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Formation of Wear- and Corrosion-Resistant Ceramic Coatings by Combined Technologies of Spraying and Micro-Arc Oxidation

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Abstract—Technological aspects of the formation of wear- and corrosion-resistant coatings on aluminum alloys and steel via an integrated use of methods of the low-temperature heterophase transfer, microarc oxidation, and magnetron sputtering. The tribological and anticorrosion properties of the coatings developed were estimated.

Keywords: ceramic, coatings, aluminum oxide, wear resistance, corrosion resistance, friction, wear, oxidation, electrolyte, magnetron

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The construction ceramic based on Al₂O₃ possesses high strength properties and exhibits corrosion-resistance in aggressive chemical media. The practical experience shows that aluminum oxide ceramic materials effectively operate in contact units of critical articles used in machine building and in marine and aviation engineering.

The existing technological approaches to fabrication of aluminum-oxide ceramic materials are based on the compaction and sintering of a mixture of ceramic powders into a monolithic article, but this process is rather expensive with the cost of the starting materials taken into account [1]. It seems that using protective ceramic coatings on metallic articles is a more rational and economical approach.

We consider here combined technological procedures for obtaining new Al₂O₃-based ceramic coatings on aluminum alloys and steel. In particular, we describe the synthesis by the method of “cold” gas-dynamic sputtering (CGDS) of an aluminum coating subjected to microarc oxidation (MAO), which yields a wear- and corrosion-resistant ceramic coating with a transition aluminum

layer to the metal. We also consider ways to strengthen the coatings being developed.

The goal of our study was to examine how wear- and corrosion-resistant coatings are formed on aluminum alloys and steel by integrated use of methods for low-temperature heterophase transfer, microarc oxidation, and magnetron sputtering and to evaluate the tribological and anticorrosion properties of the resulting coatings.

EXPERIMENTAL

As the base for the coatings served 50 × 20 × 3 mm samples fabricated from the aluminum alloys AMg2, AK7ch, A5, technically “pure” aluminum), and 12Kh18N10T steel.

The following powdered materials were chosen for performing the CGDS: aluminum powder of A-80-13 brand with addition of 40 wt % corundum powder (technological additive) of 25A brand with grain size F360; aluminum powder of A10-00 brand with addition of 40 wt % corundum powder (technological additive) of

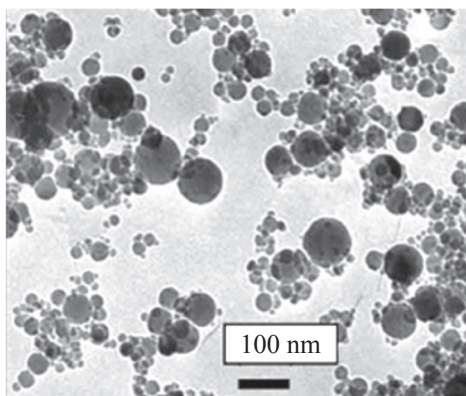


Fig. 1. SEM image of aluminum oxide nanopowder.

25A brand with grain size F360; nanopowder of aluminum oxide (nanocorundum) produced by plasma-chemical synthesis with particle size of 80–100 nm (Fig. 1).

To obtain a composite powder of the conglomerate type, the powder mixtures were subjected to a high-speed mechanical treatment in an IVCh-3 vibratory attrition grinder for 30 min. After being treated in the attrition grinder, the powders were granulated with a 2% aqueous solution of polyvinyl alcohol [2]. Then, the powders were dried, ground, and sieved to obtain the fraction necessary for the sputtering. The powders containing fraction with particle sizes of 10 to 60 μm were further used in CGDS.

The “cold” gas-dynamic spraying was performed on a Dimet-403 installation. The process consists in that particles are accelerated to a high velocity by the ultrasonic flow of air and, as a result, are deposited due to the intense plastic deformation upon an impact in the solid state at a temperature that is substantially lower than the melting point of the material being sprayed [3–5].

After the deposition of a CGDS coating and the appropriate mechanical treatment, the microarc oxidation was performed. When a high current density was passed across the metal–electrolyte interface, the conditions are created in which microplasma discharges with high local temperatures appear on the metal surface. These discharges result, under the conditions of high-intensity heat removal into the electrolyte, in that a thin-layer oxide-ceramic coating is formed [6–8]. The microarc oxidation was performed on the IPT-1000 installation.

