Technological aspects of improving adhesion of TiNiZr coating materials with thermoelastic phase transformations formed by high-velocity oxygen-fuel spraying

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Abstract. The authors discuss technological aspects of increasing the adhesion of coatings made of materials with thermoelastic phase TiNiZr transformations formed by high-velocity oxygen-fuel spraying (HVOF) with a steel base by means of using a combined method, including HVOF and electromechanical treatment (EMT). The authors presented the results of the structure and elemental composition of the surface-modified layer before and after high-frequency impulse action in the EMT process and established new possibilities of modification of the structure and properties. It is shown that in the optimal modes of EMT, the fusion zone of the coating and the base is 10-20 microns. The authors designed the statistical models of technological process, which allowed defining fusion depth and diameter of a contact core depending on technological modes of EMT, as well as a current density and frequency or pulse duration. Adhesion tests according to State Standard 98844-99 showed that the strength of the coating with the base reaches (0.3-0.4) from the tensile strength of the base, depending on the depth and size of the fusion zone. It is recommended to perform additional thermomechanical processing to ensure the functional properties of materials with shape memory effect in the TiNiZr surface layer.

1. Introduction

In modern industrial production, increased requirements are imposed to products; these requirements are: for the structure of metal, its chemical structure, mechanical properties taking into account cost of products. Taking into account the crucial role of surface layers in damage accumulation and destruction, improving performance, reliability and resource increase can be achieved by the formation of functionally oriented surface layers and compositions. In recent years, intensive work is underway on the creation of intermetallic coatings made of materials with thermoelastic phase transformations (TEPT) including shape memory effect (SME). This is explained by a unique combination of functional and strength properties (pseudoelasticity, wear and corrosion resistance, vibration damping), which are demanded for a number of potential applications [1, 2].

At present, a number of formation technologies for surface layers with multicomponent materials with SME using argon-arc and laser surfacing, plasma and high-velocity oxygen-fuel spraying (HVOF) and surfacing with explosion have already been developed; and strong and reliable surface layers of the required thickness and dispersion have been obtained [1]. These methods are distinguished by the heating type of the deposited coating material and the method of particles'
accelerating. There is one thing, which is common for all these methods: heating of the sprayed material to a high-plastic state or melting, acceleration of particles or droplets by a gas flow and subsequent interaction of particles with the treated surface. Among the specified variety, HVOF is the most universal and effective formation method of surface layers; it is characterized by a high speed of particle flight (more than 500 m/s) and a decrease in porosity (less than 2-5%) [3].

One of the problems of functional surface layers’ formation using TEPT on high-loaded products is the bonding strength of the coating to the base, which ensures the performance and durability of the hardened parts. Adhesive strength of the coating depends on a number of factors, the main of which are: preparation and cleaning of the base surface, chemical compatibility of the base and the applied layer, the difference in their coefficients of linear expansion [3]. There are different ways to improve adhesion (application of intermediate layers with high potential for interaction with both the substrate and the coating, optimization of the base temperature, of granulometric composition, of activation characteristics and thermal properties of the sprayed material, of HVOF modes, including the particles speed and the composition of combustible gas), and they depend on the coating requirements, as well as product operating conditions. Acoustic stimulation, ultrasonic action and heat treatment are used to improve adhesion; they initiate diffusion processes in the contact zone between the coating and the base [4]. However, for materials with SME, heating of the coating is not always possible to temperatures that ensure the flow of diffusion processes. This happens because it is difficult provide the necessary structural and phase state. HVOF, which is a combined process of spraying and plastic deformation of particles at the temperature of contact with the base due to high impact rate, provides adhesion of coatings made of SME materials at the level of 120 MPa without additional processing [5], detonation formation of coatings provides the bonding strength of the coating and the base up to 160 - 240 MPa, but it is not enough for high-loaded products. It is known that oxygen-fuel spraying with melting provides the strength of adhesion to the base up to 300-400 MPa [6]. This paper presents the results of a study of one of the ways to increase the adhesion strength between the base and the coating made of SME material TiNiZr, formed with HVOF and subsequent electromechanical treatment (patent № 2625508).

