

Cavitation resistance of surface composition "Steel-Ni-TiNi-TiNiZr-cBNCo", formed by High-Velocity Oxygen-Fuel spraying

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Abstract: The object of the study is a multilayered surface composition "Steel - a Multicomponent material with Shape Memory Effect - a wear-resistant layer" under conditions of cavitation effects in sea water. Multicomponent TiNi-based coatings with addition of alloying elements such as Zr in an amount up to 10% mass, allow to create a composite material with a gradient of properties at the interface of layers, which gives new properties to coatings and improves their performance significantly. The use of materials with shape memory effect (SME) as surface layers or in the composition of surface layered compositions allows to provide an effective reaction of materials to the influence of external factors and adaptation to external influences. The surface composite layer cBN-10%Co has high hardness and strength, which ensures its resistance to shock cyclic influences of collapsing caverns. The increased roughness of the surface of a solid surface composite in the form of strong columnar structures ensures the crushing of vacuum voids, redistributing their effect on the entire surface, and not concentrating them in certain zones. In addition, the gradient structure of the multilayer composite coating TiNi-Ti₃₃Ni₄₉Zr₁₈-cBN-10%Co makes it possible to create conditions for the relaxation of stresses created by the variable impact load of cavitation caverns and the manifestation of compensating internal forces due to thermo-elastic martensitic transformations of SME materials. The cavitation resistance of the coating TiNi-Ti₃₃Ni₄₉Zr₁₈-cBN-10%Co according to the criterion of mass wear is 15-20 times higher than that of the base material without coating and 10-12 times higher than that of the TiNi-TiNiZr coating. The proposed architecture of the multifunctional gradient composition, "steel-Ni-TiNi-Ti₃₃Ni₄₉Zr₁₈-cBN-10%Co", each layer of which has its functional purpose, allows to increase the service life of parts operating under conditions of cavitation-fatigue loading in corrosive environments.

Keywords: Cavitation, Surface, Multicomponent material, SME

1. Introduction

Increasing the reliability and durability of machine parts and mechanisms is primarily due to the elimination of wear caused by various types of impacts, in particular, on their surface layers. One of the types of such impact on the surface of parts working in a fluid environment is cavitation erosion of the metal, which is caused by the mechanical action of fast moving fluid particles on the surface of the metal, sand particles of solids, suspensions, gas bubbles, etc. Such influence is characterized by a high rate of loading, its small duration, locality and cyclicity. At the same time, stresses appear in the surface layers, they can be compared with the ultimate strength of the material and are concentrated in



volumes close to the dimensions of its structural components. Effective ways to improve the strength properties and resistance to corrosion-erosive effects are thermal and thermomechanical hardening treatments and the deposition of protective coatings on the metal surface [1].

Traditional materials science formation methods of structure and properties have basically exhausted their possibilities. Under these conditions, taking into account the crucial role of the surface layer in the accumulation of damage and destruction, the task of providing multifunctionality, as well as increasing reliability and resource, can be successfully solved at the final stage of processing by means of technologies based on the principles of layer-by-layer synthesis using combined, functionally oriented Macro-, micro-, and nanotechnologies. [2,3]

A promising direction in the implementation of layered synthesis technologies is the intellectualization of products using shape memory effect (SME) materials. They have a wide range of functional and mechanical capabilities: effects of thermomechanical memory and superelasticity, high strength and damping properties, thermomechanical reliability and durability, wear and corrosion resistance [4]. It was shown in [5, 6] that multicomponent TiNi-based coatings with addition of extra alloying elements such as Zr in an amount of up to 10% by weight make allow to create a composite material with a gradient of properties at the interface of the layers. This helps to impart new properties to the coatings, and significantly improves their performance characteristics. The use of materials with shape memory effect (SME) as surface layers [7] or as a component of surface layered compositions [8] allows to provide an effective reaction of materials to the influence of external factors and adaptation to external influences.

The aim of this work is to obtain quantitative data on erosion resistance under cavitation of composition surface layers with a gradient distribution of properties from a multicomponent SME material $\text{Ti}_{49}\text{Ni}_{51}$ - $\text{Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$ EPF and the wear-resistant material cBN-10% Co, which provides specified functional and mechanical properties.

