During electric arc spraying, during the transfer of molten metal by air flow, there is a significant burnout of alloying elements with the formation of a large amount of oxides, which negatively affects the adhesion of the coating to the base. A solution to the problem of increasing the adhesion strength by using pulsation of the atomizing air flow is proposed. At the optimal frequency of the pulsed flow shut-off, the time of formation of liquid metal droplets at the ends of the electrodes coincides with the frequency of pulses of the spraying flow. As a result, the droplets acquire an optimal size, they are transported by an air flow with conservation of energy, a lower mass of oxygen and, as a consequence, a significant decrease in the oxidation of alloying elements in the sprayed material. The existing test methods of sprayed coatings for adhesion strength to the base are analyzed. The design of a modernized device for determining the adhesion strength is developed and described, which provides complex loading of the coating with a combination of tear-off and shear. The tests revealed a significant (up to two times) increase in the adhesion strength of aluminum, zinc-aluminum and steel (Sv08A) coatings applied with air pulsation. This is achieved by increasing the number of fusion zones of the coating particles between themselves and with the base. It is shown that the effect of the pulsation frequency on the adhesion strength changes along a curve with a maximum corresponding to a frequency of 70-80 Hz, regardless of the coating material. It has been established that the aluminum coating has an increased tendency to oxidation, as a result of which it is 15-20 % inferior to the zinc-aluminum coating in adhesion strength. The data obtained substantiate the use of the proposed spraying technology in production

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Keywords: electric arc spraying, coating, pulsating flow, oxidation, particle, adhesion strength

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DETERMINATION OF ADHESION OF THE COATING DEPOSITED BY ARC SPRAYING WITH PULSATION OF ATOMIZING AIR FLOW

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1. Introduction

Among the variety of coating methods, the electric arc spraying process is distinguished by a set of advantages, which include high performance indicators of coatings, high thermal efficiency, and relatively low cost [1]. In arc metallization, a coating is formed from droplets of liquid metal carried by a jet of carrier gas. The material is melted due to the heat of the electric arc, the liquid metal is blown off from the ends of the electrodes, crushed by the influence of gas-dynamic and electromagnetic forces and in the form of drops moves in the direction of their resulting action [2]. In this case, a jet with a high mass flow rate of gas is used, which is necessary for the formation and transportation of droplets. In this case, preference is given to compressed air, which ensures stable atomization of the molten metal. However, the quality of such a coating does not always meet the existing requirements due to the intensive oxidation of the metal of the material with atmospheric oxygen with the corresponding burnout of alloying elements and the formation of a large number of pores and oxides. The formation of such a structure negatively affects the mechanical and operational properties of the coating. In particular, such an important indicator as the adhesion strength to the base deteriorates, which leads to local or complete detachment of the coating under load [3]. In this regard, the problem of increasing the adhesion of thermal spray coatings has not lost its relevance over the past decades, and therefore requires a solution by improving the application technology.

2. Literature review and problem statement

The formation of an oxide film on the surface of a metal particle, carried by an air flow, is a complex process, which in particular consists of compression of the film and the formation of toroidal formations that are easily separated from the surface, which leads to a decrease in the adhesion strength of the coating to the base [4]. When solving the problem of adhesion of sprayed coatings, various approaches and technologies are used. One of the areas of research is the improvement of methods for preliminary treatment of the surface on which the coating is applied, or the spraying of an intermediate layer, which provides a smooth transition from coating to base [5]. Thus, in [6], the possibility of a significant increase in the fracture toughness at the boundary of the thermal barrier coating with the surface was shown by preliminary treatment of the latter with a flow of corundum particles. A short-range approach was proposed in [7], in which a finishing surface burnishing was applied before flame spraying, which improved adhesion by inducing residual compressive stresses and reducing the number of pores on the steel surface. In [8], heating (200-400 °C) of steel was used before the thermal spray application of a WC-coating for better adhesion to the base. The authors of [9] consider it expedient to pre-apply a FeCrAl-bonding coating, which has increased adhesion to the base due to the optimal gradient of the elastic modulus. On the other hand, the authors of [10], studying the adhesion and microhardness of the nitinol layer (50 % Ni-50 % Ti) deposited on a steel base, came to the conclusion that the key factor is a careful selection of the distance from

