Improving the adhesive strength of coatings from multicomponent materials with thermoelastic phase transformations by external high-energy influences at various processing stages

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Abstract. The paper presents the results of a comprehensive study of the influence of external high-energy ultrasonic and electropulse influences on the adhesive strength of a coating from the material with thermoelastic phase transformations (TEPT) at various processing stages: preparing the base; preparing the sprayed material at the finishing stage after coating. It has been shown that as a result of complex high-energy influences at the processing finishing stage, one observes a distinct fusion of the coating from the material with TEPT (Ni-33%, Ti-49%, Zr-49%) with a base and the absence of the interface, confirmed by electron microscopic studies. The fusion zone is 10–20 μm with the coating thickness of 1 mm; there are practically no coating elements in the base material at the depth of 20 μm. The experimental studies have confirmed an increase in adhesive strength by 1.2–1.5 times up to 130–150 MPa.

1. Introduction

In modern industrial production under intense competition conditions, both on the Russian and global markets, the requirements to products are increased: by the metal structure, chemical composition, mechanical properties, geometric dimensions, the occurrence of defects accounting the quality, production time and products cost [1]. Under these conditions, taking into account the determinative role of surface layers in the damage and destruction accumulation, improving performance characteristics, increasing reliability and resource can be successfully resolved at the final processing stage on the basis of the technologies grounded on the principles of layer-by-layer synthesis using combined (hybrid), functionally oriented macro-, micro-, and nano-technologies [2].

A promising area in the implementation of layer-by-layer synthesis technologies is the functionalization and intellectualization of products using materials with thermoelastic phase transformations, including highly entropic ones with shape memory effect (SME) [3-7]. The increasingly expanding use of alloys with TEPT in engineering is connected with their exceptionally wide functional and mechanical capabilities: unique effects of thermomechanical memory, high strength and damping properties, thermomechanical reliability and durability, wear-proof and corrosive resistance [7, 8]. At present, a number of technologies have been developed for the formation of surface layers from two-component (TiNi, NiAl), three- and four-component (TiNiHf, TiNiHfCu, TiNiZr, TiNiMo, TiNiNb) [9] materials with SME using laser and argon-arc surfacing,
plasma spraying, explosion surfacing; durable and reliable surface layers of the required thickness and dispersion have been obtained [8-10]. These methods differ in the type of heating the sprayed coating material and in the method of particle acceleration. The common thing about all these methods is heating the sprayed material up to a high-plastic state or melting, accelerating particles or drops by a gas stream and their subsequent interaction with the treated surface. Among the specified variety of methods of forming surface layers, the most universal and effective ones are high-speed methods (ultrasonic gas-flame, ultrasonic plasma, gas-dynamic spraying), characterized by a high speed of particles flight (more than 500 m/s) and a decrease in porosity (less than 2-5%) [11].

One of the problems of the functional surface layers formation from materials with TEPT on high-loaded products is the coating strength adhesion to the base, which ensures the reliability and durability of the surface-modified product. The analysis of domestic and foreign information sources describing the current state of theoretical studies on adhesion of a sprayed particle and a substrate showed that most works rely on the theoretical model of describing the particle adhesion to the substrate surface. Despite this, there is currently no unified theory describing the process due to the impossibility of accounting and describing the whole variety of factors influencing the adhesion process.

The adhesive strength of coatings made from materials with TEPT depends on a number of factors, the main of which are: preparing and cleaning the surface of the base, chemical compatibility of the base and the applied layer, the difference in their linear expansion coefficients [12]. The ways to increase adhesion are diverse (applying intermediate layers, having a high potential for interaction both with the substrate and the coating; optimization of the base temperature, granulometric composition, activation characteristics and thermalphysical properties of the sprayed material, operating modes, including particle flight speed and combustible gas composition) and depend on the requirements for the coating, and the product’s operating conditions. Various external high-energy influences are used to improve the adhesion: acoustic stimulation, ultrasonic influence, thermal treatment initiating diffusion processes in the contact zone of the coating with the base [13, 14]. However, for the materials with SME, heating the coating to the temperatures ensuring the occurrence of diffusion processes is not always possible and is connected with the complexity of ensuring the necessary structural-phase state of the functional layers.

