and Cr_3C_2–Al detonation spray coatings in a 3 % NaCl solution

Material	E_{st}, V	E_c, V	i_c, A/cm²
Cr–Al–C DS coating	–0.40	–0.36	$2.0 \cdot 10^{-6}$
Cr_3C_2–Al DS coating	–0.44	–0.38	$1.6 \cdot 10^{-6}$
Steel 3	–0.54	–0.52	$2.4 \cdot 10^{-5}$
40Kh13	–0.28	–0.26	$2.0 \cdot 10^{-6}$
12Kh18M10T	–0.16	–0.18	$1.6 \cdot 10^{-6}$

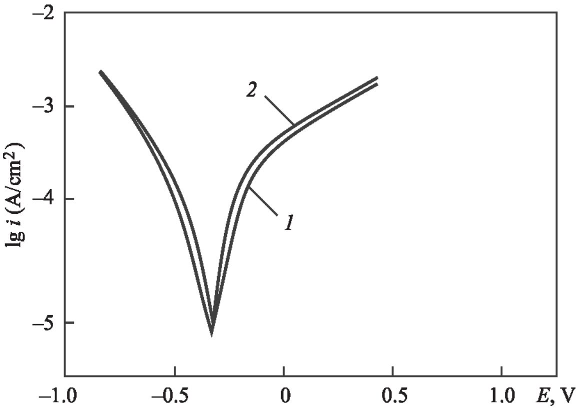

Figure 5. Polarization curves of detonation coatings in a 3 % NaCl solution: *1* — Cr–Al–C; *2* — Cr_3C_2–Al

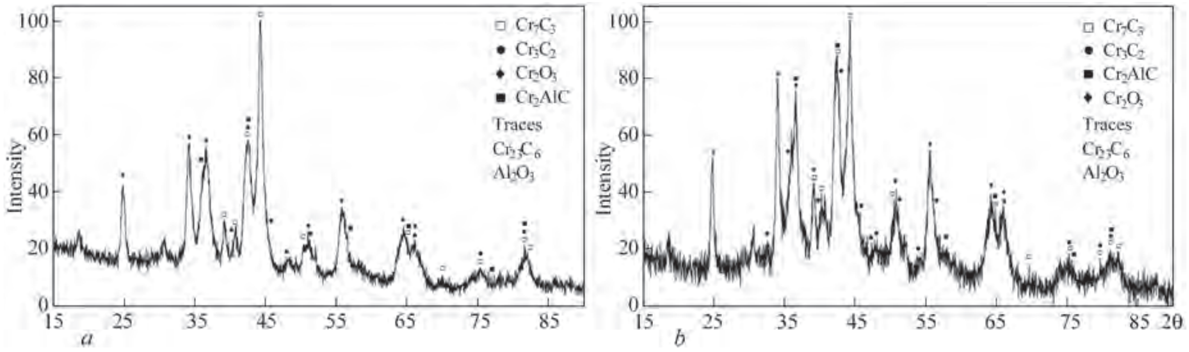

Figure 6. X-ray diffraction patterns of detonation spray coatings of Cr–Al–C (*a*) and Cr_3C_2–Al (*b*) systems after electrochemical studies in a 3 % NaCl solution

rundum modification. In contrast to MChS powders, the coatings do not contain a pure aluminium phase, which indicates its complete interaction during the spraying process with the components of Cr, C, Cr_3C_2 powders and ambient oxygen. Both types of coatings contain Cr_2AlC MAX phase, and the intensity of MAX phase peaks in Cr_3C_2–Al coating is significantly higher, which may indicate a greater amount of MAX phase in it. Also, an increase in the intensity of peaks corresponding to MAX phase on the XRD pattern of Cr_3C_2–Al coating relative to the peaks on the XRD pattern of the MChS powder is noted, which indicates the interaction of powder components during the process of detonation spraying and the formation of a coating layer with the formation of MAX phase.

The studies of the kinetics of the electrode potentials of detonation coatings of Cr–Al–C and Cr_3C_2–Al systems have made it possible to find that the value of the electrode potential of the specimens stabilizes after 25–30 min. The stationary potentials E_{st} are –0.4 and –0.44 V, respectively. The characteristic polarization curves of the coatings are shown in Figure 5; the electrochemical characteristics of the coatings are given in Table 3. For comparison, Table 3 also shows the characteristics of St3 and stainless steels 40Kh13 and 12Kh18N10T.

The analysis of the polarization curves showed that the course of cathodic and anodic polarization curves for detonation coatings of both compositions is almost the same. The corrosion current for Cr_3C_2–Al system coating is 1.25 times lower than that of Cr–Al–C system coating, which indicates its higher corrosion resistance. This is obviously predetermined by the higher content of MAX phase in Cr_3C_2–Al coating and the slightly lower porosity of this coating. After electrochemical studies, the phase composition of the sputtered coatings does not change significantly (Figure 6), i.e., no corrosion processes occur on the surface of the coated specimens. The developed coatings of both compositions are not inferior to stainless steels in terms of their corrosion resistance and are by an order of magnitude higher than carbon steel.

CONCLUSIONS

The carried out studies of the products of mechanochemical synthesis of powder mixtures of Cr–Al–C and Cr_3C_2–Al compositions showed the formation of conglomerate-type particles with a size in the range of d_{10} = 8–10, d_{50} = 16–21, d_{90} = 40–45 μm after 1.5–5 h of processing. In Cr_3C_2–Al system, the formation of Cr_2AlC MAX phase was recorded after 1.5 h of processing; in the case of Cr–Al–C system, no interaction of components with the formation of new phases occurs during the MChS process.

As a result of detonation spraying of the produced MChS powders, dense coatings with a thin-lamellar structure are formed. The presence of Cr_2AlC MAX phase, as well as chromium carbides and oxide phases Cr_2O_3 and Al_2O_3 is recorded in the coatings. The content of MAX phase in the coatings relative to the MChS powder is higher in the coatings formed from the powders of Cr_3C_2–Al system; an increase in the content of MAX phase in the coating relative to the MChS powder was found due to the interaction reactions between the starting components during the spraying process.

Based on the results of potentiostatic studies in a 3 % NaCl solution, it was found that coatings based on Cr_3C_2–Al system are characterized by a lower corrosion current ($1.6 \cdot 10^{-6}$ A/cm^2) compared to Cr–Al–C ($2.0 \cdot 10^{-6}$ A/cm^2), which confirms their higher corrosion resistance due to the higher content of MAX phase and denser structure. The developed coatings of both compositions are not inferior to stainless steels in terms of their indices of corrosion resistance and can be recommended for operation in this aggressive environment.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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