the metallizer nozzle to the base surface; this ensures the formation of the optimal size of liquid metal particles, minimizes their oxidation and promotes the formation of strengthening phases ((NiTi, Ni₃Ti, Ti₂Ni, and TiO), which increase the mechanical adhesion of the coating to the base. A similar approach was used in [11], devoted to the study of YSZ Also, the adhesion strength of metal gas-flame coatings is effectively increased by the use of vacuum post-heat treatment [3] However, the listed methods of increasing the adhesion strength significantly complicate the spraying process, require the use of specific equipment and highly qualified personnel.

Another important way to solve the problem of coating adhesion is to reduce the oxidation of metal droplets by controlling the saw air flow, which does not require additional special equipment. In this context, improving the air-spray system of a metallizer in order to reduce the oxidation of metal sprayed has long been in the focus of researchers' attention. The scientific rationale for the shape of the spray nozzles was carried out in [12], where it is recommended to use long nozzles that increase the speed of the particles in the saw stream. However, in practice, the length of the nozzle used is limited by the design features of the metallizer; therefore, its increase is problematic. Therefore, the authors of [13, 14] used an increase in the pressure of the transporting air flow to 30-40 MPa and the arc current to 1200 A, which made it possible to obtain an increase in the adhesion strength of the coating to 180 MPa and a decrease in porosity to 2-5 %. However, this technology requires the use of a complex set of equipment.

In [15], it is shown that the intensity of oxidation of the electrode metal depends on both the metallization mode and the type of saw gas and its consumption. The use of nitrogen or other gas for spraying instead of air is considered impractical, given its high costs, significantly increases the cost of the technological process [14]. So, ensuring the normal spraying mode (P=0.5 MPa, d=5-6 mm) requires 1-1.5 m³ of nitrogen per minute, which is equivalent to the consumption of 10-15 cylinders per hour of nitrogen compressed to 15 MPa. Nitrogen consumption can be significantly reduced by reducing the diameter of the saw nozzle, but this will reduce the rate of metal droplets and negatively affect the quality of the metal coating.

By studying the dynamics of a metal-air jet during metallization, it was found that in an air jet that flows out of a nozzle of a large diameter (i5 mm), metal droplets are mainly in the inner part of the jet – in its core. In this case, the peripheral layers are free of particles and serve only to maintain the velocity in the inner part of the jet [13]. Taking this into account, in order to reduce the oxidative effect of the jet, it was proposed in [16] to use a combined air-argon (nitrogen) saw jet. This leads to a decrease in the oxidative effect of the air-saw jet by 30-45 %, a decrease in porosity, an increase in the corrosion resistance of aluminum and stainless coatings by 3-4 times in comparison with coatings sprayed with the use of air. Despite these advantages, the combined mixture has not found application in production, and there are no data on its more in-depth study in the literature.

Improvement of the nozzle design can be a way to overcome these difficulties. To reduce the oxidative effect of the jet, various designs of spray heads with nozzles have been proposed, the design of which includes a conical insert. When bending around this insert, the gas-air flow creates a vacuum region at the nozzle outlet, into which an electric arc is placed. The same effect is achieved when using heads with a bifurcated air nozzle described in [16, 17].

