Properties of Al₂O₃ coatings obtained by electric arc plasma method in "dynamic vacuum"

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Abstract. The results of studies of the influence of the electrophysical characteristics of a heterogeneous plasma flow on the properties of Al₂O₃ coatings (phase composition, adhesion, porosity) during plasma arc thermal spraying on a steel grade 20 in dynamic vacuum, in the pressure range from 7 to 50 kPa and at 100 kPa are presented. As well as the results for different plasma thermal spraying modes (power, consumption rate of plasma-forming gas and powder, pressure in the chamber). For the plasma torch design in this work, it was shown that Al₂O₃ particles are deposited most efficiently when their size is up to 100 μm, with an arc current of 300 A, flow rates for powder 0.1 g/s and for plasma-forming gas of up to 1 g/s in the pressure range (2.0-3.0) · 10⁴ Pa.

1. Introduction
Recently, a lot of attention has been paid to the protection of materials with coatings. Thermal coatings are the most widespread class of coatings that protect the surface of products from various types of wear, especially parts operating at high temperatures [1-3]. The plasma thermal spraying process is carried out in several stages: plasma generation (creating a carrier stream with a high speed and temperature), heat transfer between the stream and the dispersed phase, its acceleration and heating, deceleration of the heterogeneous stream in front of the treated surface, collision and heat transfer with the surface, spreading of liquid particles, their cooling and solidification, diffusion of the particle material into the coating and the opposite process of penetration of the substrate material into the coating, this process is what is essentially meant by the term “coating formation”. Obtaining dense coatings from particles of small diameter has become possible in a controlled environment and in an environment with reduced pressure, because vacuum has a smaller effect on the saturation of sprayed particles with gases and their oxidation. In [4], it was shown that during the deposition process with a decrease in pressure in the vacuum chamber from 1·10⁵ Pa to 5·10³ Pa, increased adhesion of the coating to the substrate is observed. Thus, one of the ways to solve the problem of obtaining high-quality coatings can be the use of plasma spraying in a "dynamic vacuum", as well as the use of a plasma torch of a special design. Therefore, the aim of the work was to study the properties of the Al₂O₃ coating obtained by the electric arc plasma method in “dynamic vacuum”.

2. Methods
To spray Al₂O₃ powder on a steel substrate (after the substrate has been sandblasted), an experimental stand was constructed, the schematic diagram of which is shown in Fig. 1. As a low-temperature plasma generator (LTPG), a direct current plasma torch with vortex stabilization and an expanding channel of the output electrode is used [5, 6], where the maximum plasma temperature exceeds 2 eV
and the mass-average temperature at the outlet to the atmosphere is 4–8 kK with a plasma forming gas flow rate of 1÷5 g/s. The plasma torch design, depending on the melting temperature of the sprayed material, provides several ways of supplying particles (Fig. 2): through holes of various configurations in the cathode, through holes in the first section of the anode, and through holes in the second section of the anode. This design provides a more uniform field of velocities and temperatures of the sprayed particles when operating in the range of current strength of 100÷500 A and gas flow rate of 0.5÷5 g/s. Al₂O₃ was sprayed with a particle size of up to 100 μm at a flow rate of 0.1 g/s on a steel substrate at a flow rate of argon 0.8 g/s, or a mixture of argon and nitrogen with a flow rate of 0.8 g/s each with pressure in the chamber varying from 7 to 50 kPa.

To understand the process of plasma spraying, it is necessary to know the temperature of the plasma jet, particles size and mass, the state of the particles in the dispersed phase, as well as the velocities of the dispersed phase of the heterogeneous plasma stream, and of the stream itself at atmospheric pressure and in a rarefied medium to select the optimal plasma spraying mode [6-8].

Figure 1. Schematic diagram of the experimental setup: 1-control panel, 2-power supply, 3-vacuum chamber, 4-plasma torch, 5-cylinders with gas, 6-powder dispenser (UMP-6), 7-dispenser regulator, 8-spectrometer, 9-high-speed video camera, 10-water cooling pump, 11-heat exchanger, 12-vacuum pump, 13-control valve, 14-computer, 15-sprayed sample.

Figure 2. The gas discharge path of the plasma torch designed for spraying 1-powder feed to cathode area, 2-into the anode region, 3-below the zone of the binding of arc to anode.

