FORMATION OF STRUCTURE IN THE TINIHF SURFACE LAYERS WITH THE ASSESSMENT OF THEIR DURABILITY

ОСОБЕННОСТИ ФОРМИРОВАНИЯ СТРУКТУРЫ В ПОВЕРХНОСТНЫХ СЛОЯХ TiNiHf С ОЦЕНКОЙ ИХ ДОЛГОВЕЧНОСТИ

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Abstract: *On the basis of complex metallophysical studies, surface-modified layers (electron microscopy, spectroscopy, X-ray diffraction, calorimetry, durometer analysis), we obtained new data on nanoscale composition within the surface-modified layer, on its mechanical properties, phase composition, which determines functional properties. This allows us to find ways of their purposeful formation for different operating conditions. On the basis of experimental data of X-ray analysis of the TiNiHf alloy, we calculated energy consumption, the theoretical strength. As a result of the simulation, we constructed generalized diagrams of energy intensity and theoretical strength of the ternary alloy Ti-Ni-Hf and compiled their relationship equation.*

***KEYWORDS**: SHAPE MEMORY EFFECT, HIGH SPEED FLAME SPRAYING, DURABILITY, STRENGTH, WEAR RESISTANCE*

1. Introduction

Modern trends in science and technology development make it necessary to improve the quality and advance the functional characteristics of the existing materials in order to expand the area of their practical use [1-10]. The priority development directions of materials and technologies include the development of intelligent, adaptive materials and coatings, including materials with shape memory effect (SME), as well as development of resourceful technology for their production [11-16]. Among the alloys with SME, TiNiHf is positioned as a high-temperature shape memory alloy, it is one of the most promising alloys because of its higher martensitic transformations temperatures and low cost [17,18]. Temperature of martensitic transformation has a significant impact on the physical and mechanical properties of shape memory alloys. While the temperature changes the work against the applied stress can be done; ie, heat is converted into mechanical action, which allows us to consider the shape memory materials to be functional ones. Between voltage, temperature and deformation in shape memory alloys, there is no uniquely ultimate dependence, which requires the development of methods for calculating the mechanical behavior of alloys with shape memory effect [19].

The aim of this study is to investigate the structure of the shape memory surface layers, obtained by high-velocity oxygen-fuel spraying of mechanically activated TiNiHf powder in a protective atmosphere with the assessment of their durability.

2. The experimental procedure

To form TiNiHf surface layers on steel we used the technology of high-velocity oxygen-fuel spraying of mechanically activated powders PN37T18GF45 and PNK1-VL7. Spraying of PN37T18GF45 was carried out via an intermediate layer of pure nickel Ni (δ = 100 microns), which provides a strong bond at the interface steel - TiNiHf, upon cylindrical (diameter 10 mm, steel 1045) samples. The total thickness of the layer was varied within 0.9 ÷ 1.1 mm.

Powders Ni, TiNiHf of PNK1-VL7, PN37T18GF45 brands for high-velocity oxy-fuel spraying were subjected to mechanical activation in a high-velocity planetary ball mill AGO-2U, drum rotation speed is 1200 min^{-1}, carrier rotation speed is 900 min^{-1}, the diameter of the steel balls is 6 mm, operation time the 10-30 min.

In the process of mechanical activation of PN37T18GF45 powder we observe its fragmentation and plastic deformation. PN37T18GF45 powder particles before mechanical activation are 40-60 microns, after mechanical activation they are 0.1 - 3 microns, with nanoparticles.

High-velocity oxygen-fuel spraying was carried out on a modernized universal plasma unit GLC-720, in a protective atmosphere (argon). As a result of mechanical process and statistical processing of technological parameters, we determined optimal modes of high-velocity oxy-fuel spraying of TiNiHf shape memory materials: propane flow rate of 60-85 l / min, oxygen - 120-160 l / min, powder consumption 190-210 g / min, the carrier gas (argon) flow - 40-50 l / min, spraying angle - 70 °, the burner moving speed - 0.2-0.3 m / min, the speed of the coated workpieces 500 rev / min, spraying distance of 300 mm.

TiNiHf surface layer was under thermomechanical processing cycle including mechanical, thermal and combined thermomechanical treatment.

