Air plasma sprayed coatings of self-fluxing powder materials

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Abstract. The article discusses the structural features of self-fluxing coatings obtained by plasma spraying air from entering the hub ring and the gas-dynamic focusing powder. It was shown that, unlike the unilateral spot powder inlet into the plasma jet, the use of the annular input node allows to increase heating efficiency and to accelerate the particles in the plasma stream. By optical and scanning electron microscopy that most of the particles forming the coating, in the plasma jet is in a molten or plasticized condition. Transmission electron microscopy revealed that high cooling rates of such particles contribute to the formation of \( \gamma \)-SMC supersaturated solid solution Ni-based average grain size of 80 nm.

1. Introduction

One of the most urgent problems of modern materials science is the development of new structural materials with high technological properties and can withstand increasingly tough operating conditions. Depending on the purpose of product materials from which they are made should possess various properties. For example a high wear resistance, heat resistance, thermal conductivity, strength, corrosion resistance, electrical conductivity, etc.

Operation of machine parts is accompanied by deterioration, which in turn requires replacement and increases production costs. Furthermore, to make the entire piece of expensive material is impractical because it is related to the high cost of new materials and the difficulty of processing the workpiece surface. Effective solution to the problem of increasing the wear resistance of the surface is the formation of coatings on steel products [1]. Furthermore, coating - a way to save scarce and expensive alloying elements which are used to produce steels and alloys with special properties [1 - 3].

To improve the durability of parts and increase its service life can use various methods of surface hardening. One of the promising methods of coating formation is currently air-plasma spraying powder materials [1-6]. This technology allows you to apply coatings of different materials on the surface of any complexity or restore the most worn surfaces of the parts [2, 4].

The most common way to enter the powder into the plasma jet cross point is administered through a tube-shihtoproprov shear outlet nozzle or through a hole in the nozzle [7-9]. This method contributes to heterogeneity of the input fields of temperature and velocity of the plasma jet, which considerably reduces the quality of the formed coatings. The coatings are characterized by high porosity (15%) and poor adhesion [10, 11], which prevents their widespread use.
For the axisymmetric high-temperature heterogeneous flow in the present study used the input node of the ring of powder with gas-dynamic focusing. The prospect of such a powder inlet and the existence of the above problems have led to the development of the original node ring input and relevant research [12].

In contrast to the one-sided point of input feed conveyor ring and focusing gases does not lead to a distortion of the temperature profiles of the plasma jet, as can be seen in Figure 1, which shows the temperature profiles of air plasma jet at a distance of 5 mm from the nozzle as a free flow conveyor and focusing gases (curve 1) and in their feed (curve 2) [13].

![Temperature Distribution in Plasma Jet](image)

**Fig.1.** The temperature distribution in the plasma jet at a distance $z = 5\text{mm}$ from the edge of the outlet nozzle at the operating conditions of the plasma torch: $I = 200 \text{ A}$, $U = 270 \text{ B}$, $G_{\text{plazm.}} = 2 \times 10^{-3} \text{ kg/s}$; $G_{\text{zav}} = 0.25 \times 10^{-3} \text{ kg/s}$; 1 - GTP = Gfok = 0 kg/s; 2 - GTP = Gfok = 0.5 $\times 10^{-3}$ kg/s

Measurements of the temperature distribution in the plasma jet formed by the spectral lines of atomic copper Cu1, present in the air stream due to erosion of the copper electrode (anode). The spectra were measured for several positions line up. Scanning the diameter of the plasma jet was conducted by mechanical movement of the plasma torch 1 mm increments from the bottom up. Position $y = 0$ corresponds to the uppermost position of the jet, $y = 14 \text{ mm}$ - the lowest position of the jet, in which the visible spectral lines. The spectrum contains lines Cu1 $\lambda_1 = 5105.6 \text{ Å}$, $5153.2 \text{ Å}$, $5218.2 \text{ Å}$, $5700.2 \text{ Å}$ and $5782.1 \text{ Å}$. To measure the temperature of the plasma were selected pairs of lines: $\lambda_1 = 5105.6 \text{ Å}$, $\lambda_2 = 5153.2 \text{ Å}$; $\lambda_1 = 5105.6 \text{ Å}$, $\lambda_3 = 5218.2 \text{ Å}$.

