Conference Paper

Methods of Research of Shape Memory Effect and Superelasticity in the Alloy Ti-22%Nb-6%Zr

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ANNOTATION

Cyclic tensile tests were carried out as applied to annealed foils of the superelastic Ti-22Nb-6Zr alloy (at.%) as well as indentation of these foils with an increasing amplitude of indenter intrusion in the sample at temperatures lowering from 20° down to -60-70°C. Mechanical tests were performed on samples cut along and across the rolling direction. According to the results of measurements of mechanical properties, it is established that during cyclic stretching of foils in the rolling direction, superelasticity manifests itself, and also material training is observed with subsequent preservation of the maximal renewable deformation. When the foil is loaded in the transverse direction, no superelasticity is observed, moreover, some samples are destroyed even with a deformation of 2%. With a decrease in the annealing temperature of foils, the curve of the continuous change of loading with the depth of indenter penetration undergoes substantial changes, which indicate the appearance of a superelastic deformation under the indenter. Curves of monotonic loading and discharge undergo an inflection, and the plastic deformation region is substantially reduced. From the discharge curves in this case, we can calculate two elastic modules, typical for the usual elasticity and superelastic behavior of the alloy. In general, the main characteristics of the continuous indentation curve depend on the amount of the martensitic phase. The dependence of the modules of elasticity for foils, cooling down to -(60-70°C), and for their subsequent heating up to the room temperature is constructed.

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1. INTRODUCTION

One of the basic requirements for modern materials is working capacity under various operating conditions. Most metals and alloys require not only high mechanical characteristics, but also the ability to change their properties during operation. These materials include newly developed titanium alloys, which are characterized with shape memory effect and superelasticity.

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The effects of shape memory (SME) and superelasticity in metals and alloys have not only the scientific significance, but also the great practical importance, their application provides the solution of a number of complex technical problems. Alloys with shape memory show low values of the modulus of elasticity, close to the value of the module for bone tissue, especially for Ti-Ni alloys. This fact led to its wide application in medicine. However, the toxic properties of nickel limit its further use, since it causes Ni-hypersensitivity and allergy. At present, the most promising alloys for medical use are Ti-Nb-Zr-based alloys, characterized by high biological compatibility, corrosion resistance, low modulus of elasticity and superelasticity [1-5].

Martensitic transformations, conjugated with an SME, with the deformation and the restoration of the shape of the product, are very sensitive to the distribution of residual microstresses and crystallographic texture existing in the product [6]. Thus, the textural features of articles determine the anisotropy of the properties of the material, especially mechanical properties, such as hardness and elastic modulus. Accounting of these factors is necessary to improve the efficiency of the use of superelastic alloys in various industries. The purpose of this work was to identify the limits of variation in the properties of superelastic alloys based on titanium and zirconium and the possibilities of controlling them by changing the crystallographic texture during deformation and subsequent annealing.

2. SAMPLES AND METHODS FOR THEIR STUDY

The work was performed by Ti-22Nb-6Zr alloy (at.%) (hereinafter TNZ), characterized by the maximal reversible deformation in the system of Ti-Nb-Zr alloys. Samples for the study were smelted in an electric arc furnace "MEPhI 9", in an argon atmosphere. Further, they were homogenized in a vacuum oven at a temperature of 1100°C for 3 hours. After annealing, hardening was carried out in water to fix the β-structure, followed by hot forging to reduce the grain size. Further deformation was carried out by cold rolling (up to 90-95%) in a laboratory rolling mill with a roll diameter of 5 cm.

The properties of deformed samples as well as those annealed at temperatures of 550, 600, 650°C for half an hour were studied, followed by quenching into water to fix the β phase. According to the data of [7], this regime of thermomechanical processing corresponds to the formation in the alloy of a nanosubstructure with a subgrain size of less than 100 nm. Holding at 600°C for half an hour leads to the manifestation of the best functional fatigue life of the alloy [8]. It was noted in [9] that during the tests of the Ti-Nb–Zr alloy, a partial superelasticity manifests itself in the first cycle, especially after annealing, which leads to the formation of a fine-grained, recrystallized structure in the β-phase (600, 750°C).

