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FORMATION OF NANOSTRUCTURED SURFACE LAYERS OF A MATERIAL WITH TiNi-BASED SHAPE MEMORY BY DIFFUSION METALLIZATION

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Abstract- Results of research on the formation of the surface layers of a material with shape memory effect (SME) based on TiNi diffusion metallization in molten Pb-Bi under isothermal conditions in an argon atmosphere are presented. It is shown that this method allows obtaining of uniform surface layers in nanostructured state of internal surfaces on the articles of complex shapes with stress concentrators. Structure, chemical and phase composition of the surface layers provide a manifestation of TiNi shape memory. The average grain size of TiNi coatings ranges between 60 ÷ 160 nm.

Keywords— Diffusion metallization, Nikelid titanium surface layers, Shape memory effect

I. INTRODUCTION

Results of, research on the development of nanostructured metals and alloys for industrial purposes and modifications of their surface gained in recent years strongly suggests the feasibility of nanostructuring for dramatical improvement of the mechanical properties [1]. One of the priority directions of development of materials and technologies is the creation of intelligent, adaptive materials and coatings, which include materials with shape memory effect (SME Currently the technology of surface modification of materials with shape memory based on TiNi, NiAl, TiNiCu for products of engineering purposes, using TIG and laser welding, plasma and high-speed flame spraying [2,3] has been already developed They ensure the formation of fine-grained structure with a porosity of up to nanoscale 5%, and the adhesive strength of 50-60 MPa. Chemical and phase composition of the formed coatings provides functional properties of materials with shape memory. The studies of functional and mechanical properties of materials with surface-modified layer in the conditions of low-and multicycle, friction-mechanical loading, exposure to active media showed their appropriateness for use [4].

However, we have developed technology of modifying by materials with shape memory which allow to create a cover only for the outer surface of products. One purpose of coatings on the technology of forming products of various configurations, both on the outer and on the inner surface of almost any chemical composition is metallization diffusion technique melt of fusible metal [5]. Taking into account the potential of this technology in the formation of multi- layered coatings and the creation of composite structures, including the use of materials with shape memory effect it is possible to expect an extension of their practical use.

The purpose of this research is to study the regularities of formation of nanostructured surface layers of a material with TiNi-based shape memory by diffusion saturation from the melt of fusible metals, the study of their phase-structural state and functional-mechanical behavior.

II. TECHNOLOGY OF FORMATION OF NANOSTRUCTURE SURFACE LAYERS AND METHODS OF INVESTIGATION

Formation of TiNi surface layer was produced by diffusion metallization of the fusible metal melt under isothermal conditions in an argon atmosphere at a temperature of 1100 ÷ 1150°C. The driving force of the process is the difference in concentration of alloying elements on the surface of the workpiece and in the transport melt. Process of diffusion metallization was carried out in a modernized technological complex (patent number 2430191), which allows to form a coating on the technology described in the [6] and produce surface plastic deformation of the workpiece (Fig. 1) in a single process cycle.

The melt of lead or eutectic Pb-Bi, which elements are in saturating atomic state directly contacted with the surface of the work pieces was used as a transport medium. These melts activate product surface purified it from oxide films by providing a high wettability, which in its turn provides good adhesion. Dissolved in the melt Ti and Ni powders adsorbed onto the surface of the part, and then diffuse into the surface

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of the volume. Cementation process was carried out cyclically with lifting products from melt every 40-50 minutes. Duration of saturation process was 8-10 hours depending on the desired coating thickness.

Development of the technology was performed on samples from steel A107, 10 mm in diameter. The material used for the surface modification was NiTi powder brand PN55T45 (Scientific and Production Association "Tulachermet"). Before saturation the powder was subjected to mechanical activation in the ball mill GEFEST 2. The particle size of the powder is 0.1-20 microns.

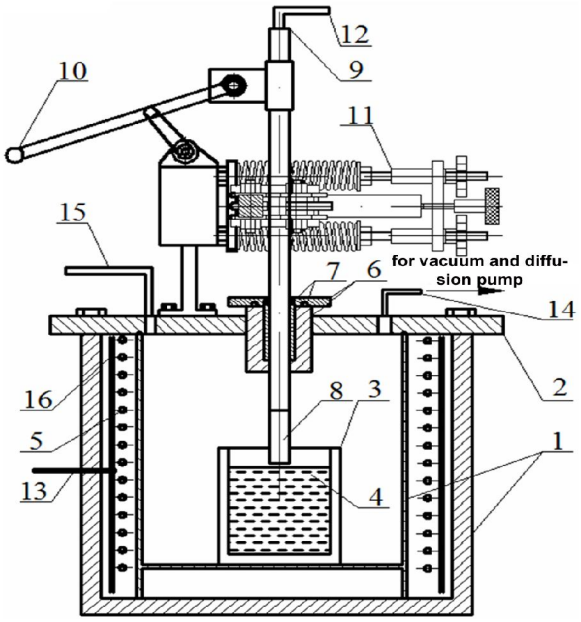


Fig.1. Technological complex for the formation of coatings: 1 - the case of the vacuum chamber, 2 – cover, 3 - metal flask, 4 - liquid metal melt, 5 - heating elements, 6 – gea, 7 - clamping unit, 8 – workpiece, 9-tube, 10 – arm, 11 device for surface plastic deformation, 12 - pipe for coolant, 13 – temperature, 14 - vent pipe, 15-tube for supplying argon, 16 - heat shields

