Study of the formation of functional ceramic coatings on metals

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Abstract. The paper presents the results of experimental studies in the field of the formation of ceramic coatings using a complex method combining the benefits of microarc oxidation and cold gas-dynamic spraying. These coatings are characterized by high hardness, wear resistance and are an economical alternative to structural alumina ceramic materials for machine supports.

1. Introduction
The functionality of engineering products is largely determined by the properties of the used structural and functional materials. The most effective protection option is the application of protective coatings. This paper discusses the informed choice of materials for coatings and the technology of their application.

Known technical solutions due to the substantial tightening of the operating conditions of marine equipment do not provide effective protection against the aggressive effects of external factors, primarily against wear and corrosion [1]. Practice shows that to effectively protect parts, it is advisable to use complex technologies that combine the advantages of several technologies. The combination of technologies of cold gas-dynamic spraying and microarc oxidation (MAO) is effective when creating coatings of the metal-ceramics system [2-3].

In this regard, an urgent task is to study the possibility of synthesizing new ceramic coatings based on Al2O3 on steel parts, on which an aluminum coating of a given thickness is formed by cold gas-dynamic spraying, containing Al2O3 ceramic nanoparticles, after which the resulting coating undergoes an MAO process, as a result which forms a wear-resistant ceramic coating that provides corrosion protection and high wear resistance.

The aim of the work is to study the synthesis of ceramic nanostructured coating on a steel substrate with the integrated use of microarc oxidation and cold gas-dynamic spraying methods.

2. Object and methods of research
Samples made of structural steel of the St45 grade, having a size of 50x20x3 mm, were used as the substrate.

For the cold gas-dynamic spraying were selected powder materials:
1. Aluminum powder grade ASD 1 TU 48-5-226-87 with the addition of alumina powder (corundum) grade 25A grain F360. Corundum is a necessary technological additive to prevent clogging of the nozzle. The composition of the original mechanical mixture of powders for cold gas-dynamic spraying: 60% aluminum (average grain size 20-60 microns) and 40% aluminum oxide (average grain size 40-120 microns). Figure 1 (a) shows a photograph of the powder for cold gas-dynamic spraying in the initial state.

2. Aluminum oxide nanopowder (nano-corundum), obtained by plasma-chemical synthesis, with a particle size of 80-100 nm, the photograph of the nanopowder in the initial state is shown in Figure 1 (b).
Figure 1. Photograph of powder for cold gas-dynamic spraying.

To obtain a composite powder of conglomerate type, the powder mixtures were subjected to high-speed machining in a vibrating eraser for 30 minutes.

Then, the powders were dried, ground, and sieved to isolate the fraction required for spraying. The powders containing fractions with a particle size of from 20 to 60 microns, later, were used during cold gas-dynamic spraying.

Cold gas spraying was carried out on the installation "Dimet-403". The process is that the particles are accelerated to high speed, due to supersonic gas flow, as a result of which they are deposited due to severe plastic deformation upon impact in a solid state and at a temperature well below the melting point of the sprayed material, using Dimet-403 aluminum particles do not exceed 60 °C [4-7].

After applying the coating by cold gas-dynamic spraying, micro-arc oxidation (MAO) is carried out. When a high-density current is passed through the metal-electrolyte interface, conditions are created when micro-plasma discharges with high local temperatures occur on the metal surface. The result of the discharges is the formation of a coating, which is a ceramic, which is formed due to the oxidation of the metal surface. [8]. The MAO process was carried out on an IPT-1000 unit.

MAO was carried out in an electrolyte based on boric acid of the following composition: boric acid 20-30 g/l; potassium hydroxide 3-7 g/l.

Measurements of the microhardness of the coatings were carried out according to the Vickers method in accordance with GOST 9450-76 on a PMT-3 microhardness tester.

The dispersion of powder materials was measured by laser diffraction analysis using a Malvern Mastersizer 2000 instrument.

The morphology and elemental composition of the particles of the powders and coatings were studied by scanning electron microscopy and X-ray microanalysis on the TESCAN Vega research complex.

The phase composition of the coatings was studied on a D8 Advance X-ray diffractometer from Bruker (Germany) using Cu-Kα radiation in Bragg-Brentano goniometry.

The adhesive strength of the coatings was determined by the method of pin tearing on an Instron 1000 tensile testing machine.

Testing of coatings for wear resistance was carried out in accordance with GOST 30480 on a machine for testing friction 2168 UMT under the "steel (grade 45) ring coated with steel (grade 45) ring" scheme. The clamping pressure was 110 kPa, the movement of the sample with the coating relative to the counterbody was 0.306 m/s, and the range was 1.1 km.

Tests for corrosion resistance was carried out according to GOST 9.308-85.
3. Aluminum coating on steel base reinforced with corundum nanoparticles

During cold gas-dynamic spraying, aluminum particles with a size of less than 5 microns are carried away from the surface, since they have a small mass and do not have sufficient kinetic energy for fixing on a steel substrate. When using a powder with a fraction of more than 60 microns, the formed coating does not have high adhesive and cohesive strength. The particles of corundum in the composition of aluminum powder in contact with the sprayed steel surface fly away from it, cleansing it from impurities, and further eliminate the oxide layer of the newly formed coating in the same way, thereby significantly increasing its cohesion. Part of the coarse corundum "coupled" with the coating, increasing its strength characteristics.

In this paper, aluminum powder was reinforced with nano-sized corundum particles. Figure 2 shows the particle obtained composite powder.