2. Experiment

2.1 Technology of formation of surface composite layer

The formation technology of a surface composition with SME material is a complex multi-operation process involving the preparation of the surface and the deposited material (milling and mechanical activation), high-velocity oxygen-fuel spraying (HVOF), and subsequent thermo-mechanical (TM) treatment (Fig. 1). Characteristics of the layers are presented in Table 1.

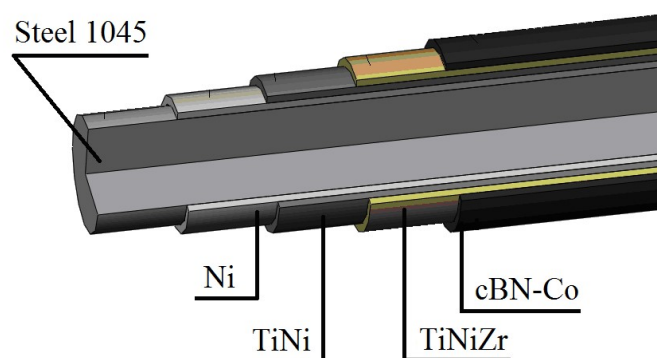


Figure 1. Scheme of the surface layer with a material with SME

Table 1. Layer characteristics

| Layers | Material | Layer thickness, μm | T, $^{\circ}\text{C}$ | M _s , $^{\circ}\text{C}$ | M _f , $^{\circ}\text{C}$ | A _s , $^{\circ}\text{C}$ | A _f , $^{\circ}\text{C}$ | Microhardness, hPa | Phase state |
|--------|----------------------------------------------------|--------------------------------|-----------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-----------------------|---------------------------|
| base | Steel 1045 | - | 20 | | | | | 1,9-2,1 | - |
| 1 | Ni | 100±10 | 20 | | | | | - | - |
| 2 | Ti ₄₉ Ni ₅₁ | 600±50 | 20 | 23 | 55 | 13 | 31 | 10,2-11,9 | austenite |
| 3 | Ti ₃₃ Ni ₄₉ Zr ₁₈ | 1000±50 | 20 | 186 | 249 | 215 | 298 | 2,1-2,9 / 9,5-12,7 | martensite / austenite |
| 4 | cBN-10%Co | 200±10 | 20 | | | | | 34,6-35,6 | - |

M_f is the temperature of martensitic transformation expiry;

M_s is the temperature of martensitic transformation onset;

A_s - temperature of austenitic transformation onset;

A_f is the temperature of austenite transformation expiry.

The outer layer in contact with the working medium must have a high wear resistance with an increased bearing and damping ability, corrosion resistance with an optimum combination of strength and toughness. To meet these requirements, it is proposed to use a combination of layers of dissimilar materials. The outer layer is a hard and wear-resistant cBN-Co material, intermediate layers of Ti₃₃Ni₄₉Zr₁₈-Ti₄₉Ni₅₁, which are in austenitic-martensitic and austenite phase state, respectively. The purpose of the intermediate layer is to relax the stresses, damping the oscillations and blocking the cracks that appear in the outer layer and propagate deep into the material. An intermediate functional layer made of materials with an ESP in the martensitic state, which has an increased elasticity, helps to reduce the stress concentration at the tip of the crack and inhibits or blocks its movement. The gradient of properties in the outer contact and functional layers of materials with ESP is provided by a gradient of the temperatures of the phase transformations, which are set by the regulation of the chemical composition and thermomechanical processing. The intermediate layer of Ni is designed to increase the adhesion strength of the functional layer and the base material (Steel 1045), since Ni and the steel base are characterized by unlimited solubility of the basic elements. In this case, the crystallochemical affinity of the base material, the connecting and functional layers takes place, and, importantly, all the components have close values of the coefficient of thermal expansion.

A composite coating was deposited on the steel samples (Steel 1045) consisting of: a 100 μm adhesive layer of nickel, Ti₄₉Ni₅₁ 550-600 μm functional layers at room temperature in austenitic state, Ti₃₃Ni₄₉Zr₁₈ with a thickness of 950 ÷ 1000 μm , located at room temperature in a martensitic state, and a wear-resistant layer of cBN-10% Co whose thickness is 200-210 μm .