Analyzing the sources on this issue, it should be noted the widespread use of the Laval nozzle [18, 19]. This type of nozzle is designed to create gas flows at supersonic speeds and is used as one of the main elements of jet engines, steam turbines, etc. The Laval nozzle is a tube of variable cross-section, which consists of a part, tapers and a part, expands. The use of this profile in Laval nozzles is due to the fact that during gas outflow at low velocities, when the gas density can be taken unchanged, the nozzle cross-section should be reduced to increase the velocity. Therefore, the inlet of the Laval nozzle is made narrowed [18]. In the narrowest section of the nozzle, the gas density decreases inversely with the flow velocity, and the latter acquires a velocity equal to the speed of sound. This section is called the nozzle throat. Further, with an increase in the flow rate, an intensive drop in its density occurs, as a result of which the nozzle cross section increases. The Laval nozzle profile is also used for electric arc metallization [19]. The choice of geometric parameters and gas-dynamic characteristics of the Laval nozzle is carried out by mathematical modeling for various conditions of the jet outflow.

A significant number of spray head designs have now been developed that can be used on most industrial arc metal plugs, such as two wire metallization. However, they rarely find wide application, despite the complexity of their manufacture and the specificity of the materials used, as well as the fact that they do not always meet the high requirements for creating a two-phase saw jet [20]. Currently, there are no system solutions for effective low-cost control of the spray air flow and reducing its oxidizing ability to prevent intense burnout of alloying elements from the metal and saturation of the coating with atmospheric gases. This poses the problem of finding appropriate effective solutions, which is the solution to which this work is aimed.

3. The aim and objectives of research

The aim of research is to reduce the oxidizing ability of the saw air flow during the formation of thermal gas coatings by controlling the air supply with a corresponding decrease in the oxidation of the coating metal to increase the strength of coatings with a base.

To achieve the aim, the following objectives were set:

 to propose a method of electric arc spraying, which ensures a decrease in metal oxidation during its transportation by an air stream and increases the adhesion of thermal gas coatings to the base;

 to investigate the strength of adhesion to the base of coatings obtained using the new technology, and to determine the optimal parameters of the coating application mode;

- to determine the features of the microstructure of the coatings formed using the new deposition technology.

4. Materials and methods of research

One of the main parameters of the operational durability of protective coatings is the strength of its adhesion to the base, since it is this that determines the operational durability of the coatings. Determination of this parameter with respect to coatings obtained with air flow pulsation was one of the main tasks of this study.

The existing test methods can be classified according to the following criteria [21]: direct or indirect, with or without glue, shear tests, pull-off tests, or a complex load when shear at a distance. When testing coatings for pull-off, a pin test is often used according to the Steffens method [21], which makes it possible to accurately determine the pull-off force. However, this method introduces a significant error in the form of pin friction on the base surface, and increases the scatter of results. In addition, during operation, as a rule, complex loads act on the coating – shear pull-off, or displacement pull-off. Therefore, it is necessary to consider test methods when working in difficult shear breakout conditions. A complex of forces acts on the surface with the applied thermal spray coating; accordingly, the research method should take into account not unidirectional forces, but the resulting vector forces that are applied to the working part of the parts. For practical purposes, not one resultant R is usually required, but its components acting in given directions. These forces are:

 $-P_z$ – acts in the cutting plane in the direction of the main movement and determines the load on the coating and base;

 $-P_y$ – radial component applied perpendicular to the axis of the base of the part. This component determines the resistance force and deflection of the workpiece;

 $-P_x$ – component that acts along the workpiece (part) axis parallel to the counter-part feed direction.

The resultant force *R* is found as:

$$R = \sqrt{P_x^2 + P_y^2 + P_z^2}.$$
 (1)

The ratio of P_x , P_y and P_z does not remain constant and depends on the geometric parameters of the working surface after spraying, the load mode, the amount of surface wear, the physical and mechanical properties of the material being processed, and the like. Under some loading conditions, the forces P_y or P_x may be absent. The P_z force always acts, therefore it is often called the main component of the cutting force.

Based on this, let's analyze the well-known method of testing coatings under a complex pull-off load with a shear (Fig. 1), developed at the Department of Equipment and Technologies of Welding Production of the Priazovskyi State Technical University (Ukraine).

