Obtaining electrically conductive wear-resistant coatings using cold gas-dynamic spraying method

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Abstract. This work presents research results of the technology development in applying electroconductive wear-resistant coatings using supersonic cold gas-dynamic spraying method.

Keywords: electrocoating dispenser, wear-resistance, quasi-crystalline compound, nano-structured coating, fraction.

Introduction

The problem of increase in materials wear-resistance while maintaining their high electrical conductivity constantly arises in producing competitive products. There are a number of methods that may increase wear-resistance of machine parts friction pairs surface (detonation spraying, plasma spraying, etc.). It is well-known that most durable coatings are metal and cerment. They provide special high mechanical and special protective properties of products. Electrochemical methods of applying protective oxide coatings, similar in properties to structural ceramics, are also common [1-6].

In thermal spraying methods of powder materials on a substrate, two-phase high-temperature flows are used to obtain high adhesion (for example, plasma, explosion energy, thermal energy of gases combustion, and electromagnetic beam).

In this case, properties are determined by the physicochemical processes which occur during interaction with the molten particles' substrate or particles close to this state of the sprayed material [7].

In the method of thermal gas deposition of metal coatings with a heterophase flow temperature of more than 3000 °C, there are a number of specific effects that limit the possibilities of using it. These effects are, formation of oxides, nitrides, carbides, structural changes, the occurrence of high thermomechanical stresses due to the difference in the coefficients of thermal expansion of the substrate, and the applied coating. These phenomena significantly reduce quality of the coating and adhesion, strength of the applied material to the substrate, and cohesion of the applied layer.

Particular difficulties arise when applying non-equilibrium, chemically active materials. At (0.4-0.6) of metal or alloy melting temperature, the initial structure degrades, brittle phases appear, and complex oxides are formed. This leads to a noticeable decrease in the technological and operational properties of the coating and the product as a whole [8]. Therefore, in the recent years, there has been an intensive search for low-temperature methods of forming functional coatings. These methods include: magnetron spraying [9-11] and high-velocity cold gas-dynamic spraying (HCGDS) [12].

Principle of the method consists in the application of metal powders or their mixtures, transported using supersonic gas flows, onto the surface to be treated. According to known technologies, the powder material which is finely dispersed particles ranging in size from 5 to 80 microns is accelerated in a supersonic nozzle by a compressed gas stream to velocities exceeding the sound velocity and directed...
to the surface to be coated. At the same time, temperature of the applied material, as a rule, does not exceed 120 °C. By changing the mass flow rate of the applied powder and introducing a plasticizer, control of the chemical composition in thickness is achieved. HCGDS method allows deposition of films and coatings with a thickness from 10 microns to several millimeters.

When applying formable materials such as Al, Cu, the spraying process takes place at particle velocities of 400 m/s. Such velocities can be achieved by using air as the working gas. Gas flow rate can be increased by 1.2–1.5 times. This rate is very effective in obtaining coatings with high adhesion. For obtaining that rate, the working gas such as air is heated by passing it through a special ohmic heater located up to the nozzle cluster. Typically, the working gas temperature does not exceed 250°C while particles temperature in the flow is 80–120°C.

The method is very promising for depositing homogeneous materials, i.e. when the substrate material and the applied layer material are close to each other in crystallographic structure and thermal expansion coefficients. However, when applying electrically conductive coatings with an electrical conductivity of the order of 10-8 Ohm m, it is possible to obtain high wear-resistance (wear of the order of 3.5x10^9 mm/km) and low porosity of the coating (about 0.5%).

Objective of the work is to develop functional coatings based on applying HCGDS method.

**Materials and equipment**

Copper powder (with grade C-01-04 and fraction 40–60 µm) is used as a starting material for spraying coatings. Copper has been used as a carrier (substrate). To ensure a stable coating process and achieve the required level of properties, the following materials are used: ZrO2 powders with a particle size of 0.1–1.0 microns, reinforcing nanoparticles of a quasi-crystalline compound of the Al-Cu-Fe system, and reinforcing particles of Y2O3. For mixing the powders, a mixer of the «Mixer-0.5» type has been used and mixing has been carried out for 15 minutes. Dispersion degree of powder materials has been measured on a «Malvern Mastersizer 2000» laser diffraction analyzer and an «Zetasizer Nano» laser diffraction nanoparticle analyzer. Coatings have been obtained using HCGDS method on the DIMET-403 installation [13]. Study of the coatings microhardness has been carried out on a microhardness tester PMT-3. Wear-resistance has been determined on a material friction testing machine 2168 UMT. Particle velocity in a heterophase flow has been measured according to the method described in [14].