Grinding and mechanical activation can be performed using a variety of equipment. Milling and mechanical activation were carried out in the modernized ball mill GEPHEST-2 AGO-2U [9], in which mechanical effect is created by a series of successive mechanical impulses (strokes). Mechanical activation is not only an effective way to optimize the particle size distribution, but also due to the large plastic deformation it allows to pump energy into the processed material forming amorphous and nanostructural states [10]. This energy is released during the formation of the coating and activates the process of nanostructuring [11]. Since the formation of coatings was carried out by HVOF by imposing separate particles – splices, which move and harden at high speed, the phase composition, structure and properties of the coatings depend on the temperature, velocity of the particles colliding with the substrate and their cooling. HVOF is accompanied by large plastic deformations and the crystallization of particles occurs at high degrees of supercooling and is accompanied by the formation of crystalline nucleating centers whose size is determined by the degree of supercooling determined by the parameters of the process [12].

2.2 Experimental

In order to assess the quality of the composition functional layers, the sprayed samples were tested for adhesion, cavitation resistance, and fatigue strength. Adhesion was measured by a pin method on an Instron-8801 test machine. The micro-hardness test was performed on the Falcon-500 hardness tester. Cavitation tests were carried out in accordance with the American Standard ASTM G32-10 (Standard Test Method for Cavitation Erosion Using Vibratory Apparatus), using an ultrasonic vibrating unit and standard statistical processing of the experimental data (Fig. 2). [13]

Ultrasonic waves were used to create the cavitation zone. The signal from the generator is fed to a magnetostrictive transducer mechanically connected to a waveguide, at the end of which an experimental sample of a cylindrical shape with a diameter of 15 mm is rigidly mounted (Fig. 3), which provides an amplitude of oscillation of the sample end surface up to $50 \pm 2 \mu\text{m}$ at a frequency of 20 kHz. The sample is immersed in a vessel with water. On the end surface of the sample, a zone with developed cavitation is formed. To assess the effect of corrosion processes on the magnitude of cavitation erosion, experiments were conducted in fresh and sea water.

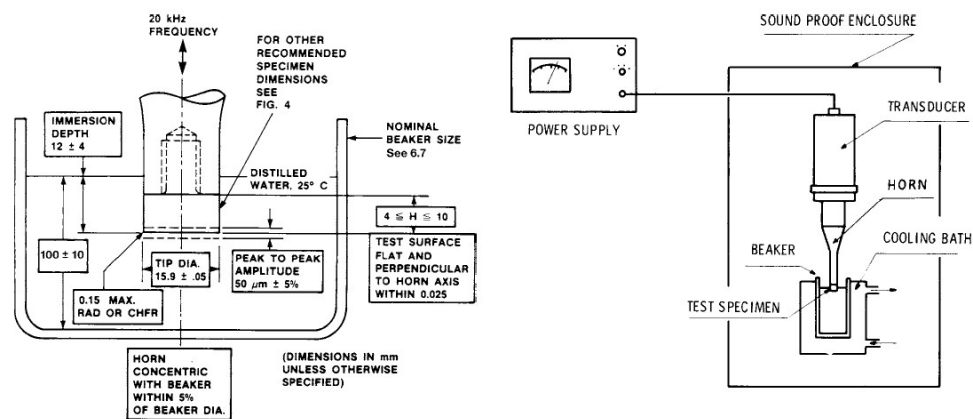


Figure 2. The test procedure for cavitation damage [ASTM G32-10].