X-ray analysis was performed on diffractometer Shimadzu XRD - 7000 in Cu-Ka radiation (λ = 1,54051). The microstructure and chemical analysis of the material steel-alloy TiNiHf was analyzed on an electron microscope of ultrahigh resolution JSM-7500F. Evaporation and heating of the sample was analyzed using arc and spark discharges, and then we carried out decrypts of the spectra and evaluation of the intensity of the spectral lines of the respective elements. Multi-cycle fatigue tests of steel 1045 cylindrical samples were carried out at the equipment MIE-6000. Quantitative assessment of durability was carried out by gravimetric method using an analytical balance WA-33. After deposition and machining to size, we held vacuum annealing of the samples: steel + TiNiHf at T = 1073K for 1 hour in order to impart the necessary functional mechanical properties to surface layer, it was subjected to thermomechanical processing by means of surface plastic deformation. Running by rollers of the cylindrical samples made of steel 1045 with TiNiHf coating was carried out under the following conditions: contact pressure (per roller) F = 3 ÷ 4 kN, roller diameter d1 = 50 mm, roller width b1 = 8 mm, the running speed v = 94 • 10-3 m / s, longitudinal feed - s = 0,08 mm / rev. Control over thermomechanical return of the samples, that were subjected to a combined treatment in a thermomechanical cycle, was carried out after heating to a reverse martensitic transformation temperature.

Structural and mechanical features of the surface layers formation using shape memory alloy. As a result of high-velocity oxygen-fuel spraying of mechanically activated powders, a layer with thickness of 1 mm (Fig. 2) is formed, it has a minimum amount of pores (less than 1%). The adhesion strength to the substrate layer increases (110-120 MPa).

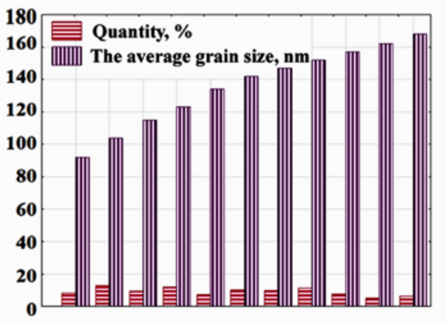
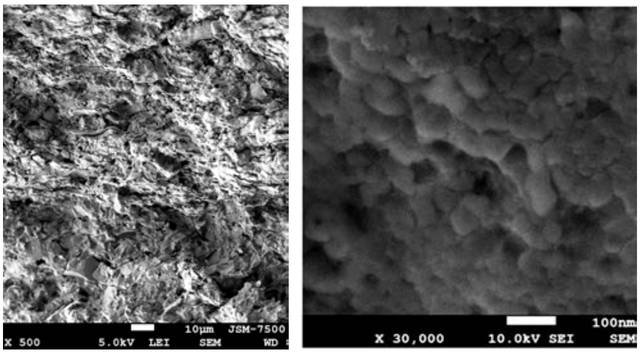


***Fig. 2.** The quantitative distribution of the grain size and their percentage in the TiNiHf layer*

Structure of a sprayed TiNiHf layer has extremely low etchability with conventional reagents, largely due to the strong grain refinement as a result of high-velocity heating, rapid cooling, and significant strain (Fig. 3); that provides specific structural effects. Due to characteristics of high-velocity oxy-fuel spraying of mechanically activated powder (high cooling rate and rapid hardening of the layer), during spraying in the cross-section of the TiNiHf layer there are no distinct columnar dendrites, the structure can be described as a nanocrystalline with grain size of 50-90 nm. Microhardness of TiNiHf layer varies $H_\mu = 9{,}7 \div 12{,}6$ GPa.



a) b)

Fig. 3. *Nanostructured TiNiHf layer formed by high-velocity oxy-fuel spraying of mechanically activated powder in a protective atmosphere: thickness - 1 mm, × 500 - a), × 30000 - b)*

3. A theoretical estimation of durability

To evaluate the durability we used an option of energy model of damage accumulation in the surface-doped material for the two-component alloys, proposed by the following authors [20,21]. Models of [20,21] are reduced to the fact that for the destruction of the material, it is necessary to spend a part of the value of the irreversible deformation work. Only a certain amount of irreversible deformation work is spent for the accumulation of damage. To establish this amount, which depends on the heat transfer conditions, the degree of deformation, etc. we must refer to physical or mechanical experiments.

The energy spent in the crystal lattice distortion is determined from the expression [21]:

$$H = \int c_p \cdot dT \tag{1}$$

where c_p – specific heat capacity, J / kg·K;
T – temperature, K;
T_{tm} – temperature of melting onset, K.

The limit energy (energy intensity), absorbed by the body, located at T, when melting, is determined from the expression:

$$Q = \int_{T}^{T_{tm}} c_p \cdot dT + L_{tm} \; , \tag{2}$$

where L_{tm} – latent heat of fusion.

The theoretical strength is determined by the formula [21]:

$$\sigma_{teor} = \sqrt{E \cdot Q} \; , \tag{3}$$

where E – Young's modulus, MPa.