X-ray analysis of the structural state of foils, including determination of phase composition, an evaluation of the structure perfection by means of the X-ray line profile analysis, texture estimation, was carried out using X-ray diffractometers DRON-3, DRON-3M and D8 Discover with the copper radiation anode. The texture was analyzed in terms of the direct pole figures {110}, {100}, {112} and {111} recorded by reflections (110), (200), (112) and (222), respectively, using the standard tilt method [10, 11].

Mechanical tests were carried out on a digital nanoscale device DNT-1/5 using the developed device, which allows to change the temperature of the test sample during testing with its simultaneous registration. The versatile electromechanical machine Instron 5966 (P_{max} = 10 kN) is used for cyclic testing of specimens when they are loaded along and across the rolling direction.

3. THE RESULTS OF THE STUDY OF THE STRUCTURAL STATE OF THE SAMPLES

The characteristic fragments of the diffraction spectra of the investigated samples are shown in Fig. 1, in which the reflection indices for α- (underlined figures) and β-phases. The α-phase is a hexagonal close-packed (HCP) structure, and the β-phase is a body-centered cubic (BCC) structure. According to the spectra shown in Fig. 1, the rolled foil consists of a single β-phase and is characterized by wide X-ray reflections, which is caused by the presence of a large number of defects in the hardened material. As a result of annealing in the temperature range 550-650°C, the crystal structure of the deformed foil is improved, as evidenced by a decrease in the width of the X-ray lines. Annealing of foils at temperatures of 550 and 600°C followed by rapid quenching made it possible to fix the α-phase in the alloy, while in the foils annealed at 650°C, the α-phase is absent (Fig. 1-d).

Fig. 2 shows the change in the direct pole figures (DPF) {110} and {100} of rolled foils from the TNZ alloy as a result of their annealing at a temperature of 600°C. Abbreviations are used in Fig. 2: RD is the foil rolling direction, TD and ND - the transverse and normal direction in the foil.

At the rolling of foil to a deformation degree of 95.3%, a two-component crystallographic texture was formed, characteristic for the BCC structure and, consequently, for the β-phase of titanium. In the rolled TNZ alloy, the rolling texture is described by two components: {100} <110>, {112} <110>, the first of which is basic. After annealing at 550 and 600°C in the TNZ alloy, the α-phase is detected and the enhancement of