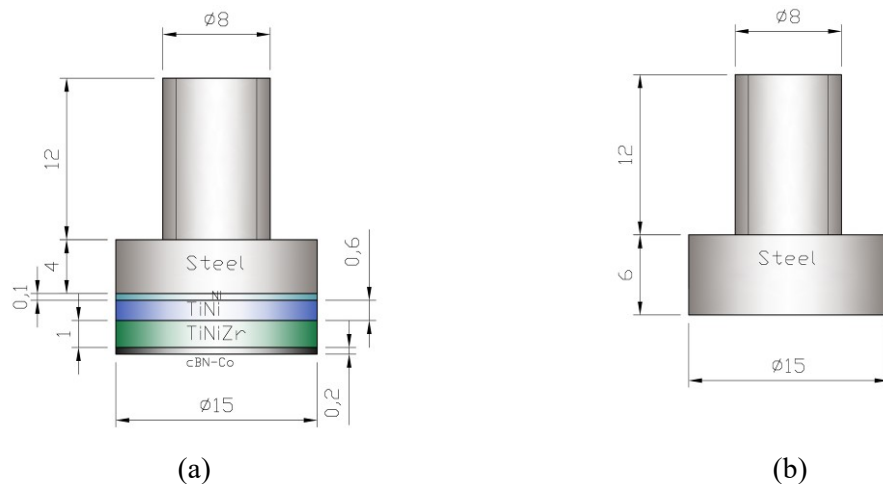


Figure 3. Configurations and dimensions of cavitation test specimen for (a) with a composite layer, (b) steel (1045 or stainless 20Cr13).

The TiNiZr functional layer, which has a high-temperature SME [5], at normal temperature has increased relaxation properties and microhardness of $9.5 \div 12.7 \text{ GPa}$ in the austenite state and $2.1 \div 2.9 \text{ GPa}$ in the martensitic state. The microhardness of the wear-resistant cNB-Co layer varies depending on the cobalt content from $17.2 \div 22 \text{ GPa}$ to $34.6 \div 35.6 \text{ GPa}$.

Damage accumulation and destruction of the samples surface was carried out with the visual inspection and area damage assessment on a stereoscopic zoom microscope MSP-1. Monitoring of the samples profile change, subjected to the cavitation fracture, as well as the damage depth was performed on the contour-tracing apparatus ABRIS PM7, the weight loss was measured on a DEMCON DL213 balance with an accuracy of ± 0.001 g. The dependence of the mass loss on the time of cavitation effect was measured; and from these data, the kinetic curves of the sample material destruction were constructed, which are characterized by the presence of the initial segment, when the destruction is small, and by the section with the maximum quasi-constant velocity.

2.3 Experimental results and discussion

The traditional criterion for resistance to material erosion is the loss of its mass over a period of time. Fig. 4 shows the study results of the cavitation resistance of uncoated samples and coated ones in fresh and sea water. In the process of cavitation in fresh water, the destruction of the surface is characterized by a classical curve of cavitation damage with an incubation period (30-60 min) and subsequent intensive loss of mass. The loss in mass of the composite coating $\text{Ti}_{49}\text{Ni}_{51}\text{-Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}\text{-cBN10\% Co}$ has a longer incubation period (more than 120 min), which is associated with an increased microhardness of the coating surface.

The presence of an aggressive component in the medium (salty sea water) somewhat smoothes the mass loss curve of the uncoated material and increases the intensity of the mass loss (Fig. 4). The materials used to form the coatings have an increased corrosion resistance, which is confirmed by the insignificant loss of weight of $\text{Ti}_{49}\text{Ni}_{51}\text{-Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}\text{-cBN10\% Co}$ coated samples and has almost no difference when tested in fresh and sea water. The results of the tests show that the surface composition $\text{Ti}_{49}\text{Ni}_{51}\text{-Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}\text{-cBN10\% Co}$ under consideration, each layer of which has its functional purpose, provides a set of properties such as high corrosion resistance, high microhardness, increased strength, and damping capacity. This contributes to the increase of stability of multicomponent coatings to cavitation erosion in corrosive environments.