This method uses samples with beveled edges at an angle α , which are installed on the movable bases of the device, providing their opposite parallel movement. The bevels of the edges form a container filled with the coating, is investigated. The device is installed in a tensile testing machine and the opposite directional movement of the samples is provided. Determine the surface area of the coating compartment F from the samples and find the magnitude of the pull-off and shear stress:

$$\sigma_p = \frac{P \sin \alpha}{F}; \ \tau_s = \frac{P \cos \alpha}{F}, \tag{2}$$

where σ_p , τ_s – the values of the pull-off and shear stresses, respectively; α – the bevel angle of the sample edges.

It should be borne in mind that at $\alpha \leq 90^{\circ}$ conditions for testing coatings are created with simultaneous shearing and tearing of the coating, and the adhesion strength indicator is calculated as:

$$\sigma_{eq} = \pm \sqrt{\sigma_p^2 + 3\tau_s^2}.$$
(3)

For this option, a large scatter of results is inherent due to skewing and wedging of the guides on moving bases (Fig. 1, b), taking into account the misalignment of the location of the samples and the axis of application of forces. It is also possible that the coating is destroyed not along the adhesion zone, but directly along the section, which leads to a large error in determining the adhesion strength of the coating to the base. In addition, an uncontrolled stress concentrator is created at the root of the coating, which leads to scattering of test results. The disadvantage is also the relative complexity of manufacturing the entire structure of the installation and the need for high-quality filling of the gap between the bevels of the samples.

Taking into account the imperfection of the existing methods for determining the adhesion strength of the applied coating, in this work an improved method of "pin test" is proposed. It significantly reduces the effect of pin friction on the body and adds the ability to quickly remove the coating and reapply it for testing. This method improves measurement accuracy due to the ease of positioning the sample in the setup and the absence of obstructions during coating. The coating itself is subjected to a complex load, working for tearing and shearing, as in real operating conditions. To create conditions that are closest to the real conditions of the coating, the angle of inclination of the coating plane relative to the central axis of the pull-off forces was chosen equal to 0° , 30° , or 45° (Fig. 2). The matrix and the pin of the research unit for testing the adhesion of the coating to the substrate are made of structural steel.

During the tests, the pin is installed in the matrix, the coating is applied at the given technological parameters and "breaks off" with force, gradually increases and is fixed with a dynamometer.



Fig. 1. A device for determining the adhesion strength of a coating under a complex shear pull-off load: a - force application diagram; b - a sketch of the device. 1 - coating; 2 - samples with beveled edges; 3 - movable bases; 4 - guides



Fig. 2. Diagram of the device for a comprehensive test method for pull-off and shear of a coating with a base:
a - pull-off at an angle of 30°; b - separation at an angle of 45°;
1 - case; 2 - pin; 3 - cover; 4 - fixing screw

The described method and device were used in this work to determine the adhesion strength of coatings obtained with pulsating air flow. The adhesion values were taken as the average of five tests for each type of coating material and spray regime.

One of the areas of application of electric arc metallization is the protection of open structures from manifestations of atmospheric corrosion, which is the main reason for the increased demand for the application of anti-corrosion coatings based

on zinc and aluminum. Therefore, aluminum (100 % Al) and zinc-aluminum (85 % Zn, 15 % Al) wires were used as a starting material for deposition. The level of adhesion strength of specialized coatings was compared with the strength of the coating obtained using wire made from low-carbon steel Sv08A. The microstructure of the coatings was investigated on a Neophot-21 microscope on a cross-sectional microsection prepared according to a standard procedure and etched with a 4 % solution of nitric acid in ethyl alcohol.