The power supply of the installation makes it possible to deliver into the bath a current of up to 100 A at a voltage of up to 1000 V and to vary the current in the bath by connecting additional capacitances, which provides in each particular case a stable occurrence of the MAO and

deposition of an oxide-ceramic layer.

The following electrolytes were used as the working solutions in the MAO.

– Silicate-alkaline electrolyte with composition (g L^{-1}): potassium hydroxide 2, liquid silica glass 8, water the rest. The MAO duration was 1.5 h in the anodic-cathodic mode at an ac current density at ac current density of 13–15 A dm^{-2} .

– Borate electrolyte with composition (g L^{-1}): potassium hydroxide 3–7, boric acid 20–30, and water the rest. The MAO duration was 1.5 h in the anodic mode with dc current density of 5 A dm^{-2} .

The magnetron sputtering was performed on a Magna TM5 installation. This method consists in the cathodic sputtering of a target in the plasma of the magnetron discharge, which is a diode discharge in cross fields.

The microhardness of the coatings was measured in conformity with GOST (State Standard) 9450–76 with a PMT-3M microhardness meter. The dispersity of the powdered materials was measured by the method of laser diffraction analysis with a Malvern Mastersizer 2000 instrument.

The morphology and the elemental composition of the materials were examined by scanning electron microscopy (SEM) and energy-dispersive microanalysis on a TESCAN Vega research complex.

The phase composition of the coatings was examined on a Bruker D8 Advance X-ray diffractometer (Germany) with CuK_α radiation in the Bragg–Brentano configuration.

The adhesion strength of the coatings was determined by the pin detachment method on an Instron 1000 tensile machine.

The wear resistance of the coatings was evaluated on an MTU-1 friction machine by the scheme with rotting 18KhGT steel rods and an immobile aluminum disk with a coating. The contact area was 1.5 cm^2 , the test duration was 20 h at a load of 1.5 MPa and rotation speed of 580 rpm.

The mass wear of the materials was determined on a GH-252 analytical balance. The measurement error was 2×10^{-4} g.

Corrosion tests of the samples with coatings on aluminum alloys were performed in a 5% aqueous solution of NaOH. Corrosion tests of the samples with coatings on steel were performed in conformity with GOST 9.308–85 in a 5% solution of NaCl (“salt spray”).