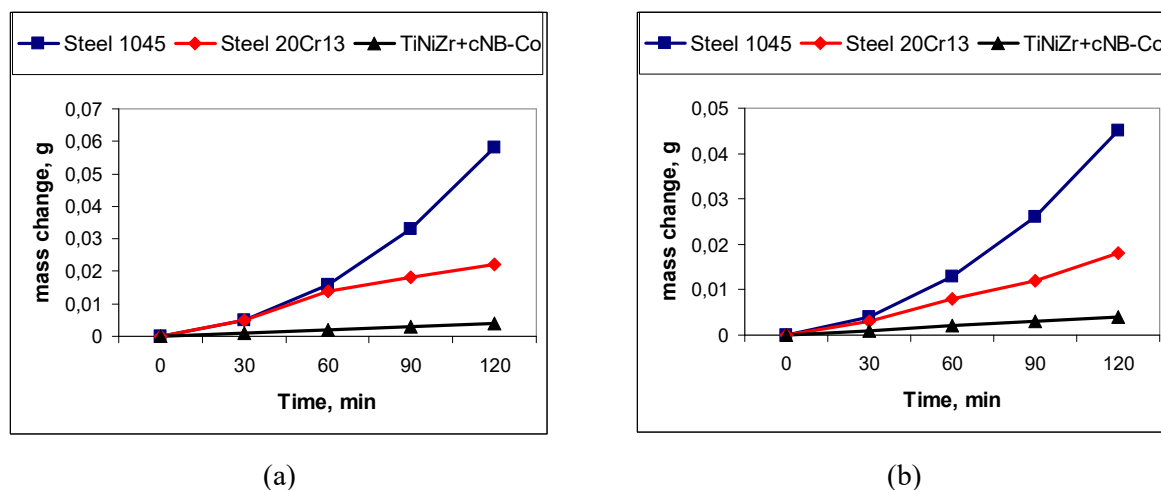


Figure 4. Dynamics of the sample mass change as a result of cavitation influences: (a) Sea water; (b) Fresh water.

The cavitation resistance of materials can be evaluated both by weight loss and by the duration of the incubation period. However, neither method allows us to investigate the mechanisms of failure, which can differ significantly depending on the chemical composition of the material, heat treatment, design features of the product and operating conditions. Being an integral characteristic, the weight wear sums the damage within the limits of the entire cavitation "spot". However, a visual examination of the "spots" can be used to establish that the wear rate of the surface in different areas is different (Fig. 5).

Within the formed "spot" of erosive destruction, three characteristic regions can be distinguished. Firstly, it is the area in which the strong destruction of the surface are observed - zone 1. The next region corresponds to moderate disruptions and represents an annular area along the edge of the "spot" - zone 2. Finally, the region lying between zones 1 and 2, which has the smallest damage - zone 3.

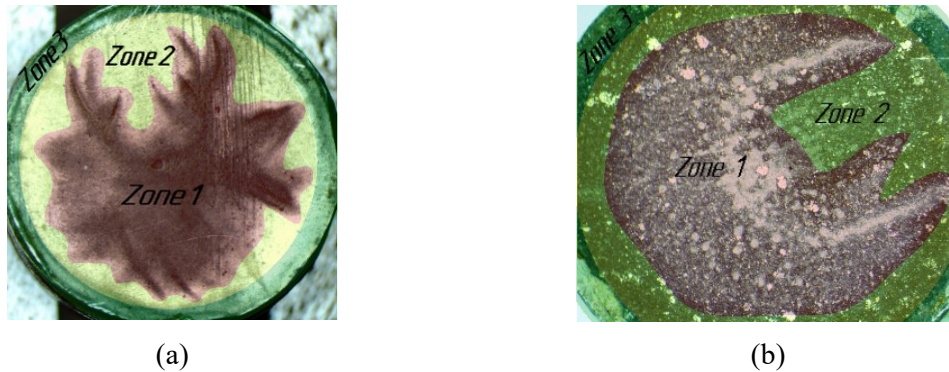


Figure 5. Erosion spot of a cylindrical sample with a flat surface: (a) uncoated; (b) coated with $\text{TiNi-Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$

The surface without coating of Steel 1045, Steel 20Cr13 and the composite coating $\text{Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$ -cBN10%Co before and after cavitation for 30 and 120 min in the sea water is shown in Fig. 6. It can be seen that the surface micro-relief practically does not change, i.e. the coating is practically not subjected to cavitation erosion.