5. Results of studies of adhesion strength and structure of coatings

5. 1. Principle of spray flow control in electric arc spraying

Nozzles of the metallizers, which are now produced by the industry, create only a straight, steady air flow. These systems are easy to manufacture and maintain, since they do not require additional mechanisms and

friction units. The use of additional types of nozzles, which are installed in the standard places of an industrial metallizer, makes it possible to form various zones and sections in the air flow until the discharge or supersonic flow rates are obtained. However, in this case, the flow itself remains constant, with a large air flow and, accordingly, with a high ability to oxidize the metal of the coating. It was proposed to use a pulsating air flow, which is formed by the so-called pulsators, which interrupt the air flow dozens of times per second, which makes it possible to reduce (regulate) oxidative processes in the air flow [22, 23]. To implement the method of arc metallization with a pulsating spray flow, taking into account theoretical conclusions and obtained practical preliminary results, a pulsator design for industrial use was proposed, shown in Fig. 3. The installation, mounted on a massive base, consists of a pulsator, a pulsator valve rotation drive (DC motor), a pulse frequency control panel, and an air supply system from the receiver to the metallizer [24, 25]. This device (pulsator) is installed in front of the spray system of the arc metallizer and does not present obstacles in the practical implementation of the arc spraying process.

By reducing the air consumption of spraying with a pulsating spray flow, it reduces the amount of oxides in the coating, improves the conditions for wetting the coating particles, the sprayed surfaces and increases the adhesion to the base. The mass of oxygen (m_{O_2}) , which takes part in the process of metal spraying using a pulsator, was determined analytically depending on the frequency of pulsations of the air flow for different positions of the pulsator valve (K), for which the expression [26] was used:

$$m_{\mathcal{O}_2} = \frac{G_s^a \cdot V_a^n \cdot T \cdot (1 - K)}{n} \cdot a_{\mathcal{O}_2} \cdot \gamma_{\mathcal{O}_2}, \qquad (4)$$

where G_p^a – total air consumption for spraying; a_{O_2} –volume percentage of oxygen in the air (taken as 21 %); V_a^n – air volume at a frequency (*n*) of the pulsator valve revolutions (or overlap frequency) during time *T* at a flow rate of 2 m³/s; γ_{O_2} – specific gravity of gaseous oxygen at a temperature of 20 °C and pressure 760 mm Hg ($\gamma_{O_2} = 1,3 \text{ kg/m}^3$).



Fig. 3. Experimental setup with a pulsator: a – general view; b – schematic diagram; 1 – coil with wire; 2 – metallizer; 3 – pulsator valve motor; 4 – pulsator; 5 – air supply system from the receiver to the metallizer

The total air consumption during the rotation of the pulsator valve (which provides a pulsating supply) was found depending on the number of valve revolutions as:

$$G_p^n = G \frac{d_c^2(\pi - \omega)}{4n},\tag{5}$$

where G – air flow rate of the metallizer; ω – angle of rotation of the pulsator valve.

Fig. 4 shows the results of calculations using expressions (4) and (5) in the form of dependences of the mass of oxygen involved in sputtering on the pulse frequency. From Fig. 4 it can be seen that the mass of oxygen in the sawing jet decreases with an increase in the frequency of pulsations by several times. The intensity of the air flow, as well as in accordance with the mass of oxygen, decreases with an increase in the degree of overlap of the pulsator nozzle channel. As the pulsation frequency increases, the difference between the oxygen mass values for different nozzle overlap levels decreases.



Fig. 4. Influence of the pulse frequency of the pulsator on the mass of oxygen in the air passing through the nozzle at different levels of overlapping of the nozzle (from 10 % to 80 %)

Thus, the pulsating flow should significantly affect the processes of interaction of oxygen with the surface of molten droplets, regulating the intensity of metal oxidation and burnout of alloying elements. The consequence of this should be the regulation of the amount of oxides in the coating and the strength of the adhesion of the coating to the substrate.