To ensure the necessary level of reactive stresses and reversible deformation defining form restoration of surface layers of alloys with shape memory effect surface plastic deformation (SPD) was carried out by run- in three roller device (running modes Pk = 5 kN, $V_{ob} = 90 \cdot 10^{-3}$ m / s, S_{pr} = 0. surface layers of alloys with shape memory effect , produced surface plastic deformation (7 mm / rev number of passages 5). A final operation of surface modification process is thermal cycling in the temperature range of martensitic transformation of TiNi: M_f = 12 °C, M_s = 86 °C, of A_s =88 °C , A_f = 121 °C (cooling to the martensitic transformation temperature, followed by heating to temperatures of Reverse martensitic transformation, 10 cycles).

Microhardness measurements were performed on a PMT-3. Structure and phase composition of the surface layer were examined by X-ray diffraction and light microscopy. XRD analysis was performed on a Shimadzu XRD - 7000 Cu-Ka radiation. Investigation of the structure was also performed on a scanning electron microscope of ultrahigh resolution JSM-7500F.

III. RESULTS AND DISCUSSION

Since the formation of the surface layers of materials with shape memory effect under isothermal conditions, based on the principle of concentration of mass transfer is multifactorial, for developing of the technology algorithmic design of experiments was used. The main parameters determining the functional and mechanical properties of the coatings are: adhesion, structure and phase composition. A preliminary analysis showed that the main process parameters that affect the structure and quality of coverage include: temperature, time of diffusion saturation, the number of cycles "tripping" the product into the melt, the chemical composition of the low-melting melt composition of the inert medium. For spectrally pure argon in the formation of coatings with SME used apparatus for individual and continuous purification of argon [7] was used.

Some of these parameters (composition of the melt and transport of inert atmosphere, the number of cycles) are made on the base of experimental studies [6]. Based on the statistical analysis of experimental data to test the technology diffusion saturation the influence of time and temperature on the thickness of the coating process TiNi (1) (Fig. 2) was determined.

$$\delta = -419{,}131+0{,}728\cdot T+21{,}595\cdot t-0{,}0003\cdot T^2+0{,}004\cdot T\cdot t- -1{,}166\cdot t^2 \quad (1)$$

where T - temperature of the melt, °C; t - time of exposure in the melt, hour.

The resulting statistical model allows to manage the process of coating formation and to optimize its parameters.

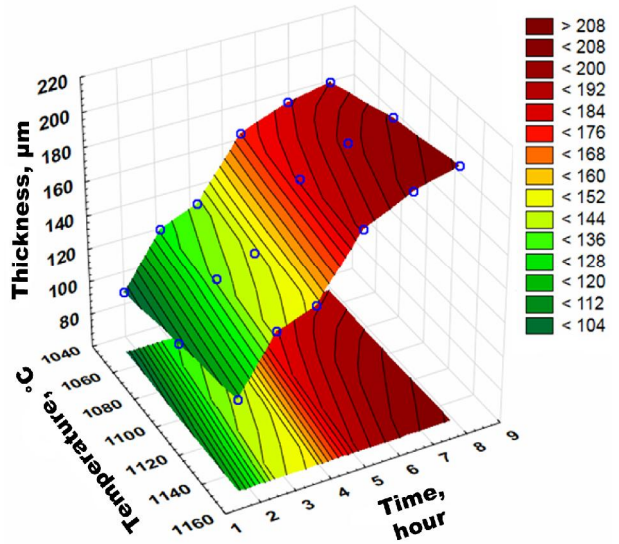


Fig. 2. Effect of time and temperature of the process of diffusion saturation on a coating thickness TiNi

Macroanalysis of the surface layers of alloys TiNi, received by a well-established technology, showed that the structure of the coating has a small transition zone of 10-20 m (Fig. 3), on the border of coating-base there are no visible defects (Fig. 4). Microhardness of the surface layer varies in thickness of TiNi layer within H_μ = 7.0 ÷ 10.5 GPa.