3. Results and Discussion

Studies have shown that the velocity of the dispersed phase at the exit of the plasma torch in vacuum is 3–6 times higher than without vacuum. With an increase in current from 250A to 300A, the particles velocity increases, and at currents of 350A and higher it begins to fall (both in vacuum and without vacuum). The characteristic values of the velocities at the exit of the plasma torches nozzle in vacuum are 100–200 m/s, without vacuum 30–35 m/s. At the same time the temperature of powder particles near the substrate at a current of 300 A is on average 2400–2500 K (the melting point of Al₂O₃ is 2317 K). Qualitative analysis and metallographic studies of aluminum oxide ceramics were carried out on specially prepared thin sections (microsections) shown on Fig. 3 in the laboratory of OOO “Melitek” [9]. As the substrate steel of grade 20 was used. Aluminum oxide (alumina) during its
plasma deposition undergoes significant phase changes and ultimately the coating consists of a whole set of phases (α-, δ-, γ- and θ- Al₂O₃), which differ in their chemical and mechanical properties. As a result, the adhesion strength of the coating is very low [3,10]. Of all forms of Al₂O₃, the trigonal α-modification of alumina is the only thermodynamically stable. Microhardness measurements of the deposited layers showed that they have phases with a hardness of HV 840-1018 (low-temperature phase γ-Al₂O₃) and with higher values of HV 1240-1460 (high-temperature phase α-Al₂O₃). Since γ-Al₂O₃ has a lower formation energy than α-Al₂O₃, tetrahedral coordination should form upon rapid cooling, i.e. cubic structure of γ-Al₂O₃. Upon slow cooling, hexagonal α-modifications of Al₂O₃ are formed. In this case, the total free energy of the system decreases. During the deposition process, alumina particles that fall into the axial, highest temperature zone of the plasma flow are heated to higher temperatures. These particles form aluminum oxide layers with the α-Al₂O₃ phase. Less heated particles located in the peripheral zones of the torch form structures consisting of the γ-Al₂O₃ phase. Analyzing the results of metallographic studies, we can say that the deposited layers consist of strongly deformed particles. The ratio of thickness to diameter can be estimated as 1/3:1/4, which indicates the heating of the bulk of the sprayed material above the melting temperature. The creation of a “dynamic vacuum” in the spraying chamber eliminated the addition of the atmospheric gasses into the plasma stream, which led to a substantial increase in the length of the torch. In addition, there is no cooling of the plasma stream.

![Figure 3](image_url). Photos of the substrate with a coating (top) and magnified coating (bottom) magnification of 50 µm and 10 µm.
Figure 4. a) The dependence of the adhesive strength of the coating on pressure and current,  
   b) Dependence of coating porosity on pressure and current

The adhesion characteristics of the coating, Fig. 4a improve with decreasing dynamic pressure: from 5÷10 MPa at a pressure above $3.0 \cdot 10^4$ Pa and 10÷20 MPa at $\approx 2.0 \cdot 10^4$ Pa to 20÷30 MPa at $\approx 1.0 \cdot 10^4$ Pa, but at this pressure the thickness of the coating was very low (up to 0.1mm), the uncertainty of determining the adhesion is high and considering the phase composition of Al2O3 this mode sub optimal. An increase in the consumption of plasma-forming gas at a current strength of 300 A does not lead to an increase in adhesive properties of the coating. An increase in powder flow rate increases adhesion by a factor of 1.5 at an optimum pressure $(2.0÷3.0) \cdot 10^4$ Pa and decreases adhesion at a low pressure $(\approx 1.0 \cdot 10^4$ Pa).

The characteristic of open porosity, Fig. 4b, has a local minimum at the most effective mode of formation of ceramic coatings in a chamber with dynamic vacuum corresponding to $(2.0÷3.0) \cdot 10^4$ Pa and particle velocities of up to 125 m/s and is 15-20%. The most effective mode corresponds to a current of 300A. A lower current (250A) leads to an insignificant increase in porosity in the region of optimal pressure, and its decrease at atmospheric pressure, which can be explained by insufficient heating of particles at high plasma flow rates. At low pressures $\approx 1.0 \cdot 10^4$ Pa, the operating mode at a current of 400A shows a lower porosity than at 300A, but greater than at 300A and optimal dynamic pressure, therefore, at a pressure of $\approx 1.0 \cdot 10^4$ Pa, a better coating quality is achieved at higher currents.

4. Conclusion
An experimental complex of plasma-electric arc thermal spraying in “dynamic vacuum” was created on the basis of a low-temperature direct current plasma generator with an expanding channel of the output electrode, in which the sprayed powder could be supplied both to the cathodic or anodic arc attachment zones and to the current-free plasma jet. Techniques for determining the speed, size, and temperature of particles under various operating conditions of the plasma torch were developed. For this plasma torches design, the optimal operating mode in a “dynamic vacuum” (power, plasma-forming gas and powder flow rate, chamber pressure) at which Al2O3 is efficiently deposited was determined.

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