5.2. Strength of adhesion of coatings to the base

The influence of the frequency of pulsations of the saw flow on the value of the adhesion strength of the coating was determined for coatings obtained using wire electrodes made of aluminum, zinc-aluminum alloy, and Sv08A steel. The test

results are shown in Fig. 5-7 in the form of experimental points and graphical representations of regression equations approximating (Table 1). For all equations, the coefficient of determination was 0.85–0.95, that is, they reliably reflect the real nature of the dependences of adhesion strength on the pulsation frequency. For an aluminum coating, the minimum values of adhesion strength are 28-22.5 MPa (depending on the angle of separation), which corresponds to sawing at a frequency of 20 Hz (Fig. 5). With an increase in frequency to 80–80.9 Hz (breakaway angles 0° and 30°) and 78.4 Hz (45°), the adhesion strength gradually increases, reaching a maximum, which is 31.9 MPa at 0° and 42.9 MPa at 45°. At all pulsation frequencies, the adhesion strength is minimum at a pull-off angle of 0° , and maximum at a pull-off angle of 45°. At higher values of the frequency, the adhesion of the coating decreases, that is, the considered dependences have a clearly expressed extreme character.

For the zinc-aluminum coating (Fig. 6), the level of adhesion strength was close to that of the previous coating (the range of experimental values is 25-48.5 MPa). Unlike aluminum and zinc-aluminum alloys, coatings made of Sv08A steel have a slightly lower (by 6-12 MPa) adhesion strength. For the last two

coatings, the same extreme character of the dependence on the pulsation frequency remained, as in the aluminum coating, with an increase in strength with an increase in the separation angle.



Fig. 5. Influence of the frequency of pulsations of the saw flow on the value of the adhesion strength of the aluminum coating at different angles of separation of the coating: $0^{\circ} - 2$; $30^{\circ} - 3$; $45^{\circ} - 4$; 1 - the strength of adhesion with the pin test [9, 10]



Fig. 6. Influence of the frequency of pulsations of the saw flow on the value of the adhesion strength of the Zn-Al coating at different angles of separation: $0^{\circ} - 1$; $30^{\circ} - 2$; $45^{\circ} - 3$



Fig. 7. Influence of the frequency of pulsations of the saw flow on the value of the adhesion strength of the coating made of steel Sv08A at different angles of separation: $^{\circ}$ - 1; 30 $^{\circ}$ - 2; 45 $^{\circ}$ - 3

The data on the coordinates of the extremum of these dependencies (the frequency corresponding to the maximum and the maximum value of σ_{eq}) are given in Table 1. The optimal range of the pulsation frequency, which corresponds to the maximum value of the adhesion strength of a particular coating for various test conditions (pull-off angles), is: 78.4–80.9 Hz – for aluminum coating, 79.8–82.8 Hz – for Zn-Al coating and 80.2–82.9 Hz – for coating made of Sv08A steel.

Table 1

Regression equations approximating the experimental dependences of the bond strength (σ_{eq}, MPa) on the pulsation frequency (v,Hz)

Separation angle. degrees	Regression equation	R^2	Function maximum (fre- quency/ σ_{eq})
Aluminum coating			
0	σ_{eq} =-3.1×10 ⁻ ³ ×v ² +0.49×v+12.83	0.88	78.4/31.9
30	$\substack{\sigma_{eq}=-3.4\times10^-\\{}^3\times\nu^2+0.54\times\nu+13.75}$	0.87	80.0/35.4
45	$\begin{array}{c} \sigma_{eq} = -4.7 \times 10^{-3} \times v^2 \\ 0.76 \times v + 12.36 \end{array}$	0.87	80.9/42.9
Zn–Al coating			
0	σ_{eq} =-2.9×10 ⁻³ × ×v ² +0.48×v+15.35	0.85	81.6/34.6
30	σ_{eq} =-3.8×10 ⁻³ × ×v ² +0.61×v+16.21	0.87	79.8/40.5
45	$\sigma_{eq} = -4.2 \times 10^{-3} \times v^2 + 0.69 \times v + 17.91$	0.88	82.8/46.7
Sv08A steel coating			
0	$\sigma_{eq} = -3.2 \times 10^{-3} \times \times v^2 + 0.51 \times v + 4.87$	0.95	80.4/25.5
30	$\sigma_{eq} = -4.2 \times 10^{-3} \times v^2 + 0.67 \times v + 2.60$	0.89	80.2/29.6
45	$\sigma_{eq} = -4.2 \times 10^{-10}$ $^{3}\times v^{2} + 0.70 \times v + 6.04$	0.90	82.9/34.9