The results of X-ray analysis showed that at room temperature coating TiNi, obtained by diffusion saturation of the melt consists of austenitic B2 phase with a cubic lattice (≈ 72-73%), the martensitic phase B19' monoclinic lattice (≈ 24-25%), Ni_3Ti (≈ 0,5-1,0%) and Ti_2Ni (≈ 0,5-1,0%) (Table 1).

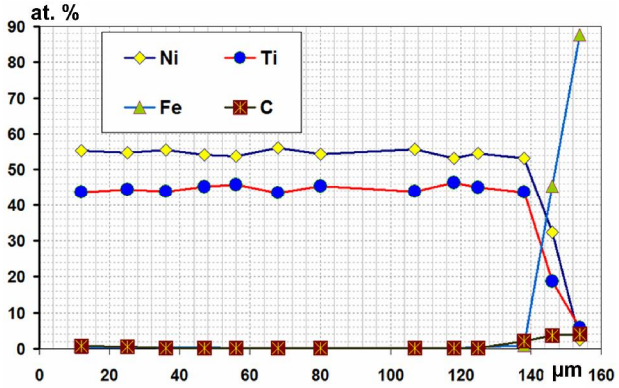


Fig. 3. The distribution of chemical elements in the surface layer of TiNi: retention time is 4 h, the temperature is 1100°C.

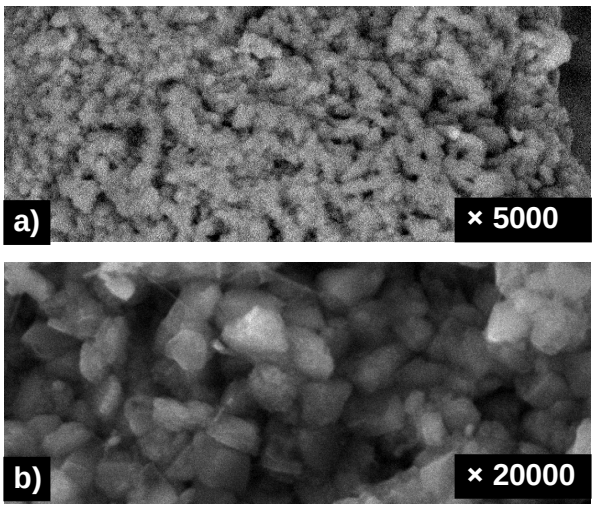


Fig. 4. The microstructure of the surface layer of TiNi phase B2):
× 5,000 s); × 20000 - b)

TABLE 1.
THE PHASE COMPOSITION OF THE COATING TINI

Phase	a, нм	$V_{яч} \cdot 10^3$	b, нм	c, нм	β, degree
B2 (cubic)	0,3015	27,41	-	-	-
B19' (monoclinic)	0,2886	54,84	0,4133	0,463	96,8
Ti_2Ni (cubic)	1,1278	143,45	-	-	-
Ni_3Ti (hexagonal)	0,5092	18,63	-	0,829	-

In previous studies [8] it is shown that the hardening phase Ni_3Ti with a hexagonal lattice has a needle or cellular morphology. To ensure shape memory effect in the alloy of TiNi it should not exceed 10-15%. The presence of this phase is due to the difference in the coefficients of diffusion of Ni and Ti, so their interaction with intermetallics compound is formed with a large content of easily diffusible element. Phase Ni_3Ti, $NiTi_2$ are distinguished in the process of crystallization and are arranged along the grain boundaries , and for their elimination a homogenizing annealing is conducted under an inert atmosphere (vacuum) at the temperature of 800-1000 ° C for 1 -2h. The presence of the structure of the phase Ni_3Ti, $NiTi_2$ (size 15-40 nm) of the particle results in a decrease in the temperature range of martensitic transformation of B2 → B19 '. Fig. 5a shows the needle structure of monoclinic phase B19 'TiNi, and Fig. 5b shows the electron diffraction pattern of TiNi, covering consisting of randomly disoriented nanoscale grains.

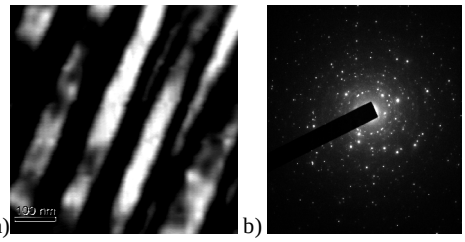
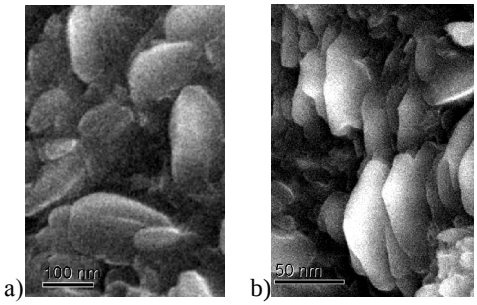


Fig. 5. The structure of the martensite phase B19', × 120 000 - a); × 150 000 - b); electron diffraction layer TiNi

Metallographic analysis revealed that the TiNi surface layer structure, obtained by diffusive saturation has extremely weak etchable conventional reagents due to the strong grinding of grains. Study the microstructure of the TiNi surface layer on scanning and transmission electron microscopy of high resolution showed that TiNi coating has nano-sized structure with a grain size of 65-160 nm (Fig. 5c).