The aim of this study is to elaborate methods for increasing the adhesion strength of coatings from the materials with thermoelastic phase transformations by external high-energy influences at various stages of processing and to develop recommendations for increasing the adhesion strength of products in specified operating conditions.

To achieve this goal we investigated:
- the influence of ultrasonic influences at the surface preparation stage on the adhesive strength of coatings from multicomponent materials with TEPT;
- the optimization of the granulometric composition of the sprayed material with TEPT at the stage of mechanical activation;
- the impact of ultrasonic influences on the adhesive strength of the coatings from multicomponent materials with TEPT at the finishing processing stage;
- the impact of complex ultrasonic, electropulse and thermal force influences on the adhesive strength of the coatings from multicomponent materials with TEPT at the finishing processing stage.

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2. Materials and research methods. Peculiarities of the forming surface layers technology from the materials with TEPT

When developing the forming surface layers technology from the materials with TEPT according to raised standards to adhesion, Steel 45, widely employed in mechanical engineering, was used as a base, and nickel, having an unlimited solubility with iron and chemical affinity with the material of the functional layer, was used as a transition layer. To form the functional layer we used a three-
component material with TEPT Ti33Ni49Zr18, possessing a high-temperature memory effect (with the following temperatures of phase transformations $M_f = 459K$, $M_s = 522K$, $A_s = 488K$, $A_f = 571K$, transformation sequence $B2 \leftrightarrow B19'$), which is in a martensitic state at the room temperature.

The surface layers formation from the materials with TEPT was carried out under conditions of high-energy influences by using a complex technology, including: preparing the base surface, dispersing and mechanical activating the applied multicomponent material with TEPT, applying adhesive and functional layers in the protective atmosphere, and subsequent thermal treatment using ultrasonic and electropulse thermal force influences, providing the formation of a nanoscale structure.

The preparation of the base includes mechanical treatment to create a surface with a developed microstructure with the following activation by surface plastic deformation with ultrasonic treatment by bead-blasting and chemical treatment consisting in degreasing the surface and etching with a mixture of hydrochloric and nitric acids. Preparation of the applied material consists in the mechanical activation (MA) of the material, which provides the necessary granulometric composition, energy state, and reactivity of the material. The mechanical activation was done in the modernized Hephaestus-2 ball mill AGO-2U [15], in which the mechanical action is done by a series of successive mechanical impulses (impacts) from actuating media transmitting portions of mechanical energy, reinforced by the ultrasonic action, to the processed material. The used planetary ball mill has the following operating parameters: the drum volume is 150 cm$^3$, the ball acceleration is 40g, the ball to load ratio is (10-15): 1, the ball diameter is 6-8 mm. The maximum loading of the drum with grinding balls is 250 g, and with the processed material is 100 g. The rotation frequency of the carrier is 630, 890, 1090 rpm; the drum rotation frequency is 1290, 1820, 2220 rpm; the centrifugal acceleration of the grinding media is 300, 600, 1000 m/s$^2$. During the scrutiny the influence of MA time on the powders’ morphology and specific surface, on the phase composition change of the powder mixture, and on the distribution of elements and their compounds in MA powders was studied.

The coating was done by high-speed gas-flame spraying (HGS), having all the advantages of high-speed coating methods, which are essentially a combined process of spraying and plastic deformation of particles at a contact temperature with the base due to the high speed of collision. The coatings made from the materials with SME were sprayed using the upgraded GLC-720 apparatus in the protective argon atmosphere. HGS provides the adhesion of coatings from the materials with SME up to 120 MPa without an additional processing [16], the detonating formation of coatings provides the adhesion strength of the coating to the base up to 160 - 240 MPa. The experience shows that for high-loaded products this adhesion level does not provide the necessary level of reliability. During the usage of products with coatings from the materials with SME, the coatings undergo both a temperature change, leading to a martensitic-austenitic transformation, and a change in the coating material structure due to atom shear. This leads to stresses occurrence at the coating – base interface and, during the repeated phase transformations, can cause delamination, which is typical for coatings with a low value adhesive strength, provided only by the adhesion mechanical component. It is known that gas-flame spraying with reflow provides the adhesion to the base of 300-400 MPa [17]. To increase the reliability of products coated with SME materials it is necessary to develop additional measures or look for alternative ways to improve the adhesion.