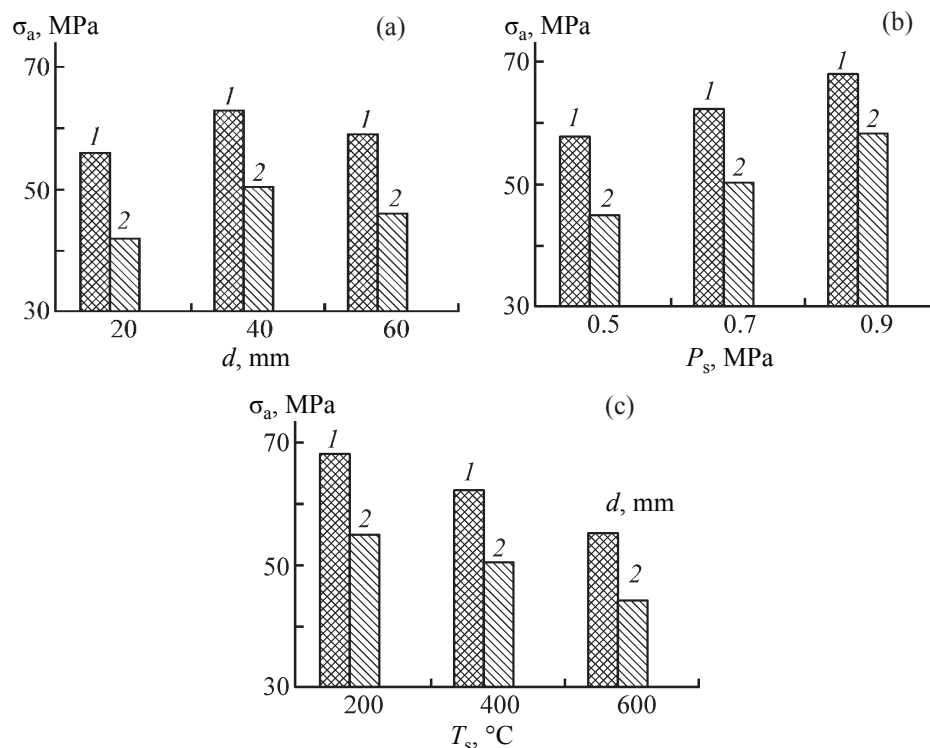


Fig. 2. Dependence of the adhesion strength of the coatings on the CGDS conditions (for the example of A-80-13 powder being sprayed): (a) on the fraction of the powder material, (b) on air pressure, (c) on air-heating temperature. Base: (1) aluminum (2) steel.

RESULTS AND DISCUSSION

Service properties of aluminum coatings formed by “cold” gas-dynamic spraying and strengthened by micro-arc oxidation. Our practical analysis demonstrated that, in “cold” gas-dynamic spraying of aluminum powders, aluminum particles with average grain diameter $d_{av} \leq 5 \mu\text{m}$ are not fixed on the surface because of having a small mass and not possessing a sufficient kinetic energy for being fixed on the metal surface. If a powder containing aluminum particles with $d_{av} \geq 60 \mu\text{m}$ is used, the coating being formed does not have a high adhesion and cohesion strength. When nonplastic particles of coarse-grained corundum in the technological additive to the aluminum powder arrive to the metal surface being subjected to a spray, the particles bounce off the surface cleaning it to remove contaminations and then remove in the same way the natural oxide film from the just formed aluminum coating, with its cohesion thereby substantially raised. Single particles of coarse-grained corundum uncontrollably adhere to the coating and thereby improve its strength characteristics.

Figure 2a shows how the adhesion strength of aluminum coatings varies with the granulometric composition of the particles being sprayed. The use in spraying

of powders having a fraction composition with $d_{av} = 20\text{--}60 \mu\text{m}$ is accompanied by the weakening of the elastic repulsion of particles, which leads to predominance of the adhesion energy.

It was found in the study that the adhesion properties of the CGDS aluminum coatings formed on metals depend of the motion velocity of particles and their temperature. It was confirmed experimentally that raising the air pressure in the spraying chamber results in that the adhesion strength of an aluminum coating becomes higher (Fig. 2b). With increasing air heating temperature, the adhesion strength of the coatings decreases (Fig. 2c).

Estimate of the wear rate of friction pairs

Material	Wear rate of a friction pair ($\times 0.01$), g h^{-1}
AK7ch + MAO	1.19
AK7ch	2.97
AMg2 + MAO	0.89
CGDS coating	4.03
CGDS coating + MAO	1.41