As seen from the graph in Figure 1, a slight decrease in temperature, feeding the carrier gas and the focusing is observed only in the periphery of the jet. The central part of the jet remains undisturbed, indicating an insignificant depth of penetration into the plasma jet of cold carrier gas and a focusing assembly using annular input powdered materials.

Earlier work by the authors showed that use of an annular input node powder, compared with a one-way point, allows to significantly increase the heating efficiency of the particles, which contributes significantly to the quality of ceramic and metallic coatings [13 - 19].

In this paper, as a material for the deposition of wear-resistant coatings of self-fluxing powder was selected on the basis of nickel. Due to the high resistance of the formed coating to abrasion and ability to work with significant impact loads, it is used in machine tool (protection guides machines). High heat resistance causes the application of self-fluxing coatings in aircraft (turbine blades and compressor of a jet
engine) and mechanical engineering (protection detachable and permanent matrices for pressing). The high corrosion resistance allows their use in the petroleum and coal industry (production of parts of mud pumps). High resistance to cavitation wear allows the use of these coatings in transport engineering (propellers river and sea vessels) [1-3, 17].

The aim of this work was to study the structure and properties of wear-resistant coatings of self-fluxing alloys formed by plasma spraying using the input node of the ring of powder with gas-dynamic focusing.

2. Materials and Methods of Research
As the material for the formation of wear-resistant coatings used self-fluxing nickel-based powder brand PR N77H15S3R2-3 dispersion 40/100 microns. The powder was sprayed onto a mild steel pipe St3 with 25 mm inside diameter and a wall thickness of 3 mm.

Plasma spraying was performed using a plasma torch PNA-50 manned annular input node of powder with gas-dynamic focusing (development of the Institute of Theoretical and Applied Mechanics SB RAS). Spraying was carried out on samples of the following modes:

Mode number 1: current - 140 A, the voltage - 265 V;
mode number 2: current - 170 A, the voltage - 258 V;
mode number 3: current - 200 A, the voltage - 250 V;
mode number 4: current - 230 A, the voltage of - 243 V.

Spraying distance was 170 mm. As the plasma gas used air as a protective (veil anode), and the focusing of the conveying gas, a mixture of air and propane-butane. Plasma gas flow was 3 g / s, shielding - 0.45 g / s, and the conveying focusing - 0.9 g / s.

Immediately before spraying, blasting the surface of the parent metal. Measuring temperature of heating the particles in a plasma jet were performed using the apparatus and methods presented in [20].

For metallographic studies using optical microscope Carl Zeiss Axio Observer A1m. Deeper structural studies were carried out on a scanning electron microscope Carl Zeiss EVO50 XVP using microprobe EDS X-Act and the transmission electron microscope Tecnai G2 FEI. To determine the phase composition of the coatings used X-ray diffractometer ARL X'TRA. The porosity of the coatings was determined by microscopic method. The microhardness of the structural components of coatings were evaluated for Wolpert Group 402MVD. Wear-resistant coatings in friction of loosely fixed abrasive particles was evaluated by comparing the wear test samples and specimens of mild steel 20 after cementation according to GOST 23.208-79 [21].

3. Results and discussion
In [15] it was shown that the formed coatings are characterized by a complex structure: there are not melted or deformed (the first type); not melted but deform plastically (second type) and molten particles (the third type). The number of particles of the first type in the coating is large, and with increasing of the arc current remains practically unchanged. This caused a slight increase in the temperature of particles in the plasma jet. Table. 1 shows the mean temperature of the spray particles in the cross section of the plasma jet at a distance of 170 mm from the nozzle.

| Deposition Mode | Average Temperature, K |
|-----------------|-------------------------|
| number 1        | 2189 ± 199              |
As a result, local microhardness measurements revealed that the maximum hardness (900 ... 1050 HV) have a third type of particle. This is due to the structural changes occurring in the particles of this type during the crystallization. Firstly, heating of the particles within the plasma stream resulting in the formation of a homogeneous melt, and rapid crystallization (solidification time of the particles - 10^-5 ... 10^-7 [1]) to the fixing metastable structures (supersaturated solid solution), which is typical during deposition of alloys a quantity of alloying elements which exceeds the limit of their solubility in the solid state. According to X-ray structure analysis in the presence of the coating was found γ-based solid solution Ni. Presumably, this supersaturated solid solution of Cr and Si in the γ-Ni. Furthermore, X-ray diffraction analysis were able to detect the presence in the coating of the reinforcing phase in the form of nickel boride (Ni$_3$B), chromium boride (Cr$_2$B and CrB), chromium carbide (Cr$_7$C$_3$), nickel silicide (Ni$_3$Si) and nickel-iron (FeNi$_3$).