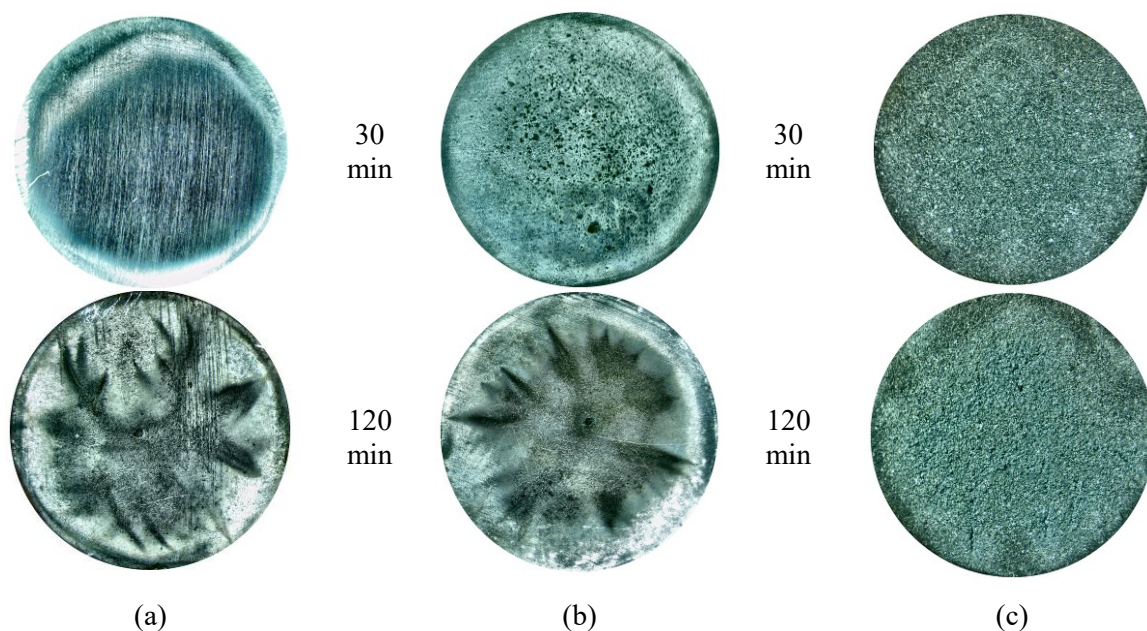


Figure 6. Destruction of the surface by cavitation for 30 and 120 min in the sea water: (a) Steel 1045; (b) Steel 20Cr13; (c) composite coating $\text{Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$ -cBN10%Co

The composite coating $\text{Ti}_{49}\text{Ni}_{51}$ - $\text{Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$ -cBN10% Co in the process of cavitation for 120 min in the sea water is shown in Fig. 7. Cavitation damage of the composite layer is only visualized after 120 minutes of impact.