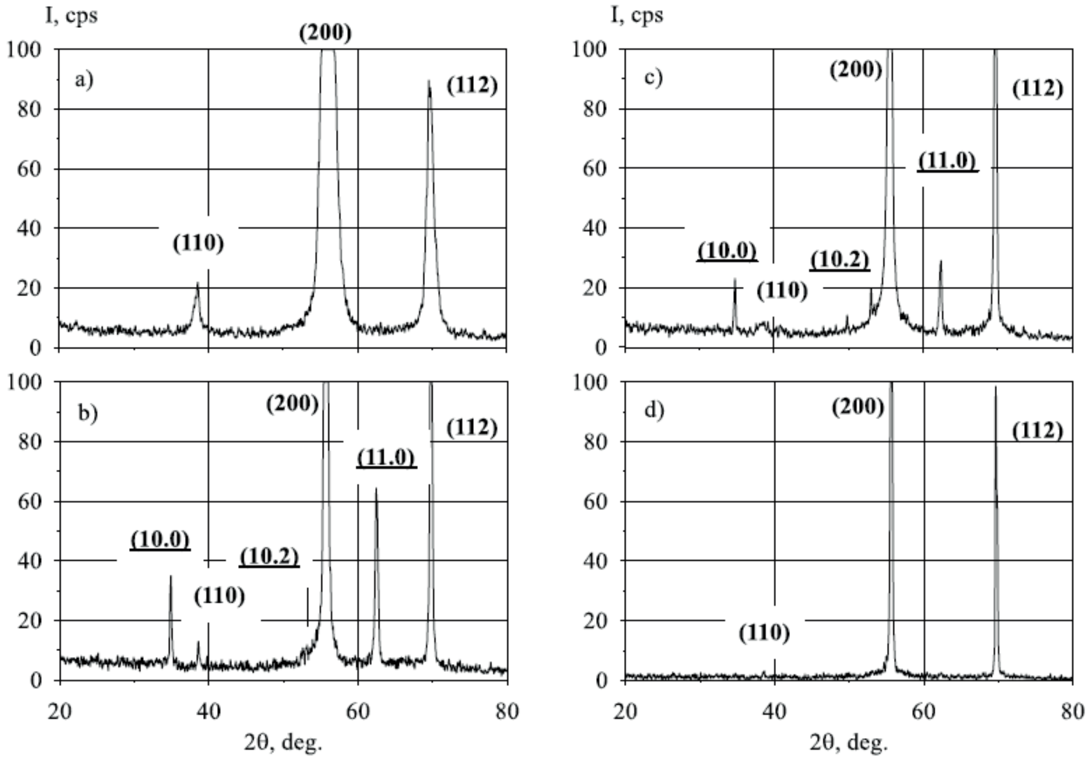

Figure 1: Change of diffraction spectra of rolled foils (a) as a result of their annealing for 0.5 h at temperatures: b – 550°C; c – 600°C; d – 650°C.

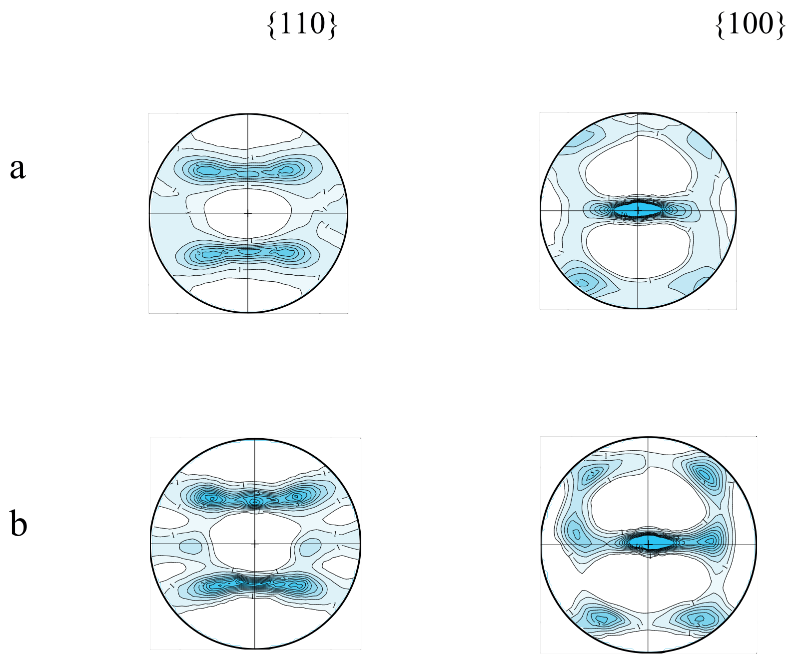

Figure 2: Change in the straight pole figures {110}, {100} of the rolled TNZ foil (ε = 95. 3%) (a) as a result of annealing at 600°C for 0.5 h (b).

the additional texture component {112} <110> is observed in comparison with the main {100} <110>. According to the literature data [12], the growth of the component {112} <110> indicates the occurrence of recrystallization in the materials with BCC structure. Strengthening the texture of recrystallization leads to an increase in the pole density at the diameter of the ND-TD of PPF {100} at a distance of 35° from the ND. From the data obtained, it follows that the recrystallization texture associated with increased component with {112} plane, is most pronounced in the case of annealing of TNZ alloy at temperature 600 °C.

4. STUDY OF SUPERLASTIC PROPERTIES BY CYCLIC TENSILE TESTS

With the purpose of revealing the superelastic properties of the investigated alloys, cyclic "loading-unloading" tests were carried out. Change of the strain diagram form, i.e. the manifestation of partial superelasticity, indicates the passing of the martensitic transformation under load [8]. Namely such cyclic tests with 5-10 loading cycles show the presence or absence of the superelasticity in the material.