Figure 2. Nanocorundum-reinforced aluminum particle.

Figures 3 (a, b) show graphs of changes in the hardness and wear resistance of coatings after applying cold gas-dynamic spraying of a reinforced composite powder with a different percentage of nanocorundum.

Figure 3. a) the change in the microhardness of the reinforced coating after cold gas-dynamic spraying with different content of nanocorundum; b) change in wear resistance of the reinforced coating after cold gas-dynamic spraying with different content of nanocorundum.
From figures 3 (a, b) it can be seen that the reinforcement of the initial powder mixture with nanoscale corundum leads to a significant improvement in the functional properties of the coating. The best indicators of wear resistance and hardness are demonstrated by coatings reinforced to 50% by weight. Adding more nanoparticles (75%) did not reveal sufficient plastic deformation, which occurs due to "flattening" of aluminum, which is part of an aluminum powder mixture with coarse corundum, to form a non-porous coating and good adhesion of the material, therefore its functional properties are worse.

In the process of spraying particles of nano-sized corundum reduce the porosity of the coating from 5% to 3% of the total volume. Figure 4 shows the microstructure of the surface of a coating of composite powder reinforced with nanocorundum at 50% by weight.

![Figure 4](image)

The white blotches (point 1) are clusters of nanoscale corundum, the monotone gray areas (point 2) are solid microdimensional alumina, fixed from a powder mixture of aluminum powder and corundum. All the rest is a composite coating of an aluminum matrix with a nano-corundum.

### 4. Microarc oxidation

To ensure high wear resistance, it is necessary that microcracks are absent in the resulting ceramic layer. Figure 5 shows the change in the morphology of the MAO coating at different current densities (i) and the processing time constant. An increase in current density leads to an increase in the power of a single microarc discharge, which in turn causes the formation of microcracks. Apparently, this is due to the more intense heating of the boundary layer of aluminum and its expansion. Based on these results, the optimal current density of 5 A / dm² was chosen for carrying out the MAO treatment of the functional-gradient coating.

![Figure 5](image)

a) i = 5 A / dm², t = 1.5 hours  
b) i = 10 A / dm², t = 1.5 hours  
c) i = 20 A / dm², t = 1.5 hours

Figure 5. Surface of MAO coatings, x1000.
Figure 6 shows the dependence of the formation of Al2O3 phases on the duration of the MAO process on the obtained coated samples after cold gas-dynamic spraying. This dependence can be traced with MDO pure aluminum.

![Graph showing the dependence of Al2O3 phase formation on the duration of the MAO process.](image)

**Figure 6.** Dependence of the process of formation of Al2O3 phases on the duration of the MAO process.

The duration of the MAO process in this work was 2.5 hours, during which time about 80% of the wear-resistant $\alpha$-Al2O3 phase was formed in the coating. With an increase in the process time up to 3 hours, an increase in the concentration of $\alpha$-Al2O3 was not observed.

At the first time point, when setting the current density on a sample of 5 A / dm2, the anodizing process took place, which had a duration of about 5-7 minutes and was accompanied by an increase in the voltage on the material before the formation of the first spark discharges. A stable MAO process was observed at a voltage of about 400 V. The growth of the oxide film was accompanied by a gradual increase in the voltage to a value of 515 V.

Coatings obtained by a combination of the method of cold gas-dynamic spraying with MAO can be divided into several layers:
- the main layer with high hardness, density and wear resistance;
- a layer obtained by cold gas-dynamic spraying, hardened with nanoscale corundum;
- metal base.

Figure 7 shows a general view of the combined coating in cross section.

![General view of the combined coating in cross section.](image)

**Figure 7.** General view of the combined coating (1 - steel substrate; 2 - transitional sprayed-MDO coating; 3 - MDO coating).
Table 1 shows the main characteristics of the synthesized wear-resistant coating:

| Table 1 - Coating characteristics |
|-----------------------------------|
| Total coating thickness, microns  | 80  |
| The thickness of the MAO coating, microns | 50  |
| Microhardness of MAO-layer, GPa   | 20  |
| Adhesion to the substrate, MPa    | 60  |
| Open porosity, %                  | 3   |
| Corrosion rate, mm/year           | 0.007 |

The results of the tribological tests show the wear of the counterbody, which is a consequence of the high hardness and wear resistance of the ceramic coating.

5. Conclusions

Reinforcement of ASD-1 aluminum powder with a fraction of up to 60 μm at 50% by weight with nano-sized corundum particles leads to the formation of a composite powder of conglomerate type, as a result, after cold gas-dynamic spraying, the functional properties of the coating, such as hardness and wear resistance, significantly increase.

In the process of applying the method of cold gas-dynamic spraying of composite reinforced powder, the accumulated particles of nano-sized corundum eliminate the pores formed, as a result, the coating porosity does not exceed 3% of the total mass.

The MAO process carried out on the surface after a cold gas dynamic spraying of a sublayer reinforced with nanocorundum in an electrolyte based on boric acid leads to the formation of a ceramic coating saturated with 80% α-Al2O3 with adhesion to the substrate, about 60 MPa and microhardness 20 GPa. The results of tribological tests confirm the high wear resistance of the coating.

Ceramic nanostructured coatings on a metal substrate, obtained by a complex of microarc oxidation and cold gas-dynamic spraying methods, are a cost-effective alternative to structural alumina ceramic materials for machine friction bearings.

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