5.3. Structure of coatings

An increase in the adhesion strength of coatings is directly related to qualitative changes in the microstructure of the coating due to the replacement of a stable air flow with a pulsed flow. An increase in adhesion strength was accompanied by an increase in the strength of the coating itself due to an increase in the number of fusion regions of metal particles. The latter is illustrated in Fig. 8, from which it can be seen that the coating obtained with a ripple with a frequency of 70 Hz (close to optimal) remained intact even after being torn away from an angle of 45° (that is, at maximum adhesion strength). This indicates a high degree of consolidation of metal particles in the area of action (Fig. 8).



Fig. 8. Appearance of an aluminum coating applied at a ripple frequency of 70 Hz, separated from the surface when tested with a pull-off angle of 45°

Fig. 9 shows the microstructure of an aluminum coating applied at different flow pulsation frequencies. In the absence of pulsation (Fig. 9, a), a fine-grained structure with chaotically located parts and a small number of fusion zones between particles is observed in the coating; but the number of oxide inclusions is large. When the flow pulsates with a frequency of 43 Hz, the amount of oxides remains almost unchanged, but no particle coarsening is observed. With an increase in pulsations to 70 Hz (approaching the extremum $\sigma_{ea} = f(v)$) the coating acquires a stable directionality in the arrangement of particles with the presence of pronounced fusion zones; a decrease in the content of the oxide component is also observed. At an increased pulsation frequency (105 Hz), the volume fraction of the oxide phase in the structure increases, that is, these coating conditions are already beyond the optimal pulsation frequency range.



Fig. 9. Microstructure (×500) of an aluminum coating applied at different pulsation frequencies: a - without pulsations; b - 43 Hz; c - 65 Hz; d - 105 Hz

The oxide component, which usually occurs in the form of thin films along the boundaries of particles, reduces their mechanical adhesion and prevents the formation of fusion zones. This is especially important for the "coating/ base" boundary, since it is here that the zonal stresses from the coating shrinkage are concentrated, facilitating the development of cracks along the boundary. In addition, the presence of oxides determines the local concentration of stresses during operation, stimulates the detachment of microparticles, accelerating the wear of the coating. Taking this into account, it was found by microscopic analysis that a decrease in the volume fraction of oxides in the structure of the coating is a key factor in ensuring its high reliability and durability.

6. Discussion of the results of studying the adhesion strength of coatings with the base

The research results presented in Fig. 5–9 show that the proposed method of electric arc deposition of protective coatings using a pulsed air flow has significant advantages over known methods. First of all, they consist in improving the structural state of the coating, which becomes denser and less saturated with oxides due to a decrease in the oxidative effect of the spray flow. In turn, this allows to significantly increase the strength of adhesion to the base, is the key to high performance characteristics of the coating.

When testing the coating for separation, it was found that a common feature for all three materials is the extreme nature of the dependences of the adhesion strength on the frequency of air pulsation (regardless of the angle of separation of the coating). With a pure separation, when the angle is equal to zero (coincides with the separation axis), the adhesion strength is minimal, and at a pulsation frequency of up to 40 Hz, their increase is insignificant. At low pulsation frequencies of the air supply, an increased accumulation of liquid metal at the end of the electrode is possible in the absence of flow actions, which leads to an increase in the particle size or to a short circuit. With a further increase in the frequency of pulsations, the adhesion strength of the coating increases more intensively, which is explained by a general decrease in the oxidative potential of the saw stream. In this case, the time of formation of liquid metal droplets at the ends of the electrodes coincides with the frequency of the saw flow pulses, and the particle size is optimal. At a frequency of 70–80 Hz, these processes reach their optimum, providing the maximum level of adhesion strength. At higher frequencies of the flow pulsation, the liquid metal does not have time to accumulate at the ends of the electrodes during the pause between pulses, and its breakdown by the air flow is carried out with repeated (several times) exposure to the saw flow. In this case, the value of the mass of the liquid metal is determined by the energy of the arc, and no significant effect of the frequency of the pulsating flow on the dispersion of particles is observed.