Cyclic tests were carried out as follows: the sample was stretched to 2.5% deformation, followed by complete removal of the load. After the sample was completely unloaded, it was stretched again. This cycling was carried out 5 times. Mechanical tests were performed on samples cut along (RD) and across the rolling direction (TD). Typical curves of stress-strain diagrams of superelastic samples are shown in Fig. 3.

From the shown diagrams, it can be seen, that the samples cut out along and across RD behave differently. That is, the anisotropy of properties is manifested due to the texture features of the material (different values of reversible deformation in different crystallographic directions).

It should be noted that with each subsequent cycle of "load-unloading", the restoration of the form is increasingly approaching the initial value (the residual deformation tends to zero), that is, the material "trains". The appearance of plasticity at the first stages of stretching the samples along RD may be due to the reorientation of the grains with initial orientation corresponding to the component {111} <112>, which were at the beginning of the test in an orientation unstable with respect to the acting load. These grains are forced to entrust until the coincidence of <110> with the direction of stretching. This component is stable in the case of deformation along RD, which coincides with the original direction of extension.

From the diagrams obtained for various samples, it can be concluded, that the TNZ alloy has superelastic properties after annealing at temperatures of 600 and 650°C for 0.5 h, since the samples completely restore their original shape after the load is

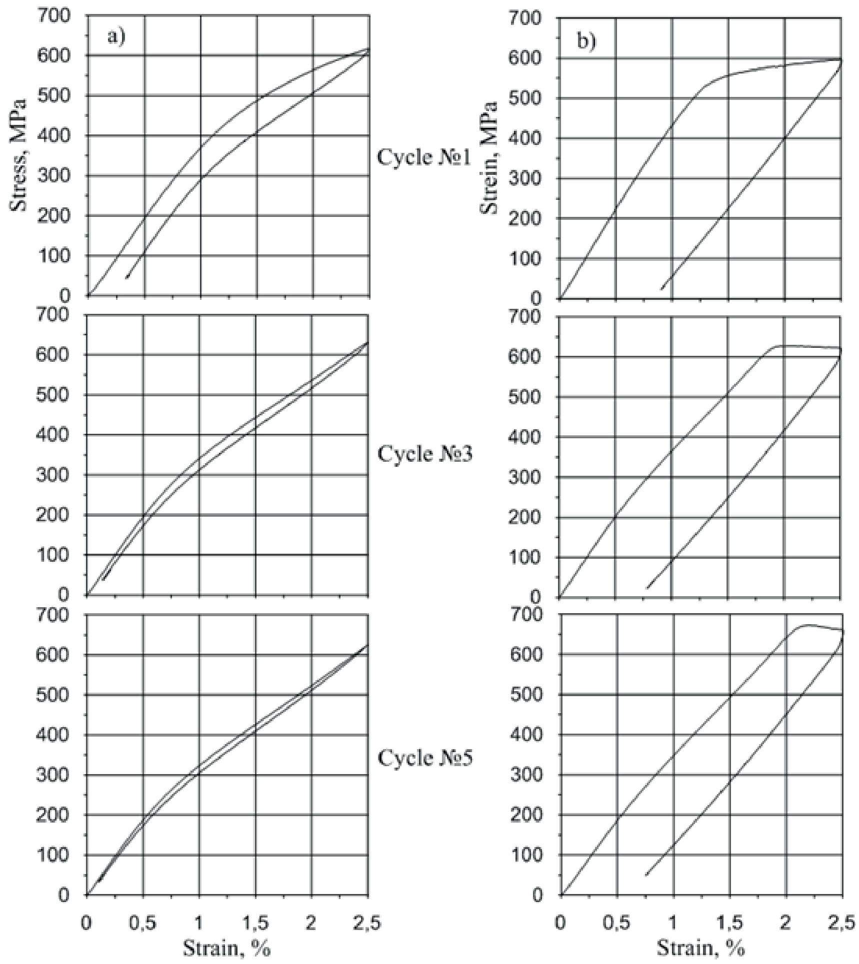

Figure 3: Change in the shape of the stress-strain diagram after cyclic tensile testing of foils made of TNZ alloy annealed at 650°C for 0.5 h, along (a) and across (b) RD.

removed. The most stable superelasticity appears in this alloy after annealing at 650°C, which is probably due to the absence of the α-phase.

