Tribological properties of multifunctional coatings with Shape Memory Effect in abrasive wear

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Abstract: The article gives research results of the abrasive wear process on samples made of Steel 1045, U10 and with applied composite surface layer "Nickel-Multicomponent material with Shape Memory Effect (SME) based on TiNi". For the tests we have chosen TiNiZr, which is in the martensite state and TiNiHfCu, which is in the austenitic state at the test temperature. The formation of the surface layer was carried out by high-speed oxygen-fuel deposition in a protective atmosphere of argon. In the wear test, Al2O3 corundum powder was used as an abrasive. It is shown that the wear rate of samples with a composite surface layer of multicomponent materials with SME is significantly reduced in comparison with the base, which is explained by reversible phase transformations of the surface layer with SME. After carrying out the additional surface plastic deformation (SPD), the resistance of the laminated composition to abrasion wear has greatly enhanced, due to the reinforcing effect of the SPD. It is recommended for products working in conditions of abrasive wear and high temperatures to use the complex formation technology of the surface composition "steel-nickel-material with high-temperature SME", including preparation of the substrate surface and the deposited material, high-speed spraying in the protective atmosphere of argon, followed by SPD.

Keywords: Abrasive wear, Surface, Multicomponent material, SME

1. Introduction

One of the most dangerous types of wear is abrasive wear [1-3]. The destruction of the workpiece surface as the result of abrasive wear occurs due to the interaction with solid particles which plastically and elastically deform the surface of the parts, as well as scratch, scrape and cut the material. When free abrasive particles get into places of details interface, they perceive the load transmitted through an interface pair and hit or squeeze into the surface details. The process of abrasive wear is an extremely complex phenomenon and is often accompanied by shock-droplet [4], erosion corrosion [5], the cavitation effect [6,7] and its distinctive feature is rapid development, leading to destruction of the surface. Currently, there are various ways to control abrasive wear: technological and operational ones. One of the promising control areas of abrasive wear is the introduction of new technologies of surface engineering, implemented in the integrated high-energy effects: laser, plasma, high-velocity flame ones[8,9].

High-energy impact allows to increase speed of heating and cooling that leads to the creation of the maximum non-equilibrium structures, which, under certain conditions, can provide the required complex of physical-mechanical and operational properties. Structure management of materials of a given composition, in conditions which are far from thermodynamic equilibrium, allows to ensure the
required durability of the product in extreme conditions when exposed to high contact and dynamic loads, abrasive and impact-abrasive wear. It is known that the materials with high hardness are more resistant to abrasive wear. This is due to the fact that the higher the hardness is the smaller the depth of a cut or a crumple under the impact of the abrasive particles with the surface is. The interaction of abrasive particles with the surface is accompanied by surface deformation and causes the hardening that increases the hardness of the outer layers, and, as a consequence, increases the resistance to abrasive wear. However, further accumulation of defects, such as scratches and cracks, leads to intense destruction of the workpiece surface [3,10,11]. Studies proved the dependence of abrasive wear resistance and energy consumption of the material, which is defined as the product of tensile strength and relative residual contraction [12,13]. This allows us to conclude that abrasive wear resistance depends on the optimal combination of strength and plasticity.

In the present work in order to control abrasive wear, we proposed to use smart, intermetallic nanocrystalline and layered structures, which also include materials with reversible phase structure, in particular, materials with shape memory effect (SME). The use of SME materials [14], in order to form surface layers or layered structures [15] which are multi-functional, can provide an effective response of tribomaterials to active influence of external factors [16], including the conditions of abrasive wear. The special tribological properties of SME alloys based on TiNi in combination with high damping capacity and resistance to corrosion-erosion effects have determined the Ni alloy as a "frictional phenomenon" - "a new tribo-material" and "tribo-composite" [17,18]. High wear resistance of alloys with SME has got not only high hardness values, but also special functional-mechanical properties. On the workpiece surface made of SME materials, as a result of abrasive particle deformation at a voltage that exceeds the limit of elasticity, there is a nonlinear plastic deformation, which remains as a residual one and may accumulate in the case of conventional material after removing the tension. In the case of SME material, when elastic deformation is too high, the further deformation is non-linear and takes place due to thermoelastic martensitic transformation (austenite-martensite). This deformation is removed completely when the load is restored by the reverse martensitic transformation (martensite-austenite), in this case there is a phenomenon of pseudo elasticity [10,14-16,19]. Therefore, the damage accumulation in SME materials is much slower than that of the conventional materials. However, the production of workpieces from SME materials is not economically feasible. Therefore it seems promising to use SME materials in order to form the formation of the surface layers, resistant to this type of fracture.