Comparison of the adhesion strength of aluminum and zinc-aluminum coatings shows that the maximum values for pure aluminum applied by arc metallization are less by 9-14% (Table 1). This indicates an increased tendency of alloys with a high aluminum content to oxidize during deposition, and to a certain extent is explained by the lower strength of aluminum in comparison with zinc. This should be taken into account when choosing a coating material designed to protect exposed structural elements from the weather.

The results obtained in this work differ from the results of the "pin test" in greater stability and repeatability. This is a positive consequence of the application of the proposed test method for adhesion strength, which is characterized by a significantly lower manifestation of uncontrolled friction forces between the sample and the device body during testing. In this regard, this method is worth wider use in the practice of thermal spraying.

The results presented show that the proposed method of electric arc spraying with the use of a pulsating air flow is promising, taking into account the need to obtain reliable adhesion of coatings to the base. However, this method still has certain limitations associated with a narrow range of alloys on which research has been carried out and the effectiveness of the new technology has been proven. In the case of spraying alloys of other alloying systems, the parameters of the regime used may turn out to be far from optimal and will require improvement. Therefore, this direction requires additional in-depth studies of the effectiveness of this method in obtaining coatings from high-alloy steels and special alloys for various functional purposes. This is relevant for these materials, since it is in them that significant burnout of alloying elements (for example, chromium) is observed, which negatively affects the characteristics of the coating, first of all, their corrosion resistance and heat resistance. When carrying out such studies, it will be necessary to eliminate the shortcomings of this work, which consist in the absence of the use of modern metal-plastic physical methods of analysis to assess the state of the coating. Obtaining such data on the phase-structural composition of the coating, the distribution of chemical elements between its phase components, etc., can deepen the understanding of the reasons for the increase in the adhesion strength of the coating due to the pulsation of the saw stream.

7. Conclusions

1. The technological principle of the implementation of electric arc spraying with metal materials, based on the forced controlled pulsation of the saw air flow, has been formulated. The pulsation limits the supply of oxygen to the arc burning zone, prevents intense oxidation of the surface of metal droplets, as a result of which the amount of oxides in the coating decreases, and the fusion of particles between themselves and with the base improves.

2. Using a modernized test method that combines pulloff and shear, the adhesion strength to the base of aluminum, zinc-aluminum and steel (Sv08A) coatings applied by a pulsating air flow was investigated. With the indication of the quantitative indicators of the test results, the extreme nature of the influence of the pulsation frequency on the adhesion strength was revealed. It was found that at the optimal pulsation frequency, which varies for different coating materials and test conditions within 78.4–82.9 Hz, the adhesion strength doubles relative to a steady air flow, reaching 42.9 MPa (aluminum), 46.7 MPa (Zn-Al alloy) and 34.9 MPa (Sv08A steel).

3. It is shown that in the absence of pulsation of the air saw flow, a fine-grained structure with chaotically located parts and a small number of fusion zones between particles are observed in the coating; but the number of oxide inclusions is large. With a slight increase in frequency (40 Hz), the amount of oxides remains almost unchanged, but no particle coarsening is observed. With an increase in pulsations to 70 Hz, the coating acquires a stable directionality in the arrangement of particles with the presence of pronounced fusion zones, and a decrease in the content of the oxide component is observed. With a further increase in the pulsation frequency, the volume fraction of the oxide phase in the structure increases.

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