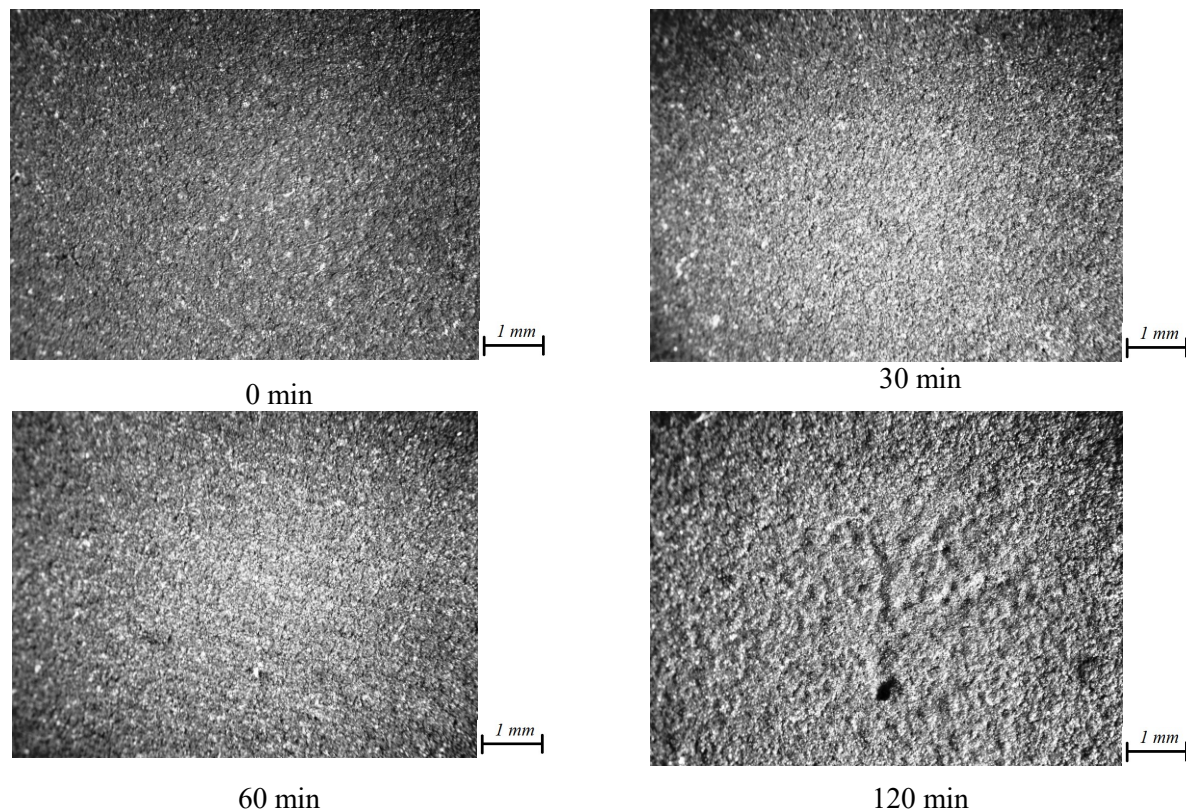


Figure 7. Cavitation destruction of the composite layer $\text{Ti}_{49}\text{Ni}_{51}$ – $\text{Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$ –cBN10%Co.

For a qualitative description of the cavitation fracture of a surface, it is expedient to investigate the parameters of the surface profile. The most characteristic factor for assessing the degree of surface cavitation wear is the following one: R_z is the height of the unevenness of the profile by ten points and R_{\max} is the highest profile height at the base length of 7.5 mm.

Table 2 shows the dynamics of surface roughness variation within zone 1 on different samples during the cavitation effect in the sea water environment. The surface roughness of the samples with coatings is much higher than the initial roughness of the uncoated sample. This is due to the formation technology of surface coatings by the method of HVOF by the powder material particles, which forms a characteristic surface micro-relief.

Figure 8 shows the distribution of depths of the asperities from erosion fracture surface of tested samples for the three time values of cavitation (after 30 and 120 min, from top to bottom). The distribution was obtained by computer analysis of the measurement results of surface roughness in different areas of the samples. In the above diagrams the depth of erosion destruction of the surface was determined by the depth of asperities.

Table 2. Change in surface roughness (R_z / R_{\max}), μm

| | Process time, min | | | | |
|---------------------------------------------------------------------------------------------|-------------------|-------------|-------------|-------------|-------------|
| | 0 | 30 | 60 | 90 | 120 |
| Steel 1045 | 0,27/1,56 | 5,23/18,54 | 9,56/28,14 | 13,88/44,48 | 16,25/47,2 |
| Steel 20Cr13 | 0,35/1,72 | 1,05/4,18 | 1,43/12,65 | 4,87/21,42 | 8,48/32,18 |
| Ni– $\text{Ti}_{49}\text{Ni}_{51}$ – $\text{Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$ –cBN10%Co | 61,76/79,36 | 63,14/80,12 | 65,86/80,67 | 67,24/81,04 | 69,21/85,60 |

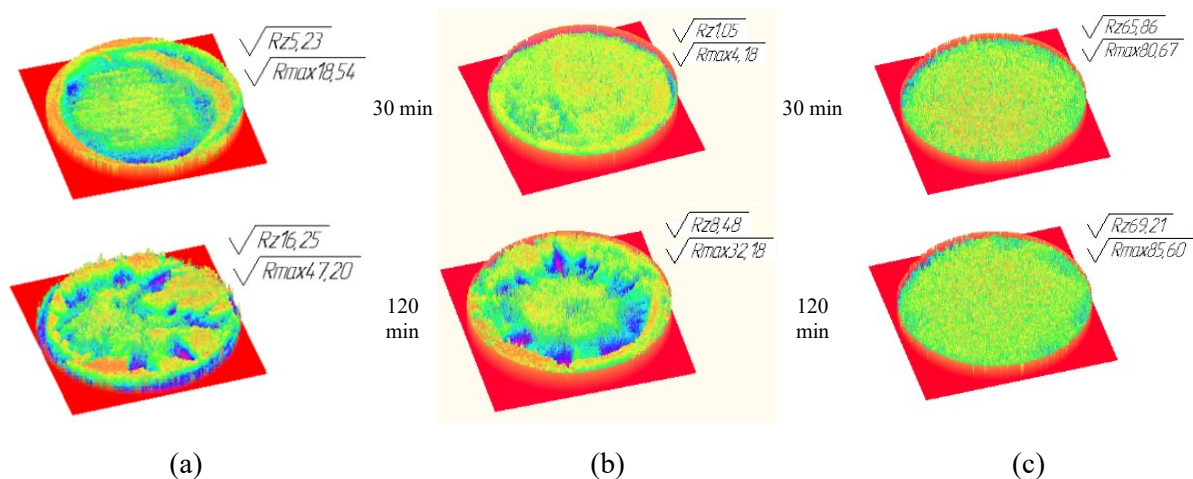


Figure 8. Destruction of the surface by cavitation for 30 and 120 min in the sea water: (a) Steel 1045; (b) Steel 20Cr13; (c) composite coating $Ti_{33}Ni_{49}Zr_{18}$ -cBN10%Co