In [26, 27] it is shown that multicomponent coatings on the basis of TiNi with additional alloying elements such as Zr in an amount of up to > 10% allow us to create a composite material with a gradient of properties at the interface between the layers, which allow to obtain new properties and to increase their performance. Use of materials with shape memory effect (SME) as the surface layers [25] or as a part of the layered compositions [27] allows to provide the effective response of materials to external factors and adaptation to external influences.

As a technology we selected High Velocity Oxygen Fuel spraying (HVOF) in the protective argon environment [15,20,21]. Surface layers formed by HVOF in a protective environment are characterized by high adhesive strength (90-100 MPa) and low porosity (less than 1%). As SME materials for the formation of surface compositions in the present work, we selected composite materials TiNiZr, TiNiHfCu, which have different structural-phase states [22-24]. As materials for results comparison, we applied structural steel 1045 and tool steel U10.

2. Experiment

2.1 Technology of formation of surface composite layer

As the basis were used Steel 1045, which is widespread in mechanical engineering, the transition layer is Nickel, which has unlimited solubility with iron and chemical affinity with the material of the transitional and functional layers, which provides increased adhesive strength. In order to for functional layers, we used SME materials, which have significantly different temperature phase
transformations: Ti$_{33}$Ni$_{49}$Zr$_{18}$ alloy, which possesses high temperature memory effect and at temperature of 20°C is in the martensitic state [23]; Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_5$ alloy at temperature of 20°C is in the austenitic state [28]. The characteristics of the materials are presented in Table 1.

| Material samples | Diameter, mm | Weight, g | T, °C | Microhardness, GPa | Phase state     |
|------------------|--------------|-----------|-------|-------------------|-----------------|
| Steel 1045       | 50,39        | 145,735   | 20    | 1.9-2.1           | -               |
| U10              | 50,24        | 158,943   | 20    | 5.7-6.5           | -               |
| Steel 1045–Ni–Ti$_{33}$Ni$_{49}$Zr$_{18}$ | 50,53 | 154,176 | 20 | 2.1-2.9 | martensite |
| Steel 1045–Ni–Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_5$ | 51,12 | 155,214 | 20 | 9.5-11.9 | austenite |
| Steel 1045 – Ni – Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_5$ + (SPD) | 50,87 | 155,663 | 20 | 11.7-14.2 | austenite |

Formation technology of surface composition involves several stages: preparation of the base and coating material, application of transitional and functional coatings by High-velocity oxygen-fuel spraying (HVOF), thermomechanical treatment (TMT).

Base preparation is a comprehensive machining, which includes creation of a surface with well-developed microstructure, followed by shotblasting, and chemical treatment, which consists of degreasing and surface etching with a mixture of hydrochloric and nitric acids.

Preparation of coating material is mechanical activation (MA) of a powder material, which provides necessary granulometric composition, energy state and reactivity of the material. Mechanical activation was carried out in the upgraded ball mill Gefest-2 of AGO-2U [30], in which the mechanical effect is carried out by a series of mechanical pulses (beats) of working bodies, that transmits a portion mechanical energy to the processed material.

The coating was carried out by HVOF at the upgraded device GLC-720 in a protective argon atmosphere [8, 29].

![Figure 1. Device for coating by HVOF in a protective atmosphere](image-url)

Integrated TMT was carried out to give pseudo elastic properties or the properties of shape memory to a surface layer and to impart functional properties and increase the adhesion strength. Integrated treatment is assigned depending on the thickness of the composite layer. For coatings with thickness up to 1 mm we carried out comprehensive treatment consisting of surface plastic deformation (SPD) and ultrasonic treatment (UST). For coatings with thickness greater than 1 mm we carried out comprehensive treatment consisting of SPD and resistance spot welding [31].
Study of the deformation behavior influence of the samples (steel and composite surface layer of SME alloys) in conditions of abrasive wear was carried out on a modernized testing machine friction CMT-1-2070, which is equipped with a special chamber for abrasive. Figure 2 shows a diagram of abrasion testing. A device consisting of two disks of equal diameter, revolving in the opposite direction, is placed in hermetically sealed camera.