A device for the implementation of ultrasonic processing in one cycle with the coating by the high-speed gas-flame spraying method (Figure 1a), and the subsequent electropulse treatment with the thermal force of the coated substrate is presented in Figure 1b.
Figure 1. The scheme of the formation of surface layers with improved adhesive strength (1 – a burner for a high-speed gas-flame spraying; 2 – an ultrasonic source; 3 – a detail) - a); a fastening scheme for a detail of surface layers with improved adhesive strength (1- a detail; 2- three-roller SPD mechanism; 3- a welding transformer) - b).

The electropulse treatment with a thermal force influence is a combined treatment based on electrical, thermal and mechanical influence [18]. It is implemented by passing the pulsed electric current of high density in direct contact with the treated surface, using a conducting deforming element in the form of a roller. The depth of the thermal action zone is limited by the plastic deformation zone and depends on the pulses frequency, current density, time of thermal pulse influence, or the detail rotation speed, and the speed of the deforming element movement. The direction of motion of the electrodeforming tool is determined by the direction of the maximum stresses action in the product during usage. The optimization of the indicated technological parameters allows providing a sufficient reflow zone along the depth of the coating and the base to ensure the adhesion of the coating to the base at the value level of 0.4 - 0.5 of the ultimate base strength. For products such as shafts, operating under the conditions of cyclic loading, it is reasonable to implement the deforming element movement along a helical line.

The pin method was used to assess the adhesion strength of the coating to the base. The tensile test was done on the machine Instron 8801 according to State Standard 28844-90 "Gas-thermal, reinforcing and restoring coatings". Electron-microscopic studies were carried out on the microscope JSM-7500F. The X-ray spectral analysis was done on the diffractometer DRON-7M using Cu-Kα radiation, the stereoscopic studies were done on the microscope MSP-1.

3. Discussion of the results
To form a strong physicochemical bond at the coating – base interface the base surface was activated, including surface plastic deformation by rolling and ultrasonic treatment (UST) by a strengthening spherical element. The mechanical SPD influence and the physical UST influence contribute to the destruction of oxide layers on the base surface and to a sharp increase in the number of defects in the surface layer. Due to cold work hardening and the increase in the number of defects, coming to the base surface, SPD increase the number of setting areas during coating spray and create compressive residual stresses in the base material, which can partially decrease due to a base temperature increase under certain coating application conditions. The combined action of mechanical and physical activation allows increasing the density of dislocations, increasing the number of vacant sites, which are active centers on the base surface, enhancing the flow of physical and chemical processes at the “coating-base” interface and contribute to bulk diffusion of the materials. Thus, ultrasonic treatment is one way to activate the base surface before coating. The ultrasonic treatment machinery is shown in Figure 2. After the base surface activation the samples underwent a chemical treatment, including surface degreasing and etching with a mixture of hydrochloric and nitric acids.
Figure 2. The machinery for ultrasonic treatment: 1 – an ultrasonic generator; 2 - coated sample; 3 – a waveguide with an indenter; 4 – a magnetostrictive transducer; 5 - a water cooling system; 6 – wires.

The preparation of the applied material with SME consisted in mechanical activation (MA) with ultrasonic influence, done in a water-cooled ball mill Hephaestus-2 AGO-2U. The investigation of the granulometric composition evolution, phase transformations, and structure evolution in multicomponent materials with an electron-phase transformation of Ni-33%, Ti-49%, Zr-18% at different stages of the MA process are shown in Figure 3. The industrially produced powders of titanium-nickel (PN55T45) with a fraction up to 20 microns, and zirconium (PZrK-1) with a fraction up to 40 microns were used as the initial materials. The initial powders were prepared by removing excess moisture by drying at the temperature of 100-110 °C during an hour. After that the components were dosed by weight to create a mixture with the necessary ratio of elements: Ni-33%, Ti-49%, Zr-18%. Figure 3 shows the particle size distribution based on the image analysis using the ImageJ program as well as the elemental composition of the powder at various stages of mechanical activation.