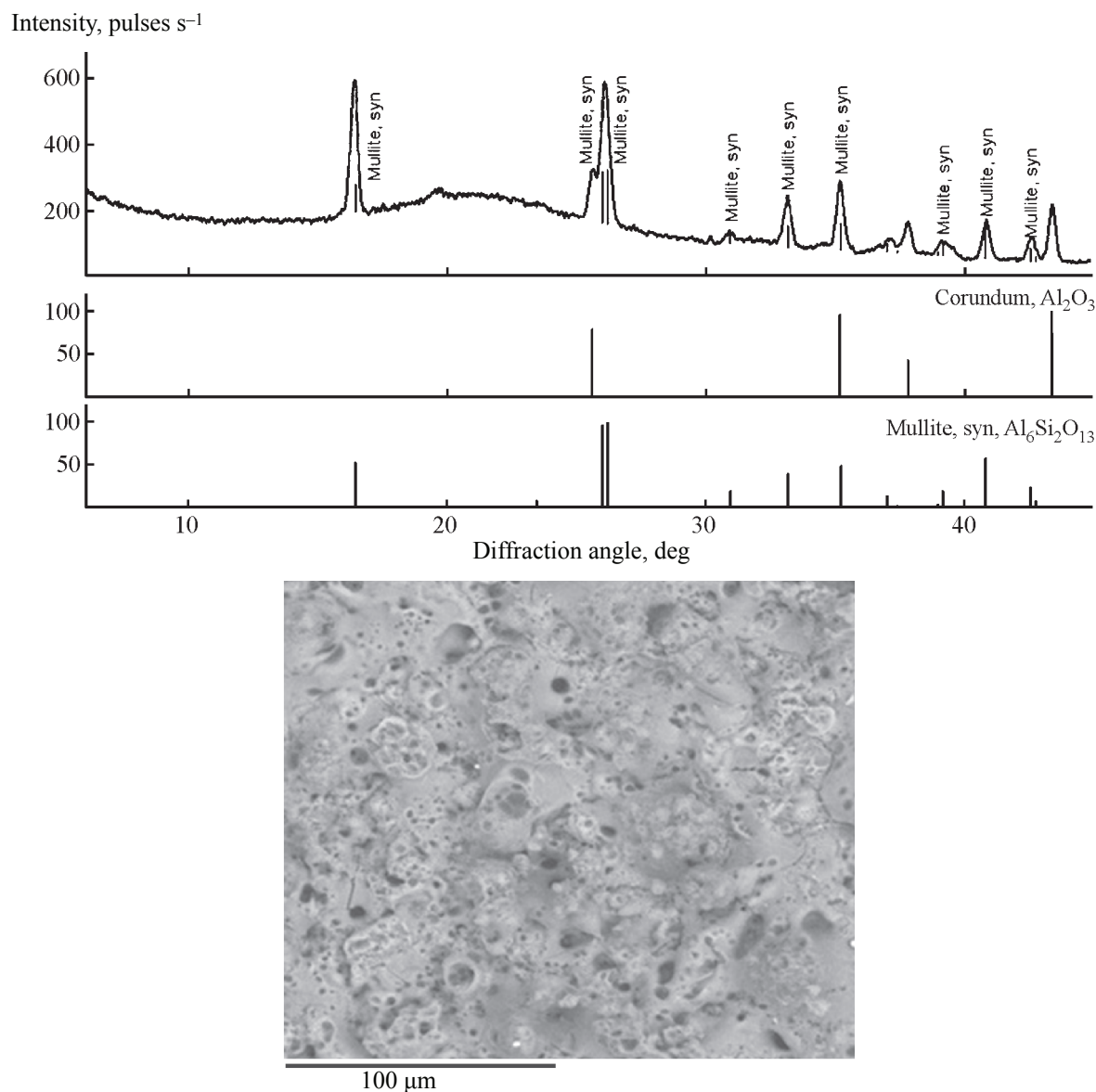


Fig. 3. SEM image of the microstructure of a ceramic coating and X-ray diffraction pattern of the coating surface.

In the first stage of the study, aluminum coatings with thickness $h = 200 \mu\text{m}$ were formed from powder materials A-80-13 on the surface of the aluminum samples. The surface strengthening by microarc oxidation in a silicate-alkaline electrolyte resulted in that an external composite ceramic layer was formed, with the thickness of the transition aluminum layer to the base was $h \approx 70 \mu\text{m}$. The phase composition of the ceramic layer is represented by the mullite phase and corundum. Also present on the surface was amorphous SiO_2 , which is frequently interpreted in the literature as a technological layer that requires smoothing (Fig. 3) [9]:

Element	O	Na	Al	Si
Content, at %	66.88	1.95	8.31	22.86

It was found that the wear resistance of MAO-hardened aluminum coatings formed by “cold” gas-dynamic spraying is approximately 3.1–3.3 that of the unhardened coatings and is 2.2–2.5 times the wear resistance of AK7ch aluminum alloy, taken to be a reference [10–12] (Table 1, Fig. 4). It should be noted that the wear resistance of MAO-strengthened aluminum coatings is somewhat lower than that of oxide-ceramic coatings obtained on aluminum alloys.