The final stage of the process of formation of the TiNi surface layer is SPD tested in the temperature range of martensitic transformations M_s-M_f. As a result, SPD grinding grain size and more uniform distribution on the depth of the layer occurs, a homogeneous nanoscale layer directionally oriented structure TiNi 60-140 nm (Fig. 6a , b) is made.



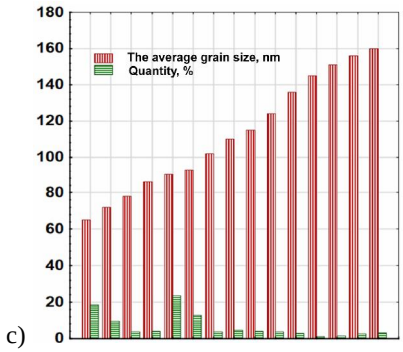


Fig. 6. Structure of the coating after complete processing cycle, including PPD - a, b); distribution of grains in the coating TiNi and their percentage - c)

To assess the functional and mechanical properties of the surface layers of TiNi, obtained by diffusion metallization from melt Pb-Bi the reversible strain (Fig.7 have been determined and the investigations of wear resistance of the coating were made. The maximum value of the reversible strain is 3.9%.

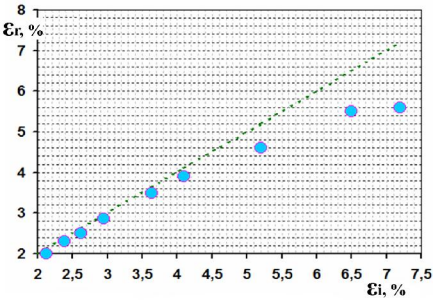


Fig. 7. Dependence of the reversible strain induced deformation of ε_O ε_N TiNi layer after complete processing cycle

Evaluation of wear resistance of the surface layers was carried out at TiNi was performed at dry friction of the coated sample of the hard disk rotating at 2070 SMT-1 testing machine at a speed of disk rotation v= 0,5÷2 m/s and the pressure P=2÷12 MPa, with the registration of temperature in the contact zone. Evaluation of the wear rate was made on the basis of experimental data using the application package Statistica v6.0 environment SPSS (Fig. 8).

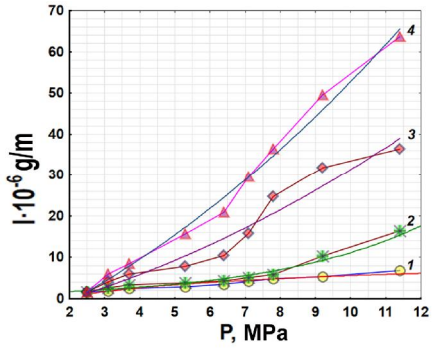


Fig. 8. The dependence of the wear rate I of the pressure disk P: disk sliding speed of 0.5 m/s -1, 1 m/s -2, 1.5m/s -3, 2 m/s -4

The obtained dependences are described by equations of the general form:

$$I = 4{,}049 - 0{,}3101 \cdot T + 1{,}8 \cdot P + 0{,}008 \cdot T^2 - 0{,}09 \cdot T \cdot P + 0{,}301 \cdot P^2 \quad (2)$$

where I - intensity of wear, P - pressure disk, T-temperature in the friction zone.

The results showed that an increase in wear resistance after diffusion metallization of steel A107 TiNi was (~ 50-80%), as a result of the full cycle of thermomechanical processing 2-3. This is explained by the fact that the nanostructured surface layer having a significant SME (3.9%), blocks the penetration of surface microcracks in the depth in development of material deformation martensite in the process of loading.

IV.CONCLUSION

The developed technology of diffusion metallization of steel in the melt of fusible metals allowed to form a nanostructured surface layers of TiNi, chemical and phase composition of which corresponds to the manifestation of SME (3.9%), offers improved performance and mechanical properties of products: adhesive strength due to diffusion bonding coating-base, microhardness (10.5 GPa), durability under conditions of friction (2-3 times). These results confirm the usefulness of the surface modification of TiNi for durability and extend the functionality of machinery products of complex shape with stress concentrators and give reason to believe that the use of multi-component for the surface modification of materials with shape memory effect will enhance prospects for their practical use in providing of resource.

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