**Research results**

A method for applying nanostructured wear-resistant electrically conductive coatings has been developed. This method includes feeding a powder composition with reinforcing particles from four dispensers into a supersonic flow of heated gas with forming a heterophase flow and applying a powder composition to the surface of the product (Figure 1). At the same time, the following procedure is applied. First, reinforcing ultrafine ZrO2 particles with a fraction of 0.1 to 1.0 µm are introduced from the first dispenser into the supersonic flow of heated gas. Surface of the product is treated until a juvenile surface is formed. After that, a powder composition based on Cu is applied to the surface of the product with a preselected ratio components by feeding powder from four dispensers. Reinforcing ultrafine ZrO2 particles are fed from the first dispenser, Cu powder from the second dispenser, reinforcing nanoparticles of a quasi-crystalline compound of the Al-Cu-Fe system from the third dispenser, and reinforcing Y2O3 particles from the fourth dispenser. Velocity of the heterophase flow when applying the composition based on Cu varies in the range from 450 to 750 m/s.
Figure 1. Appearance and scheme of operation of «Dimet 403» when applying electrically conductive coatings

In this case, velocity of the heterophase flow of the heated gas with reinforcing ultrafine ZrO$_2$ particles is varied in the range from 320 to 450 m/s. Mass flow rate of the powder from the dispensers is selected in the range from 5% to 80%. Total mass flow rate of reinforcing particles in relation with the Cu powder is not less than 20% and not more than 80%. Moreover, a powder is supplied from the first, third and fourth dispensers. This powder consists of particles with the following ratio of fractions: a particle diameter of 5-50 microns in an amount from 50 to 99% of the volume, and with a particle diameter of 50-800 nm in an amount from 1 to 50% of the volume.

At the first stage of application, non-metallic ultrafine ZrO$_2$ particles with a fraction of 0.1 to 1.0 μm are preliminarily introduced into a supersonic flow of a heated gas (for example, air) from dispenser 1. Surface of the sprayed product is processed until a juvenile surface is formed, the heterophase flow velocity at this stage is 320 to 450 m/s after which the dispenser 1 is turned off. At the second stage the heterophase flow velocity is 450 to 750 m/s. At this stage, a powder composition with a preselected ratio of components based on Cu and using nanoparticles of a quasi-crystalline compound of the Al-Cu-Fe system is applied to the juvenile surface of the sprayed product from dispensers 2, 3 and 4 and metal oxides ZrO$_2$, Y$_2$O$_3$. The purpose of applying this powder composition is obtaining a nanostructured wear-resistant electrically conductive coating.

At a flow velocity (at the second stage) less than 450 m/s, kinetic energy of the incident flow of particles is insufficient for forming a nanostructured coating. At a flow velocity above 750 m/s, elastic collision and «rebound» of the sprayed particles from the substrate surface are observed.

To obtain a nanostructured coating with adjustable wear-resistance while maintaining a high electrical conductivity of $2.2-2.8 \cdot 10^{-8}$ Ohm·m, mass flow rate of powder from any dispenser varies from 5 to 80%. Moreover, the total mass flow rate of the reinforcing nanostructured powders of the system Al-Cu-Fe and metal oxides ZrO$_2$ and Y$_2$O$_3$, in relation with the base powder, should not be less than 20% and not more than 80%. With an increase in the mass flow rate of reinforcing powders above 80%, a sharp decrease in the electrical conductivity of the coating occurs. There is no increase in the wear-resistance of the sprayed coating when reinforcing powders consumption decreases below 20%.