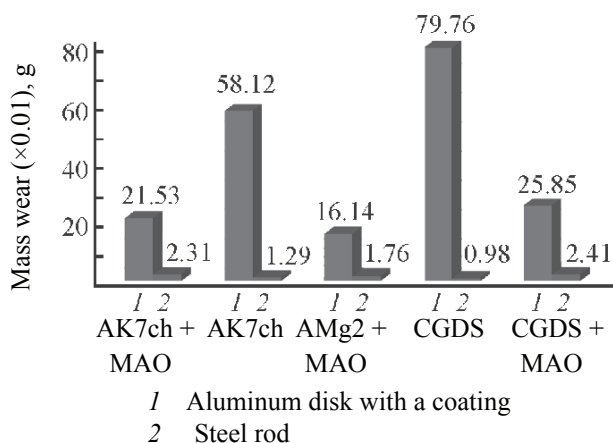


Fig. 4. Results of tribological tests.

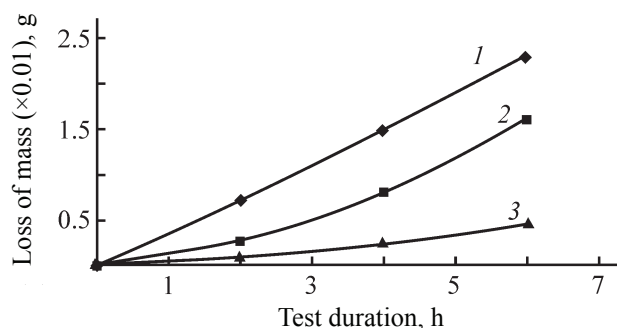


Fig. 5. Dependence of the loss of mass by sample of A5 aluminum alloy on the duration of corrosion tests in an alkaline medium. (1) Without a coating, (2) CGDS + MAO, (3) CGDS + MAO + fluoroplastic film.

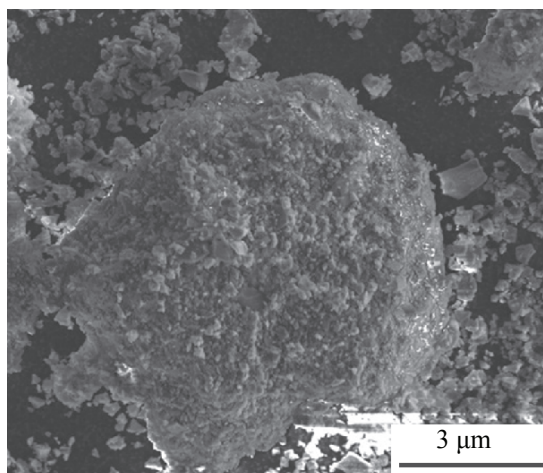


Fig. 6. SEM image of an aluminum particle reinforced with nanocorundum.

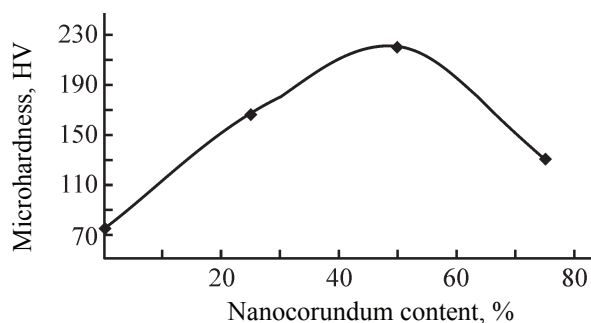


Fig. 7. Effect of the nanocorundum content on the microhardness of aluminum coatings produced by cold gas-dynamic spraying.

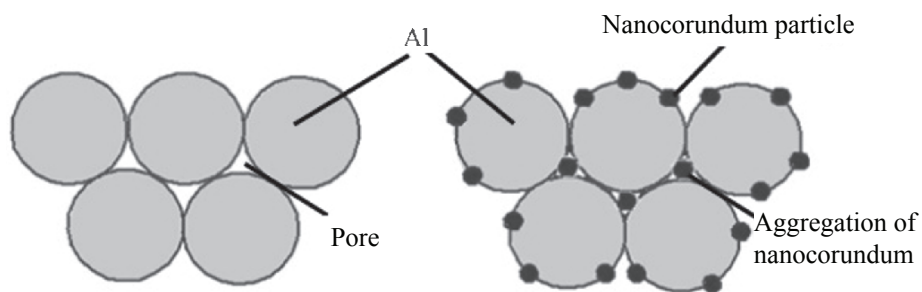


Fig. 8. Cross-sectional packing scheme of aluminum particles after the “cold” gas-dynamic spraying of a mixture of powders with and without reinforcement with nanosize corundum.