Latent fusion heat is determined from the equation [21]:

$$L_{tm} = \Delta S_{tm} \cdot T_{tm} \; , \tag{4}$$

where ΔS_{tm} – change in entropy of the body when it is melting.

Entropy of the melting is determined by the expression [21]:

$$\Delta S_{tm} = A_1 \cdot \Delta S_1 + A_2 \cdot \Delta S_2 \; , \tag{5}$$

According to the formula of the Neumann-Conn, heat capacity of alloys with shape memory effect is calculated using the formula [10]:

$$c_p = A_1 \cdot c_{p1} + A_2 \cdot c_{p2} \; , \tag{6}$$

where c_p^1 и c_p^2 – the specific heat of the component alloy.

We carried out the calculation of energy consumption and the theoretical strength of the multi-component SME material TiNiHf, obtained by high-velocity oxygen-fuel spraying in a protective atmosphere (argon). Calculation of entropy and heat capacity was performed for each of the phases (Figure 4), included in the composite SME layer TiNiHf, according to formulas (5) and (6). Further calculation was made according to the formulas (1), (2), (3) and (4).

The results of X-ray analysis showed that at room temperature, the initial phase state of TiNiHf layer after a high-velocity oxygen-fuel spraying of mechanically activated powder is an austenitic TiNi B2 phases with a cubic lattice, martensite TiNi phases B19' with monoclinic lattice, intermetallic phases Ti_2Ni with a cubic lattice, HfNi phase with orthorhombic lattice, $HfNi_3$ phase with rhombohedral lattice, Hf0.24NiTi0.76 phase with a cubic lattice, we also observed a small amount of titanium oxide TiO, less than 3% (Fig. 4).

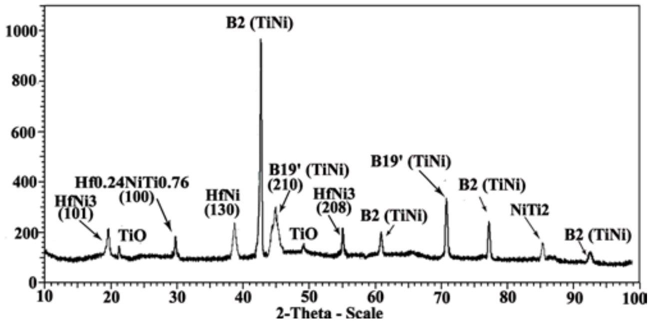


Fig. 4. *X-ray analysis of the TiNiHf alloy, after a high-velocity oxygen-fuel spraying with a local protection in argon atmosphere*

For phases TiNi, HfNi, Ti_2Ni, $HfNi_3$, Hf0.24NiTi0.76, TiO we counted (the energy of H, spent on the distortion of the crystal lattice; the ultimate energy Q, the energy absorbed by the body located at T, when it melts; σ_{teor} theoretical strength). Thus, the energy of H, spent on distortion of the phase crystal lattice Ni3Hf is equal to 23.9 MJ / kg; ultimate energy Q, the energy absorbed by the body is equal to 29.7 MJ / mol; σ_{teor} theoretical strength is 16,08GPa. We determined target values H, Q, σ_{teor} for all phases components and on the basis of statistical processing, we compiled the following equation:

- maximum Q, the energy absorbed by the body at the temperature T at its melting

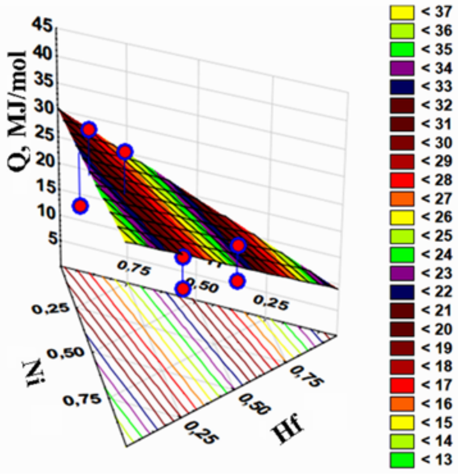
$$Q = 37{,}0238 \cdot Ni + 9{,}1063 \cdot Hf + 30{,}3113 \cdot Ti \quad (MJ / mol), \tag{7}$$