To reduce porosity of the resulting coating, Nano-sized particles of a quasi-crystalline Al-Cu-Fe compound of the sprayed powder are introduced. This thing makes it possible to provide the most dense packing. Introducing Nano-sized particles into composition of the powder mixture is provided by the following technological method. It is represented by the fact that powder compositions are prepared for each of the reinforcing powders which consist of a mechanical mixture of reinforcing powders with a fraction of 5-50 microns and 50-800 nm. These powders are poured into dispensers 2, 3, 4 and fed into
gas stream together with the powder bases (Cu) in the following sequence. At the beginning, dispenser 1 (ZrO₂) is turned on. The surface of the sprayed product is processed until a juvenile surface is formed and after that, dispenser 1 is turned off. Then, all the four dispensers are turned on. A powder composition with a preselected ratio of components is applied to obtain a nanostructured wear-resistant electrically conductive coating. This composition is based on Cu (dispenser 2) using nanoparticles quasi-crystalline compound of the Al-Cu-Fe system (dispenser 3) and metal oxides ZrO₂ (dispenser 1) and Y₂O₃ (dispenser 4).

The result is a wear-resistant electrically conductive coating with adjustable wear-resistance while maintaining high electrical conductivity: (2.2-2.8)·10⁻⁸ Ohm·m. At the same time, phase boundary of the applied layer is absent due to the regulation of powder consumption from the autonomously operating dispensers. In addition, introducing ultrafine particles of various fractions in a given ratio, makes it possible to obtain coatings of a denser packing which reduces number of pores (porosity is about 0.5%). Wear-resistance is determined by the wear of a product in a «disk-disk» installation with a counterbody made of steel 40, which is (1.5-3.5)·10⁻⁹ mm/km for coatings obtained under different modes.

When developing the proposed method using a laser Doppler velocity meter based on a spherical Fabry–Pérot interferometer, it was found that a significant increase in flow turbulence was observed at velocities of 600 m/s and more. At the same time, energy of the dispersed particles meeting with the barrier increases. Accordingly, the adhesive and the cohesive strengths of the coating increase and use coefficient of the powder also increases. However, this effect is reduced when using coarse powder over 50 microns. When it is used as a base powder of a material corresponding to the chemical composition of the sprayed product surface, a minimum change in the thermal expansion coefficient in the obtained layers of the gradient coating is ensured. It ensures high adhesion strength of the applied dispersed material. The results are presented in table 1.

| Composition mixture, % | Cu  | ZrO₂, Y₂O₃, Al-Cu-Fe | Particle velocity, m/s | Specific electrical resistivity 10⁸, Ohm·m | Hardness, HV | Porosity, % | Wear-resistance, mm/km |
|------------------------|-----|----------------------|------------------------|-------------------------------------------|-------------|------------|------------------------|
| 90                     | 10  | 350                  | 1.2                    | 60                                        | 1.2         | 3.5        |
| 80                     | 20  | 400                  | 1.8                    | 85                                        | 0.7         | 3.1        |
| 70                     | 30  | 500                  | 2.3                    | 130                                       | 0.8         | 2.4        |
| 50                     | 50  | 650                  | 2.8                    | 200                                       | 0.5         | 1.5        |
| 40                     | 60  | 700                  | 2.4                    | 180                                       | 2.5         | 1.9        |

From the given data in Table 1, it can be seen that the claimed technical effect (increased wear-resistance of the coating while maintaining high electrical conductivity and the possibility of its regulation) is achieved with the specified technological parameters. These parameters are heterophase flow rate, fraction size, and fraction content in the powder composition. The best results are obtained using a composition with a ratio Cu: (ZrO₂ + Y₂O₃ + Al-Cu-Fe) = 50:50 at a coating spraying velocity of 650 m/s. This coating is recommended for practical use in the elements and assemblies of equipment [15].

Conclusions
1. A technology has been developed for producing electroconductive wear-resistant coatings using the method of high-velocity cold gas-dynamic spraying.
2. Spraying is carried out from four autonomously working dispensers. The first dispenser contains ultrafine ZrO₂ powder to create a juvenile substrate surface. The second dispenser contains pure copper powder for applying an electrically conductive layer. From the third dispenser, a reinforcing Nano-sized quasi-crystalline Al-Fe-Cu is deposited while Y₂O₃ is deposited from the
fourth dispenser. Combination of the dispensers operations provides a functional coating with the required level of properties.

3. The coating is recommended for use in elements and assemblies of modern devices.

Acknowledgments
The presented material was obtained within the framework of the Russian Science Foundation grant "Conducting research by world-class scientific laboratories in the framework of the scientific and technological development priorities implementation of the Russian Federation" of the President's program of research projects implemented by leading scientists, including young scientists under agreement № 21-73-30019.

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