An analysis of [13] was used to consider technological aspects of the possibility of obtaining thin fluoroplastic films with thickness $h = 1\text{--}2\ \mu\text{m}$ on MAO coatings by magnetron sputtering.

Figure 5 presents the results of corrosion tests of “technically pure” aluminum A5 without a coating and with composite protective coatings. An intense

dissolution of aluminum is observed in the alkaline medium. The presence of an MAO coating strongly hinders the development of corrosion. It can be assumed that the alkali interacts with aluminum via pore channels in the oxide layer. As a result, aluminum is slowly etched off and the CGDS–MAO adhesion interface is disrupted, with stratification and disintegration of the oxide-ceramic

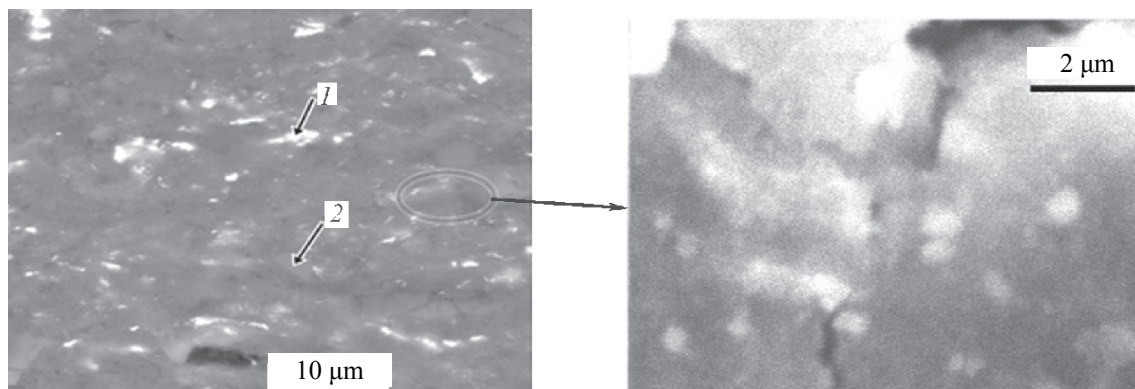


Fig. 9. SEM image of the surface microstructure of a coating formed from a composite powder reinforced with nanocorundum.

coating occurring in 3 h of corrosion tests. The best results are demonstrated by an MAO coating with a film of fluoroplastic, which fills open pores of the oxide layers and makes smaller the zone within which aluminum interacts with the alkali.

Methods for strengthening of composite ceramic coatings on a steel base. To obtain strengthened composite coatings on steel materials, we suggested a new method in which the aluminum layer formed by “cold” gas-dynamic spraying is additionally reinforced with corundum and the aluminum surface with nanocorundum particles is subjected to microarc oxidation in a borate electrolyte.

In the second stage of the study, we deposited coatings on steel samples. For the CGDS, we developed a composite powder that was based on A10-00 and was reinforced with nanocorundum particles (Fig. 6).

Practical tests demonstrated that introduction of nanocorundum substantially raises the hardness of the coatings (Fig. 7). As, however, the content of nanocorundum is raised to more than 50 wt %, a softening of the coating is observed. Probably, the low adhesion is due to the insufficient plastic deformation of composite aluminum particles for their being fixed on the surface.

In the spraying, particles of nanosize corundum not subjected to reinforcement via mechanical synthesis form an aggregation of conglomerates and reduce the coating porosity from 5 to 3% relative to the total volume (Fig. 8).

Figure 9 shows the surface structure of a coating formed from a composite aluminum powder reinforced with nanocorundum to 50 wt %. The white inclusions (point 1) are aggregations of nanosize corundum, and monotonic gray areas (point 2) are constituted by solid microsize aluminum oxide fixed from the powdered mixture of aluminum and corundum particles. All the

rest is a composite coating constituted by an aluminum matrix with nanocorundum.

Aluminum coatings with thickness of 200 μm, with 50 wt % nanocorundum, were produced on the steel surface by CGDS. The adhesion strength of these coatings to the steel base was 50 MPa. The sprayed coatings were oxidized in a borate electrolyte. It was found that, upon replacement of silicates by borates in the microarc oxidation of aluminum, corundum coatings are formed, with the possibility that secondary phases can be formed ruled out, as previously demonstrated in [14–16].