![Figure 2. Scheme of test for abrasive wear](image)

The chamber is filled with a powder of abrasive material to a level above the interface plane disks of 15 mm, which ensures a permanent contact of the powder particles in the contact zone of the two samples. We can see from the diagram that in the contact samples experience different effects: rolling friction, abrasive wear and sliding friction. This experiment may mimic the operation of a gear pair or crushing station rolls.

As the abrasive we used aluminium oxide $\text{Al}_2\text{O}_3$ (corundum) with a hardness of 25 GPa [1]. The average particle size of the $\text{Al}_2\text{O}_3$ powder is 120-180 µm.

The frequency of rotation of a pair is $300 \text{ min}^{-1}$, pressing force is 250 N, the test time is 2 hours, the interval measurement is every 15 minutes. The nucleation and growth dynamics of surface damage was observed using the stereomicroscope stamps LOMOM SP-2, with magnification 25-50, which is provided with a scale for measurement. Mass wear of the discs is determined by the gravimetric method (balance "DEMCOM DL") with a measurement accuracy of 0.001 g. The measurement of the diameters of the disks were performed with a micrometer with an accuracy of up to 0.005 mm., the wear rate was determined according to GOST 27674-88.

The study of coating hardening from existing forces in the process of cylindrical specimens rolling was carried out on microhardness tester Falcon 500.

To determine the resistance of the coating to the contact stresses we carried out their estimation based on the method described in [32].

![Figure 3. Scheme of deformation of surface layers during rolling of two cylinders](image)

The contact patch has the form of a narrow rectangle whose length is equal to the width of the disk – 10 mm, and the width is determined by the formula:


\[ b = 2.15 \left( \frac{1}{\frac{E_1}{R_1} + \frac{1}{E_2}} \right)^{1/2} \]

For alloy Ti33Ni49Zr18 Young's modulus in the martensitic condition are \( E = 28 \) GPa, pressing force is 250 N on the length of 10 mm, therefore, a distributed load is equal to \( q = 25000 \) N/m

\[ b = 2.15 \left( \frac{25000}{1} \frac{28 \times 10^9 + 1}{25 \times 10^{-3}} \frac{1}{25 \times 10^{-3}} \right)^{1/2} = 329.15 \times 10^{-6}, \text{m} \]

For alloy Ni44Ti36Hf15Cu5 Young's modulus in the martensitic condition is \( E = 80 \) GPa.

\[ b = 2.15 \left( \frac{25000}{1} \frac{80 \times 10^9 + 1}{25 \times 10^{-3}} \frac{1}{25 \times 10^{-3}} \right)^{1/2} = 190.03 \times 10^{-6}, \text{m} \]

The greatest compressive stress acting at points of the axis of contact area, for alloy Ti33Ni49Zr18 is

\[ \sigma_{max} = 1.27 \frac{q}{b} = 0.418 \left( 2 \times \frac{q}{E_1 + E_2} \frac{R_1 + R_2}{R_1 \times R_2} \right)^{1/2} = 98.9 \text{ MPa} \]

The greatest compressive stress acting at points of the axis of contact area, for alloy Ni44Ti36Hf15Cu5 is

\[ \sigma_{max} = 1.27 \frac{q}{b} = 0.418 \left( 2 \times \frac{q}{E_1 + E_2} \frac{R_1 + R_2}{R_1 \times R_2} \right)^{1/2} = 167.2 \text{ MPa} \]

Analysis of the stress state shows that the dangerous point is located at a depth equal to 0.4 of the width of the contact area. The principal stresses at this point have the following meanings:

контакта. Главные напряжения в этой точке имеют следующие значения:

\[ \sigma_1 = -0.180 \times \sigma_{max}, \quad \sigma_2 = -0.288 \times \sigma_{max}, \quad \sigma_3 = -0.780 \times \sigma_{max} \]

The main stress Ti33Ni49Zr18

\[ \sigma_1 = -17.802 \text{ MPa}, \quad \sigma_2 = -28.483 \text{ MPa}, \quad \sigma_3 = -77.142 \text{ MPa}. \]

Shear stress

\[ \tau_{max} = 0.3 \times \sigma_{max} = 29.67 \text{ MPa} \]

The main stress Ni44Ti36Hf15Cu5

\[ \sigma_1 = -30.096 \text{ MPa}, \quad \sigma_2 = -48.44 \text{ MPa}, \quad \sigma_3 = -130.416 \text{ MPa} \]