After annealing at 550°C, the manifestation of superelasticity is not observed after 0.5 h. The sample does not restore the original shape. Moreover, a sample cut across RD has collapsed during the second loading cycle.

The diffractogram of the "trained sample" (Fig. 4), i.e. after cyclic tests, indicates the appearance of an additional orthorhombic phase in it, which evidences the realization of the superelastic effect by martensitic transformations of the BCC ↔ face-centered orthorhombic structure.

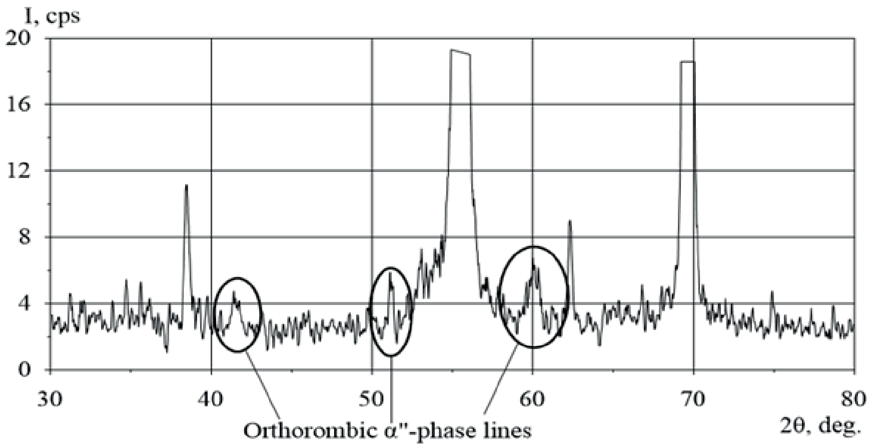

Figure 4: Diffraction spectrum taken from the sample after cyclic tests.

5. THE STUDY OF SUPERLASTIC PRIPERTIES BY THE METHOD OF LOW-TEMPERATURE INDENTATION

Fig. 5 shows the continuous indentation curves recorded at a constant load for different test temperatures.

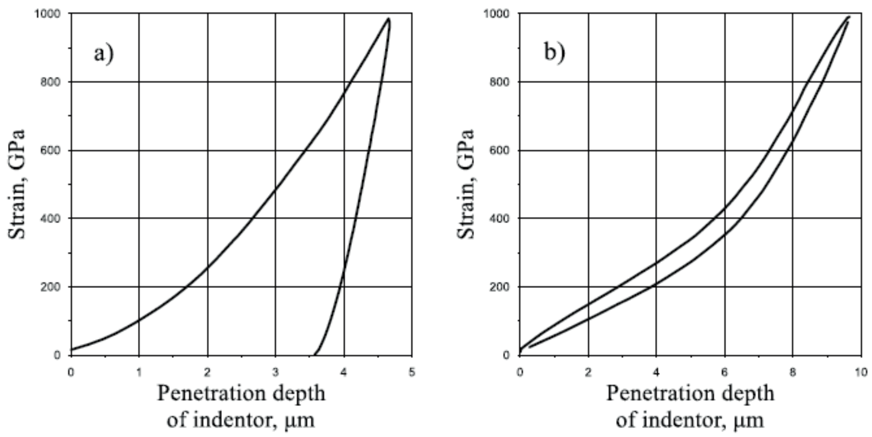

Figure 5: Dependence of the penetration depth of indenter for test temperatures of 18°C (a) and –50°C (b), depending on the applied constant load for a sample of TNZ annealed at 600°C – 0.5 h.

It can be seen from the figures presented that with increasing depth of penetration of the indenter on the curve of unloading at room temperature, there are no specific features, but when the temperature is lowered to –(50-70)°C, there are inflections that indicate the presence in the material of two elastic components due to the usual elastic component and the superelastic component associated with the martensitic transformations. In this case, the area of plastic deformation is substantially reduced. From the discharge curves in this case, we can calculate two elastic moduli [13], which are typical for the usual elasticity and superelastic behavior of the alloy.