- theoretical strength σ_{teor} is described by the equation

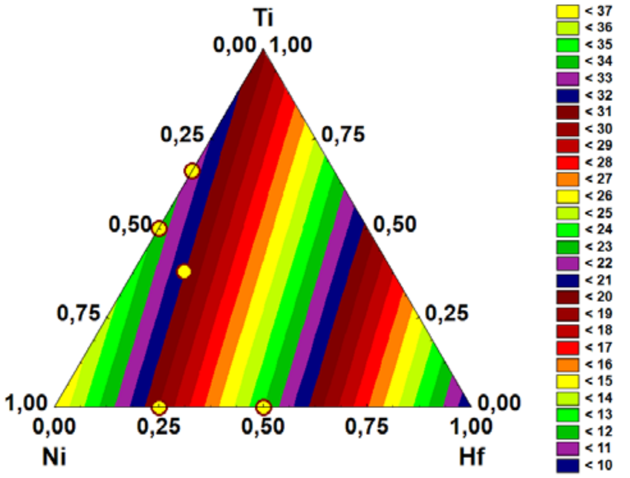
$$\sigma_{teor} = -23{,}9847 + 5{,}3837 \cdot Q - 3{,}3905 \cdot H - 0{,}1314 \cdot Q^2 + 0{,}0833 \cdot Q \cdot H + 0{,}0314 \cdot H^2, \tag{8}$$

where Ni, Hf, Ti – the percentage of SME in TiNiHf (at.%).

Fig. 5 shows the power consumption of system Ti-Ni-Hf alloys (a, b). Fig. 5 shows that power consumption value for the alloy system Ti-Ni-Hf, Ti-Ni-Zr with SME slightly differs from other connections of the system.



a)



b)

__Fig. 5.__ Power consumption of system Ti-Ni-Hf: three-dimensional (a) and two-dimensional model (b)

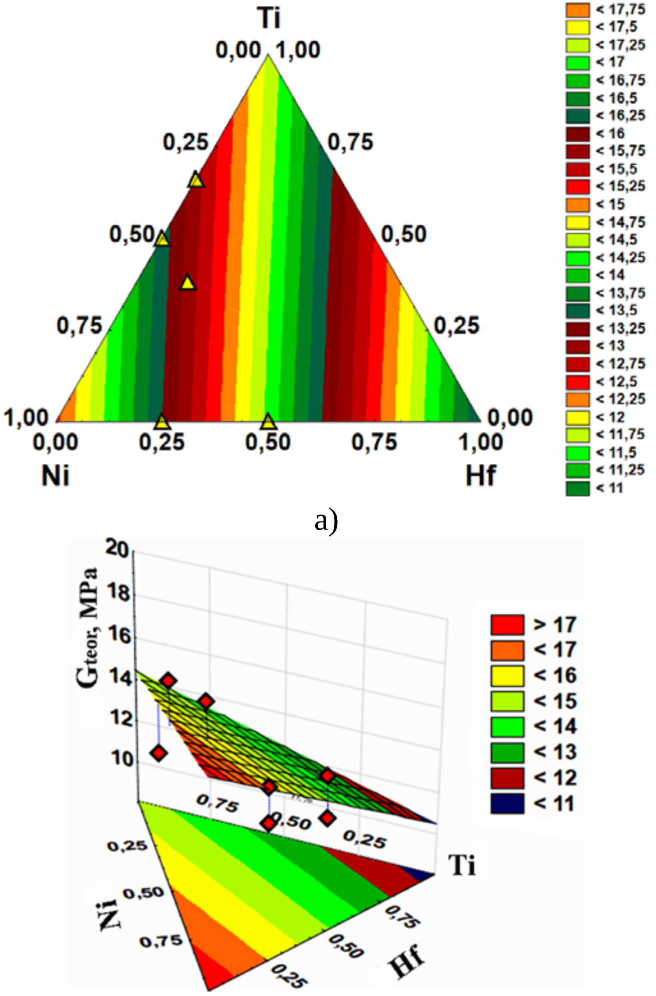
As a result of statistical processing of the calculated data, the limit energy Q, absorbed by the body located at temperature T when it melts is described by the equation

- for the layer Ti-Ni-Hf

$$Q = 37{,}0238\cdot Ni + 9{,}1063\cdot Hf + 30{,}3113\cdot Ti \quad (MJ/mol), \tag{9}$$

where Ni, Hf, Ti – the percentage of cells with SME, (at.%).

Fig. 6 shows a model for calculating the theoretical strength of the alloy system Ti-Ni-Hf.