The ceramic coatings formed on steel have the following characteristics: surface-layer microhardness 11–12 GPa, open surface-layer porosity not exceeding 3%, MAO layer thickness of up to 50 μm, and high corrosion resistance of the coating (Fig. 10).

The coatings formed by combined technological procedures are promising for improving the functional characteristics of critical aluminum and steel articles. The results obtained are practically important and can be used to develop domestic technologies, which is particularly important in the import-substitution conditions.

CONCLUSIONS

(1) The wear resistance of aluminum coatings formed by “cold” gas-dynamic spraying and hardened by microarc oxidation is approximately 3.1–3.3 times that of the unhardened coatings and 2.2–2.5 times the wear resistance of aluminum alloys.

(2) The microarc processing in a silicate-alkaline electrolyte of aluminum coatings formed by “cold” gas-dynamic spraying improves the anticorrosion properties of aluminum alloys in an alkaline medium. An additional

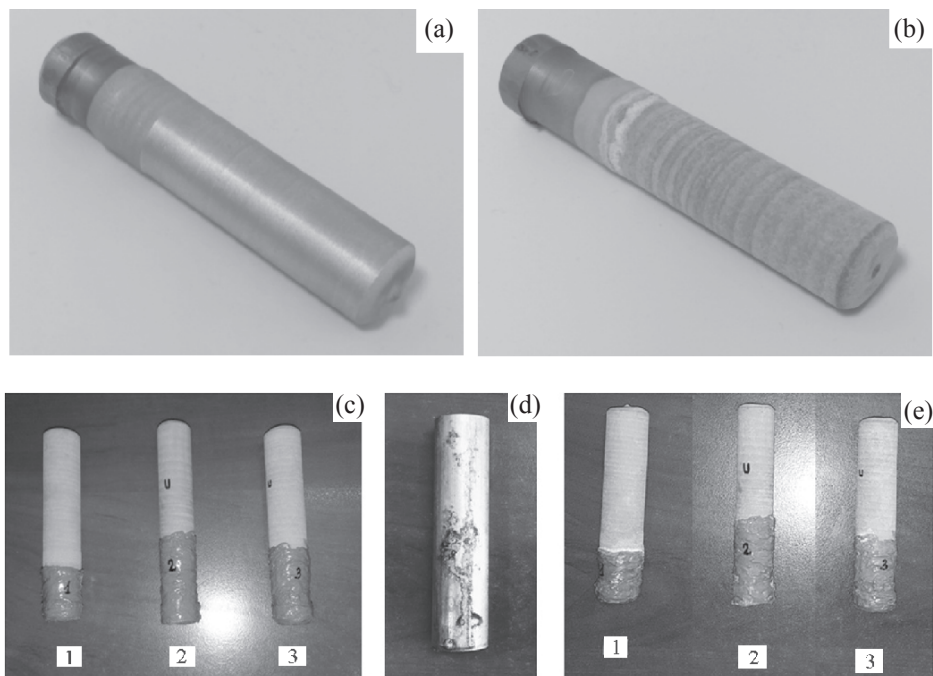


Fig. 10. Results of corrosion tests of simulating 14Kh17N2 steel samples. (a) General view of a sample with hardened aluminum coating; (b) general view of a sample with an MAO coating formed in a borate electrolyte; (c) set of samples before the corrosion tests; (d) witness sample without a coating, kept in a salt spray for 1000 h; (e) set of samples after the corrosion tests with keeping for 1000 h in a salt spray.

corrosion protection is provided by the formation of a fluoroplastic film with thickness $h = 1 \mu\text{m}$ by magnetron sputtering on the surface of an oxide-ceramic coating.

(3) Functional ceramic coatings on steel materials were developed on the basis of the advantages of combined methods of “cold” gas-dynamic spraying of composite aluminum powders and microarc oxidation in a borate electrolyte. Use of coatings of this kind improves the anticorrosion properties of 12Kh18N10T steel.

CONFLICT OF INTEREST

The authors state that they have no conflict of interest to be disclosed in the present communication.

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