As a result of measuring the continuous loading curves of the sample as a function of temperature, the following temperature dependences of the hardness and modulus of elasticity are obtained (Fig. 6, 7).

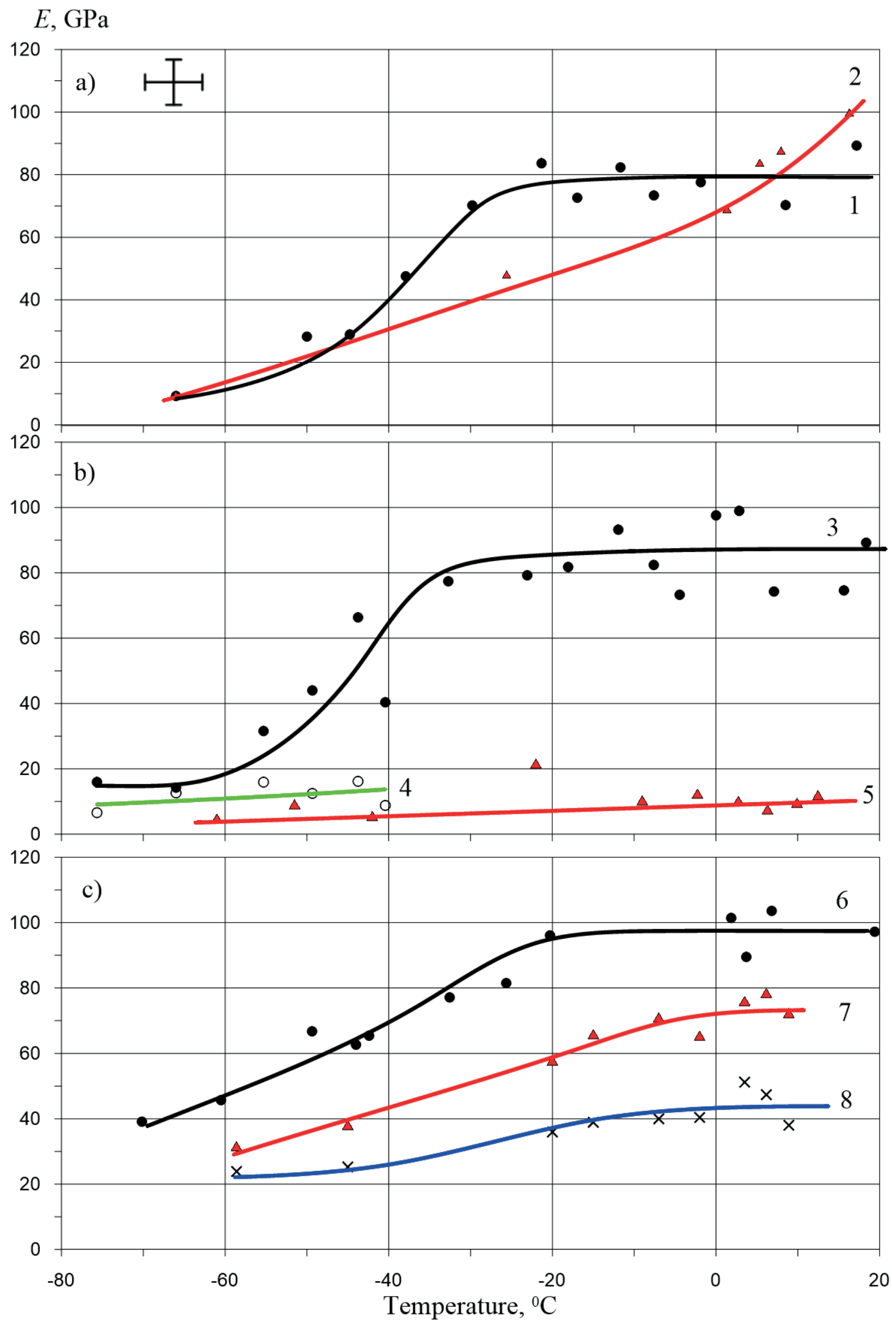

Figure 6: Dependence of the elastic modulus of foils annealed at 550°C (a), 600°C (b) and 650°C (c) on the test temperature: 1, 3, 6 – cooling; 2, 4, 5, 7, 8 – heating.