2. Materials and methods
When working out the formation technology of surface layers from SME materials with high requirements for adhesion as a basis, we took Steel 45, which is widely used in mechanical engineering. We also took nickel as a transition layer, because it has unlimited solubility with iron and chemical affinity with the material of the functional layer. For the functional layer formation, we used three-component material with TEPT Ti$_{33}$Ni$_{49}$Zr$_{18}$, which has high temperature memory effect and at a temperature of 20˚C is in the martensitic state. The formation technology of the surface composition includes several stages: preparation of the base and the applied material, depositing a transition layer of adhesive destination and functional material with TEPT using high-velocity oxygen-fuel spraying in a single technological cycle, and subsequent electromechanical treatment (EMT) to improve adhesion.

Preparation of the base includes machining to create a surface with a developed microstructure followed by shot blasting, and chemical treatment consisting of degreasing the surface and etching with a mixture of hydrochloric acid and nitric acid. Preparation of the applied material consists in mechanical activation (MA) of the material, providing the necessary granulometric composition, energy state and reactivity of the material. Mechanical activation was carried out in the modernized ball mill Gefest-2 AGO-2U, in which the mechanical action is made by a series of successive mechanical pulses (shocks), which transmit portions of mechanical energy to the processed material. Coating was carried out on the upgraded GLC-720 system in the protective atmosphere of argon [Patent No. 2502829]. The device for realization of the subsequent electromechanical processing is given in figure 1.
Electromechanical treatment is a combined treatment based on electrical, thermal and mechanical action. It is carried out by passing a pulsed electric current of high density in direct contact with the treated surface with the use of a conductive deforming element in the form of a roller. The rollers are arranged at an angle of 120˚ to each other with respect to the axis of the processed shaft symmetry, which allows to evenly distribute the load on all rollers and direct the applied force to the deformation of the coating, without disturbing the shape of the detail, i.e. without bending the detail. In this case, two rollers are made of ball bearing steel, and the third one is made of Nickel, to which the electrode is supplied. The depth of the heat-affected zone is limited to the plastic deformation zone and depends on the pulse rate, current density, the time of the heat pulse impact or the rotation speed of the part and the displacement speed of the deforming element. The deforming force given by the three-roller mechanism was 3000 N. The movement direction of electrical-deforming tool is determined by the direction of maximum stresses in the product during the operation. Optimization of these technological parameters allows providing a sufficient melting zone at the depth of the coating and the base to ensure the adhesion of the coating to the base at a level of 0.4-0.5 from the tensile strength of the base. For products such as shafts operating under cyclic loading, it is advisable to carry out the movement of the deforming element along the helix.

The most common methods for assessing the adhesion strength of the coating to the substrate are tensile and bending tests. According to State Standard 28844-90 "Thermal spray, strengthening and restoring Coatings ", pin and glue method is used. When working out the technology to improve the adhesive properties of the coating, we used the pin method. The tests were carried out on the machine Instron 8801.

Figure 1. 3D model of equipment for the surface layers formation with increased adhesive strength – (a,b); control panel-(b); implementation of electromechanical processing (d): 1-lathe, 2-power supply, 3-three-roller deforming device, 4 - tailstock, 5-caliper, 6 – conductor, 7-sample-base, 8 – coating TiNiZr, 9-roller-electrode, 10- deforming rollers 11-dynamometer
Electron microscopic studies were carried out on scanning electron microscope JSM 7500F. X-ray spectral analysis was made on pulsed nuclear magnetic resonance spectrometer JNM-ECA 400 and stereoscopic research was carried out with the microscope Olympus SZ61.

3. Experimental results and their discussion
In the process of electromechanical treatment, the pulse effect of the current is accompanied by a significant heating of the coating in the defect area and on the coating-base boundary, as well as by rapid heat removal to the base volume. The force acting on the electrical-deforming tool (roller-electrode) thickens the coatings and thus reduces the defect. As a result of such thermodeformation influence, the structural and stress-strain state of the surface layer is changed, which leads to the residual stresses. To relieve residual stresses after EMT, we carried out annealing at a temperature of 650˚C in argon atmosphere. Electron microscopic analysis of EMT influence area showed a clear fusion of the coating with the base and the absence of the interface, which is observed after spraying (Figure 2), as evidenced by the results of X-ray spectral analysis.

![Figure 2](image)

Figure 2. Area of electromechanical impact on the border of Steel 45-coating Ti33Ni49Zr18 formed by high-velocity oxygen-fuel spraying: a) before electromechanical treatment x1000, b) - after electromechanical treatment x5000; C) - after electromechanical treatment x10000.