Shear stress is

\[ \tau_{max} = 0.3 \times \sigma_{max} = 50.16 \text{ MPa} \]

According to the fourth theory of strength equivalent stress for the composition Ti33Ni49Zr18 is

\[ \sigma_{equ} = \left( 0.5 \left( (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right) \right)^{1/2} = 54.84 \text{ MPa} \]

According to the fourth theory of strength equivalent stress for the composition Ni44Ti36Hf15Cu5 is

\[ \sigma_{equ} = \left( 0.5 \left( (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right) \right)^{1/2} = 95.54 \text{ MPa} \]

Contact stresses are dependent on the contact force of the rollers. For the selected contact force of the rollers of 250 N maximum contact stresses occur at the depth of the composition Ti33Ni49Zr18 at 0.131 mm, Ni44Ti36Hf15Cu5 at 0.076 mm from the surface. Due to the fact that the adhesion strength of the coating layers is comparable to the magnitude of contact stresses, it is necessary to control the thickness of the top coat layer so that the interface between the layers was beyond the point of occurrence of maximum contact stresses.

2.2 Experimental results and discussion

During the test on abrasion wear, we monitored nucleation and accumulation of damages in the surface layers. Fig. 4 shows the pattern of damage accumulation through time for the studied materials, where more saturated colors correspond to the greater depth of the damage. Thus, on the Steel 1045 sample form the first minutes damages in the form of dings, tears, cuts and scratches appear on the surface. Areas with damage comparable to the size of Al2O3 particles, are highlighted in blue, and areas with damages that exceed the size of the abrasive particles are highlighted in red.
(Fig. 4). It should be noted that focal accumulation of damages (defects) under these test modes was observed only during the first 100-120 minutes, then the difference in depth of defects is reduced and intensive wear is observed throughout the sample surface. Similar tests on the abrasive wear of tool Steel U10 showed a decrease in intensity of the accumulation of defects and their depth compared with Steel 1045. The wear rate is reduced by about 30%. It is shown in figure of wear intensity (Fig. 5, a and b) and confirmed by other sources [1-7].

The deformation behavior of samples with a composite surface layer of a SME material with high temperature "Ni – Ti_{33}Ni_{49}Zr_{18}" (MF = 459 K, MS = 522 K, As = 488 K, AF = 571 K) [22-23] in the conditions of abrasive wear, showed that the emergence of deep damage is detected much later (after 60 minutes of testing); the speed of accumulation of defects is reduced as compared with the material without coating; with coating hardness of Ti_{33}Ni_{49}Zr_{18} in the martensitic state two times less than the hardness of tool Steel U10, the intensity of wear is in 2 times less than that of Steel U10 (Fig. 5). Test temperature (20 C) corresponds to the martensitic condition of the coating material Ti_{33}Ni_{49}Zr_{18}.

Steel 1045  U10  Ni – Ti_{33}Ni_{49}Zr_{18}  Ni – Ni_{44}Ti_{36}Hf_{15}Cu_{5}

The original surface condition

The surface of the samples after 15 minutes of testing

The surface of the samples after 120 minutes of testing

Ni – Ni_{44}Ti_{36}Hf_{15}Cu_{5} + SPD

Initial state  30 minutes  60 minutes  120 minutes

**Figure 4.** The accumulation of surface damage of the samples during the tests on the abrasive wear

To assess the effect of structural-phase state of SME materials on the wear rate at abrasive impact we carried out tests of samples with surface functional layer "Steel 1045–Ni–Ni_{44}Ti_{36}Hf_{15}Cu_{5}" after a full cycle of treatment: MA, VHOF, TMT and SPD in the test conditions in the austenitic state [24]. Analysis of the surface composition "Ni–Ni_{44}Ti_{36}Hf_{15}Cu_{5}" at various stages of the test (Fig. 4) showed
that process of surface defects of considerable size formation slows down (after 90 minutes of the test). The wear rate is reduced by 50% compared to the wear of the coating "Ni–Ti$_{33}$Ni$_{49}$Zr$_{18}$" which is in the martensitic condition and more than 6 times than that of the base material (Steel 1045).