Figure 3. The mechanical activation of the composite mixture Ni-33%, Ti-49%, Zr-18% during: a) 60 min; b) 90 min; c) 120 min.
The mechanical activation of the mixture of powders Ni-33%, Ti-49%, Zr-18%: MA during 60 min does not significantly reduce the fractional composition of the mixture (up to 16.1 μm). A decrease in the average particle size to 12.2 μm occurs after MA during 120 min, and then the particle size stabilizes and further MA does not give a significant reduction in particle size; with an increasing mill drum rotational speed, the stabilization occurs earlier.

The analysis of the average particle diameter changes at MA of Ni-33%, Ti-49%, Zr-18% and at the carrier rotation frequency of 800 rpm-1 showed that an average particle size of 10 μm is achieved over a large period of time, approximately 150 minutes.

The electron microscopic analysis combined with the energy dispersive X-ray spectral analysis allows determining the possible formation of phases during the mechanical activation and mechanosynthesis. At MA and mechanosynthesis not only particle grinding, but also the formation of compounds occurs. So, after a two-hour MA of the powder mixture, conglomerates are formed from particles smaller than 1 μm in size, and the chemical composition corresponds to the already defined set of chemical compounds Zr2Ni, NiZr, TiNi, Ti2(NiZr). Zr atoms dissolve well in titanium; a continuous series of solid solutions is formed without the formation of intermediate phases. Only insignificant amounts of these elements dissolve in nickel, and a number of intermediate intermetallic compounds are formed (Figure 4).

Figure 4. The diffraction pattern of the coating Ni-33%, Ti-49%, Zr-18%, obtained by high-speed gas-flame spraying -a); the microstructure of the coating Ni-33%, Ti-49%, Zr-18% × 100,000 - b)

Based on the study of the MA process of multicomponent materials with SME, it was found that: an increase in the MA time leads to obtaining a finer powder; homogenization is observed, a particle size is reduced, and due to cold work hardening, the strength characteristics improve; new powder material compositions are formed that in chemical composition correspond to the material necessary to obtain coatings, this is confirmed by chemical analysis of the surface layers formed by HGS MA powder. The analysis of the experimental results showed that with increasing fineness of grinding, the number of active centers increases. However, this tendency is observed up to a certain specific surface area value, after which the process slows down significantly. An intensive increase in specific surface TiNiZr area value, when dispersed in a ball planetary mill, is observed during 1.5 h [15]. According to the results of the study, the modes of mechanical activation and HGS are recommended [7], which ensure the formation of a nanoscale structure (Figure 4, b).

After the formation of the TiNiZr coating at the finishing stage, in order to increase the adhesion and the formation of the functional properties of the material with TEPT, the samples underwent ultrasonic, electropulse and force influences. The electropulse influence of the current is accompanied by a significant heating of the coating in the defects’ area, and at the coating-base interface, and rapid heat removal to the bulk of the base, and the force influencing the electrodeforming tool (roller electrode) compacts the coatings and, thus, reduces the imperfection. As a result of such thermal
deformation influence the structural and stress-strain state of the surface layer changes, leading to the residual stresses occurrence. To relieve residual stresses annealing was performed at the temperature of 650 °C in the argon atmosphere. The electron microscopic analysis of the exposure zone showed a pronounced fusion of the coating with the base and the absence of the interface that occurs after sputtering (Figure 5); this is confirmed by the results of the X-ray spectral analysis. The elemental analysis, performed in three zones – in the coating after HGS, at the base – coating interface after finishing processing and in the main material, showed that the fusion zone or contact spot is 10–20 μm with the coating thickness of 1 mm (Figure 5). In the base material at the distance of more than 20 microns, there are practically no alloying elements of the coating.