Transmission electron microscopy revealed that the amount of discharge of the hardening phase is from 5 nm to 50 nm. Since sputtering was performed in air, in the structure of the coatings were also found nickel nitride (Ni$_3$N) and nickel oxide (Ni$_2$O). Furthermore, it was found that the particles of the third type is formed submicrocrystalline structure with an average grain size of 80 nm.

One disadvantage of plasma spray technology with a point entering the powder coating is a high porosity (15%). Porosity of coatings formed by means of plasma spraying with an annular entry, far below (Table. 2). This phenomenon can be explained by the fact that entering the annular powder provides a dense axisymmetric heterogeneous flow, which in turn contributes to the maximum flow rate of the plasma and the maximum penetration of the powder particles.

Significant differences between the formation of heterogeneous flows in the ring and dot powder inlet are clearly visible in the photographs presented in Figure 2 [13].

![Annular input powder with gas dynamic focusing](image1)

![Spot administered powder](image2)

**Fig.2. Photos of high flows in heterogeneous ring and point inputs of the powder material**

It is clearly seen that, in contrast to a point input, the input ring with gas dynamic focusing provides dense axisymmetric heterogeneous stream (with the correct mode, all the powder particles pass through a high-temperature and high-axial region of the plasma jet).
Coatings formed on mode number 1 have the lowest porosity (0.96%), in contrast to the coatings obtained on the mode number 4 (~ 5%). This phenomenon can be explained by the increase in the degree of superheat of the particles. As noted above, the majority of sputtered particles are melted or plasticized (particles of a first or second type). Subsequent crystallization of the particles occurs with a decrease in volume, which contributes to pore within the particle, and on the interfaces therebetween.

Table 2.

| Number mode | Porosity, % | Pore size, microns |
|-------------|-------------|-------------------|
|             | < 5         | 5 – 10            | 11 – 20          | ≥ 30 |
| 1           | 0.96        | 52                | 28               | 20   | 0    |
| 2           | 1.95        | 29                | 29               | 36   | 5    |
| 3           | 3.11        | 18                | 28               | 44   | 10   |
| 4           | 4.95        | 21                | 22               | 37   | 20   |

The pore size distribution according to the mode of plasma spraying are presented in Table 2. In the coatings formed on the mode number 1, more than 50% of the pores have a size less than 5 microns. Such pores often occur either within the unmelted particles (defect inherent to the powder as well in the initial state) or at the interfaces between particles. Pore size greater than 30 μm is observed in contrast to coatings produced at 230 A (20%).

Note that the wrong mode selected deposition may contribute unstuck. High speed cooling of the molten particles contribute to the formation of tensile residual stresses in the coatings. When the residual stresses exceed the strength of adhesion, coating peels off spontaneously. As follows from the analysis of the structures of the transition zone “basecoats” adhesion of the coating obtained on the mode number 1 (less overheating particles) is high enough. Increasing the arc current contributes to higher residual stresses in the coatings.

The results of comparative tests of coatings on the wear resistance of the friction loosely fixed abrasive particles showed that the tribological properties of the coatings significantly reduced with increasing current arc plasma torch, which correlates well with the results of measurements of porosity. Wear resistance of the coatings formed at 70% higher wear resistance of specimens of steel 20 after cementation.

Conclusions

1. The plasma spray technology using the input node of the ring of powder with gas-dynamic focusing allows you to create high-quality coatings with low porosity, high wear resistance, hardness and adhesion.

2. High speed cooling of the particles on the substrate contribute to the formation of γ-SMC supersaturated solid solution Ni-based average grain size of 80 nm. Furthermore, in the coating are allocated reinforcing phase nickel boride (Ni₃B), chromium boride (Cr₂B and CrB), chromium carbide (Cr₇C₃), nickel silicide (Ni₃Si), nickel-iron (FeNi₃), the dimensions of which are from 5 to 50 nm.

3. The tribological properties of the coatings slightly decreased with increasing arc current, which correlates well with the results of measurements of porosity. Wear resistance of the coatings formed at 70% higher wear resistance of specimens of steel 20 after cementation.

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