![Graphs showing wear rate vs frequency and time for different surfaces](image)

**Figure 5.** The wear intensity of specimens examined: (a) Steel 1045, (b) Steel Y10, (c) coating Ni–Ti$_{33}$Ni$_{49}$Zr$_{18}$, (d) coating Ni–Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_{5}$, (e) coating Ni–Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_{5}$ at high velocity, (f) coating Ni–Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_{5}$ + SPD

Full cycle processing of SME materials, including TMT and SPD is accompanied by strain hardening, which increases the hardness, creating a nonuniform stress-strain state (SSS) and is primarily focused on the formation of pseudo elasticity properties. The increased hardness of the surface layer, from one hand – increases the resistance to abrasive wear, and from another hand – leads to its embrittlement, and together with the heterogeneity of SSS, leads to the formation of defects at an early stage of testing of break type of and fractures. It is considered that the hardness of the SME materials is not the
determining factor in the improvement of wear resistance, although it significantly affects abrasive wear (Fig. 5, c).

To assess the influence of abrasive wear on the distribution of hardness along the depth of the coatings, we conducted a study of samples’ cross-section for microhardness after 120 min of testing (Fig. 5, a). From the diagrams of the distribution of hardness it can be seen (Fig. 5, c) that after 120 minutes of testing the test coating does not accumulate hardening. Microhardness on cross sections is distributed quite evenly. This suggests that after the load is removed the material returns to their original state.

The study of microstructure of the surface layer $\text{Ni}_{34}\text{Ti}_{36}\text{Hf}_{15}\text{Cu}_{5} + \text{SPD}$ on a raster electronic microscope of high resolution showed that the layer has a nanoscale structure with a grain size of 95 - 140 nm (Fig. 5, b). Nanoscale structure causes a decrease of critical transition temperature and an increase in the interval of temperatures within which it occurs [33].

**Figure 6.** The distribution of hardness along the depth of the coating: (a) picture of microhardness measuring on the sample coated with Ni–Ni$_{34}$Ti$_{36}$Hf$_{15}$Cu$_{5}$ + SPD, (b) the microstructure of the coating Ni–Ni$_{34}$Ti$_{36}$Hf$_{15}$Cu$_{5}$ + SPD, (c) graphs of hardness distribution of the investigated coatings

Materials with SME, being the materials with reversible phase structure, have the unique ability to phase transformations under the action of load and temperature. When load is applied to the product, which is in the austenitic state, there is a direct austenitic-martensitic transformation, and at the termination of loading, the reverse martensite-austenite transformation takes place. The mechanism of
abrasive wear of Ti-Ni alloy is considered in [11]. The TiNi alloy has a limited temperature interval of phase transformations, as a rule, not exceeding 373K. For articles exposed to abrasive wear in the conditions of higher temperatures, it is economically and technologically expedient to use the surface modification of multi-component materials with SME Ti$_{33}$Ni$_{49}$Zr$_{18}$, Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_5$ providing a high temperature of SME. The most effective ways of increasing wear resistance and durability of the products in the conditions of abrasive wear is the formation of surface layered functionally graded compositions "the basis - transition layer – functional layer". As a transitional layer in the present work we used Nickel, which has a chemical affinity with material bases and the functional layer, providing a reliable adhesion. A transition layer of Nickel having a high ductility and toughness, is a relaxation layer that inhibits the movement of propagating defects, slowing down the process of destruction. Surface functional layer made of materials with SME on the basis of TiNi has a high abrasion resistance, sufficient hardness and ability to adapt to loading conditions by displaying pseudo elasticity properties during phase transformations.

3. Conclusion

Intensive development of smart materials have greatly increased modification and coating technologies with desired tribological and physical-mechanical properties used in the friction units. It was shown that the development of a new generation of coatings with SME materials, which is a multi-layered surface composition with alternating layers of different functional purposes, enhances operational properties of working surfaces of products. Study of deformation behavior of samples with a composite surface layer of multicomponent SME materials, formed under high-energy impact during abrasive wear showed a significant reduction of wear rate depending on the structural-phase state of the coatings and technology of their formation. We confirmed experimentally a decrease in the wear rate of the samples with composite surface SME layer: "Ni - Ti$_{33}$Ni$_{49}$Zr$_{18}$," which is in the martensitic state, by 3 times; "Ni–Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_5" which is in the austenitic state, by 6 times; "Ni–Ni$_{44}$Ti$_{36}$Hf$_{15}$Cu$_5", after a full cycle TMT and rpm, by 30 times. The basis of improving the wear resistance of the surface composition of SME materials in the conditions of abrasive wear is the effect of pseudo elasticity and ability of SME materials to adapt to external influences due to reversible phase transformations.

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