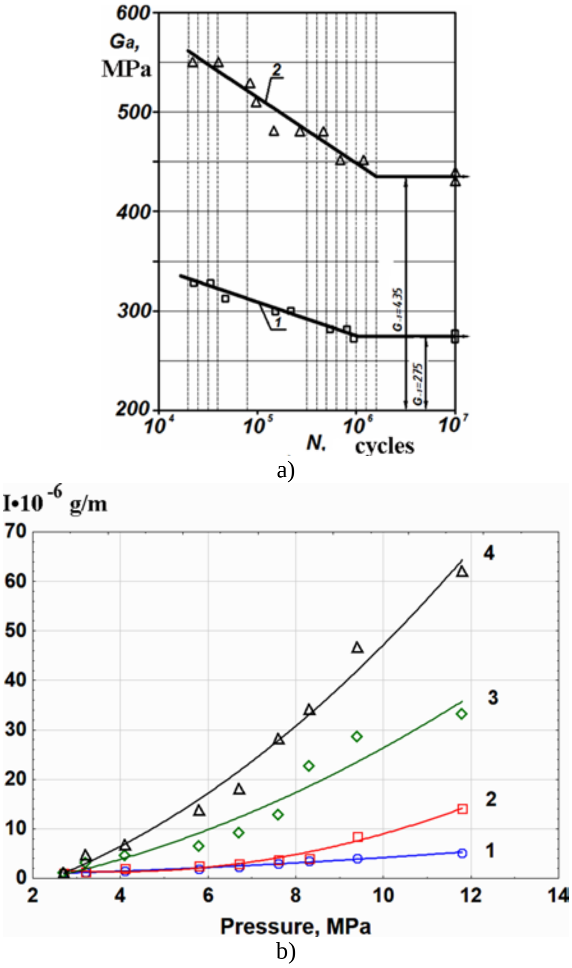
a)

b)

__Fig. 6.__ The theoretical strength of the systems Ti-Ni-Hf: a two-dimensional (a) and the three-dimensional model (b)

4. The performance properties of the layers with shape memory alloy TiNiHf

In this paper, as showed the steel samples tests (steel 1045 + layer TiNiHf), on high cycle fatigue in bending with rotation, we can see increase in durability (Fig. 7) endurance limit (σ_{-1}) of steel 1045 without coating was 275 MPa, and after the surface modification with shape memory alloy TiNiHf - 435 MPa (increased by 36.8%). During the wear test of the samples with a surface layer TiNiHf, we observed increase in the surface temperature in the friction zone, causing austenite-martensite transformation. Large pressures, occuring at friction, cause the effect of transformation plasticity, due to the formation of martensite stress. The combination of these processes determines the durability of the sample. Improved wear resistance after full processing cycle is due to the considerable reversible plastic deformations (2.2%). Experience shows that the higher the reversible deformations, the higher the wear resistance. Increased wear resistance of steel 1045 with a surface SME layer TiNiHf is 2.6 times than that compared to steel 1045 (Fig. 7 b).



a)

b)

***Fig. 7.** Cycle fatigue curves of steel 1045: no cover (1), after surface modification with shape memory alloy TiNiHf (2) - a); dependance of wear intensity I of TiNiHf layer from P drive pressure at the disk sliding speed of 0.5 m / s-1; 1 m / s -2; 1.5 m / -3; 2 m / s -4 - b)*

Increase of samples durability with nanostructured surface layer TiNiHf is explained both by features of nanostructured materials destruction, which is the slowdown in destruction at the grain boundaries, and movement obstruction cracks branching due to borders hardening, and by the pseudoelasticity of TiNiHf surface layer, inherent to materials with shape memory effect. Accumulated deformation by the surface layer is capable of recovering during cyclic loading and, thus, does not accumulate in the material, which increases its durability.

5. Summary

Complex formation method of a surface-modified layers using shape memory materials, which includes a high-velocity oxygen-fual spraying of mechanically activated powders based on TiNiHf, subsequent thermal and thermomechanical treatment allowed to form the nanoscale state in the surface layers, which have elevated level of functional, mechanical and performance properties. It is shown that preliminary mechanical activation of TiNiHf powder has reduced coatings porosity (less then 1%) and provided a bonding strength of the coating with the base (110-120 MPa). After the high-velocity oxygen-fual spraying in protective atmosphere of mechanically activated powder with shape memory efect based on TiNiHf, the cyclic durability under multi-cycle fatigue has increased by ~ 37% and the wear resistance - by 2.6 times, compared with steel 1045.

On the basis of complex metallophysical studies, surface-modified layers (electron microscopy, spectroscopy, X-ray diffraction, calorimetry, durometer analysis), we obtained new data on nanoscale composition within the surface-modified layer, on its mechanical properties, phase composition, which determines functional properties. This allows us to find ways of their purposeful formation for different operating conditions. On the basis of experimental data of X-ray analysis of the TiNiHf alloy, we calculated energy consumption, the theoretical strength. As a result of the simulation, we constructed generalized diagrams of energy intensity and theoretical strength of the ternary alloy Ti-Ni-Hf and compiled their relationship equation.

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