Figure 5. The zone of electropulse exposure at the interface "steel 45 - coating Ti33Ni49Zr18" formed by high-speed gas-flame spraying: a), b) - x 50; c), d) - x 10000.

To assess the effectiveness of the described technological operations using UST at various stages of the coating formation from materials with SME Ni-33%, Ti-49%, Zr-18%, the adhesion strength tests with fracture surface analysis - x 50 were performed. Figure 6 shows the workplace for profilometric studies of the samples surface. A stereoscopic panoramic microscope MSP-1 (1) is installed at the workplace, this allows shooting the front part of the sample. The profilometry results are displayed on the computer using the AMSu program (3). The surface roughness of the samples under study was measured using the «Abris PM7» profilograph-profimeter (2).
**Figure 6.** The workplace for studying profilometry of the sample surface: 1 - microscope stereoscopic pancreatic MSP-1; 2 - profilograph-profilometer "Abris PM7"; 3 - computer with a working software.

**Figure 7.** The moment of the sample destruction when being tested for adhesive strength by the pin method - a); profilograms of destroyed samples: before coating - b); after coating - c); after coating of the material with an SME Ni-33%, Ti-49%, Zr-18%, using ultrasonic influences at different stages of processing - d, e).

Figure 7a shows a sample for testing adhesion by the pin method at the time of destruction and the results of profilographic studies of the samples before and after applying coatings with SME Ni-33%, Ti-49%, Zr-18% by high-speed gas-flame spraying using UST at various stages of processing.

The analysis of the obtained profilograms indicates that an ordinary viscous fracture with the initiation of fracture on the surface is characteristic of a sample of steel 45 without coating. This section is marked by a brighter color on the profilogram (Fig. 7, b). A specimen with a HGS coating without UST has a mixed fracture, the coating is brittle-destroyed, the middle part of the sample is characterized by a more even distribution of protrusions and depressions, the presence of coating...
material is observed on the protrusions (Fig. 7c); this indicates an increased value of the adhesive strength. The highest adhesive strength is achieved by the implementation of the technological operations with UST described above. Fig. 6d, e shows that less than 50% of the fracture surface occurred at the base-coating interface; this allows concluding that adhesion is increased, but the cohesion strength is insufficient. Since the reliability of the base-coating compound is ensured by the mechanical and chemical components, the result obtained indicates the prevailing influence of the mechanical component on the adhesive strength during high-speed gas-flame spraying. UST, being a powerful stimulating factor for the intensification of diffusion mass transfer, increases the chemical component of adhesion. The significant spread in the values of adhesive strength is due to the need for careful testing of UST modes.

The considered sequence of technological operations during the formation of coatings from a multicomponent material with thermoelastic phase transformations Ni-33%, Ti-49%, Zr-18%, HGS using external high-energy influences at various stages of processing, including ultrasonic, electropulse and thermal force influence, is an effective way to improve the adhesive strength of coatings and, as a result, the reliability of coated products.

4. Conclusions
A comprehensive study of the impact of external high-energy ultrasonic and electropulse influences on the adhesive strength of a coating from the material with thermoelastic phase transformations at various processing stages: preparing the base; preparing the sprayed material at the finishing stage after coating.

The ultrasonic treatment of the base before coating can be characterized as a method of mechanical activating the base surface before coating.

The analysis of the granulometric, elemental, and phase composition of the applied material in the process of mechanical activation made it possible to determine the optimal parameters of mechanical activation that ensure the formation of a nanoscale coating structure.

As a result of complex ultrasonic, electropulse and thermal force influences, at the finishing stage of processing, we may observe a distinct fusion of the coating from the material with TEPT Ni-33%, Ti-49%, Zr-18% with the basis and the absence of the interface, confirmed by electron-microscopic studies. The fusion zone is 10–20 μm with the coating thickness of 1 mm; there are practically no coating elements in the base material at the depth of 20 μm. The experimental studies have confirmed an improvement in adhesive strength of 1.2-1.5 times up to 130-150 MPa.

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