Analysis of Table 2 and Fig.8 shows that the change in the roughness of the samples with coatings is less than the change in the roughness of the sample without coating by 1.5-2 times. As we know, cavitation as a phenomenon, is associated with the discontinuity of the moving fluid, the formation of vacuum voids (caverns) in it, followed by their closing, accompanied by large hydrodynamic impacts. According to the ideas of a number of cavitation phenomena researchers [11,14,15,14], the cause of cavitation destruction of parts is the fatigue destruction of micro-volumes of a material due to repeated exposure of high-frequency pulses both as a detachment action (during formation and detachment of cavitation caverns) and shock action accompanying their clamping. In this case, the application site of the cavitation action pulses is so limited that the process of cavitation destruction should be considered from the point of the cyclic strength of individual structural components or local micro-volumes of the metal. Microvolumes of metal, damaged by cyclic loading and cavitation effect, weakened by loss of communication with the neighbouring micro-volumes, easily subject to erosion by the flow, forming deep relief cavitating surface, activating the cavitation processes to an even greater extent [14].

The surface composite layer cBN10%Co has high hardness and strength, which ensures its resistance to shock cyclic influences of collapsing caverns. The increased roughness of the surface of a solid surface composite in the form of strong columnar structures ensures the crushing of vacuum voids, redistributing their effect on the entire surface, and not concentrating them in certain zones. In addition, the gradient structure of the multilayer composite coating $Ti_{49}Ni_{51}$ - $Ti_{33}Ni_{49}Zr_{18}$ -cBN10%Co makes it possible to create conditions for the relaxation of stresses created by the variable impact load of cavitation caverns and the manifestation of compensating internal forces due to thermo-elastic martensitic transformations of SME materials.

The increase in the performance characteristics of samples with a composite surface layer “steel – adhesive layer with a Ni – relaxing SME layer $Ti_{49}Ni_{51}$ – a functional reinforcing SME layer $Ti_{33}Ni_{49}Zr_{18}$ – functional wear layer of cBN-10% Co” under conditions of cavitation erosion is explained by the special functional properties of SME materials, which are manifested in the ability to adapt to the loading conditions, which is provided by the formation technology and processing of the surface layer. The increase in the wear-and-fatigue characteristics of the surface composition is explained by the pseudoelasticity of the layer made of SME materials with the $Ti_{33}Ni_{49}Zr_{18}$ and the decrease in the stress concentration due to its relaxation capacity.

The field of use of the above surface composition can be expanded by controlling the functional properties of the layers composing the composition by varying the chemical composition and controlling the phase composition by thermal and thermomechanical processing.

3. Conclusion

According to the experimental data, the surface of a composite layered material, especially hardened by a hard wear-resistant composite, has a high resistance to surface defects as a result of cavitation processes. The cavitation resistance of the $\text{Ti}_{49}\text{Ni}_{51}\text{-Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}$ coating according to the criterion of mass wear is 1.5-2 times higher than that of the base material without coating (steel 1045). The cavitation resistance of the coating $\text{Ti}_{49}\text{Ni}_{51}\text{-Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}\text{-cBN10\%Co}$ according to the criterion of mass wear is 15-20 times higher than that of the base material without coating and 10-12 times higher than that of the $\text{Ti}_{49}\text{Ni}_{51}\text{-TiNiZr}$ coating. The proposed architecture of the multifunctional gradient composition, "steel- $\text{Ni-Ti}_{49}\text{Ni}_{51}\text{-Ti}_{33}\text{Ni}_{49}\text{Zr}_{18}\text{-cBN10\%Co}$ ", each layer of which has its functional purpose, allows to increase the service life of parts operating under conditions of cavitation-fatigue loading in corrosive environments.

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