The element analysis was performed in three zones: in the coating after HVOF, on the border of the coating base after electromechanical treatment and mainly showed that the fusion zone or contact spot is 10-20 microns with a coating thickness of 1 mm (figure 3). In the material of the base at a distance of more than 20 microns, there are practically no alloying elements of the coating.

![Figure 3](image)

Figure 3. The results of elemental analysis on the connecting edge base – coating after electromechanical processing: fusion zone of the basis –coating–a); zone of base metal –b)

Figure 4 shows the characteristic cross-sectional fracture and the stereoscopic image of the fracture surface of the Ti33Ni49Zr18 surface layer specimens formed by the combined treatment (MA –HVOF –
EMT) after the post-adhesive assay test by the bayonet method. On the fracture and cross-section of the destroyed sample, the particles of the fusion zone are visible, which confirms the increase in the adhesive strength of the coating. Analysis of the test results showed that the described method of formation of the coating allowed to increase the strength of the coating with the base 1.5 -2 times up to 180-200 MPa.

Figure 4. The nature of the sample fracture in assessing the adhesion strength of the coating with the base by the pin method: vertical blue line in figure (a) corresponds to the middle line of the pin; stereoscopic picture of the destroyed sample (1, 2-metal particles from the surface of the pin; 3 - particle fusion zone)

Observations of the samples’ destruction in the process of technology development for steel surface modification showed that the nature of the destruction depends on the chemical composition and properties of the coating material and the thickness of the modified layer. Studies have shown that the optimum thickness of the coatings obtained in HVOF, on the sample with a diameter of 10 mm does not exceed 0.9-1.0 mm. When the thickness of the coating is more than 1 mm, the adhesion is reduced; sometimes there is delamination of the coating. Subsequent electromechanical treatment prevents the effect of coating detachment during operation [7] and influences the adhesive strength (Figure 4). The rate of adhesion in the EMT process is influenced by the parameters of electrical and power exposure.

Figure 5. A statistical model of electromechanical treatment "coating Ti<sub>33</sub>Ni<sub>29</sub>Zr<sub>18</sub> - base": the dependence of the fusion zone depth formed from the current and the duration of its effects – a); the dependence of the diameter of the core fusion of the current density and duration of its impact - when stress on electrodeposite roller 3000 N, the thickness of the steel of 10 mm and a coating thickness of 1 mm
To optimize the technological modes of EMT, statistical modeling was performed taking into account the main electrical parameters of the process at a constant value of the force on the electro-deforming tool: current density and current transmission duration. The depth and diameter of the fusion zone are selected as optimization parameters. Figure 5 shows the statistical model of the technological process.

From the analysis of the obtained dependences (Figure 5A, b) it follows that in the initial period of electromechanical action, the intensity of the increase in optimization parameters is high, then it decreases, reaching relative stabilization. The values of exposure duration at 0.2 can provide not a point core, but a continuous area of fusion with the coating thickness up to 1 mm. The creation of such a linear fusion zones can serve as an analog of reinforcement that will affect the stress-strain state in the composite construction of the surface layers. Taking into account these features makes it possible to manage not only the structure, but also the architecture of the surface composition to ensure the necessary operational properties [8]. After the formation of the surface layer Ti$_{33}$Ni$_{49}$Zr$_{1}$ by a combined treatment, including HVOF and EMT, it is necessary to carry out annealing in inert media at a temperature of 650˚C to remove residual stresses. If it is necessary to ensure the properties of the coating material with SME, the additional thermomechanical treatment according to the modes given in the work can be carried out [4].

4. Conclusion
As a result of studies of the structure and elemental composition of the surface – modified layer "Steel 45-functional layer of the material with thermoelastic phase transformations" before and after high-frequency pulsed action in the process of electromechanical treatment, we discovered new possibilities for modification of the structure and properties. We designed statistical model of the EMT process, determined processing parameters, ensuring the fusion zone of the coating to the substrate of 10-20 microns. It is shown that the variety of factors that determine the quality of the surface layer and the required level of performance properties of products, explain the necessity of a more in-depth study of their compositional design processes. Formation of functional surface layers or compositions from materials with thermoelastic phase transformations should be carried out on the basis of a comprehensive analysis of electromechanical and temperature-force conditions of their formation, taking into account the characteristics of the stress-strain state arising as a result of complex high-energy effects.

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