Measurements of microhardness and elastic modulus at different temperatures have shown that the superelastic properties exhibit samples annealed at 600 and 650°C for 0.5 h, which agrees perfectly with the results of cyclic tests. It should be

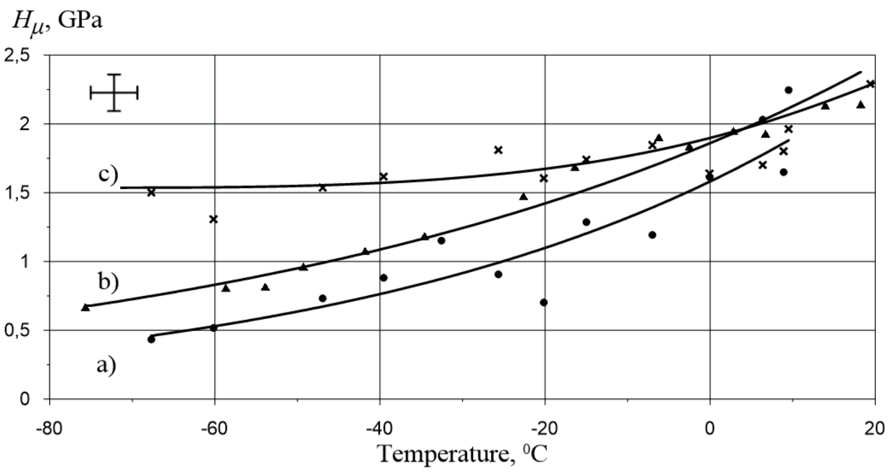

Figure 7: Dependence of hardness on test temperature: annealed at 550°C (a), 600°C (b) and 650°C (c) on test temperature.

noted that samples exhibiting superelasticity, after heating, retained a low value of the modulus of elasticity, which is not observed in samples annealed at 550°C - 0.5 h.

As it can be seen from the presented graphs (Fig. 6), the dependence of the Young's modulus *E* on the test temperature is of a complex character. The nature of this dependence is not yet fully understood. However, the fact that the Young's modulus of the material under study decreases with decreasing temperature shows that the martensitic transformation is proceeding, although an inverse relationship is observed for most pure metals and other (not superelastic) materials (*E* increases with decreasing temperature) [14].

From the graphs of the hardness versus test temperature (Fig. 7), it can be seen that the microhardness decreases with decreasing test temperature. The greatest decrease in hardness is observed in a single-phase alloy, and in the presence of an additional phase, a larger difference in the values is observed with a decrease in the indentation temperature.

6. CONCLUSIONS

1. Texture formation in the Ti-22%Nb-6%Zr (at.%) alloy during cold rolling proceeds in accordance with the laws characteristic of most BCC metals, in which the textural component {100} <011> is stable for deformation degrees less than 80%, and with its increasing up to 90-98% the component {111} <011> is enhanced.

2. When using a cyclic load with a strain amplitude (up to 2.5%), it is shown that TNZ alloy foils are subjected to "training", as a result of which the shape of strain-strain

curves during loading and unloading indicates the appearance of superelasticity effect in the material. At room temperature, the superelasticity effect was observed only in foils of Ti-22Nb-6Zr alloy annealed at temperatures of 600 and 650°C and stretched only along the direction of initial rolling.

3. In the diffraction spectra of samples subjected to "training" and possessing the effect of superelasticity, reflections of the additional phase were detected, on which it was possible to identify a face-centered orthorhombic structure.

4. It is shown that the superelasticity effect is orientationally and structurally dependent, as does the anisotropy of mechanical properties.

5. The results of low-temperature tests of the investigated samples using continuous indentation curves indicate the occurrence of martensitic transformations in the samples, which appear in the fall of the elastic modulus with decreasing temperature and the presence of hysteresis when the sample is heated. The temperature of the commencement of the martensitic transformation under a load of the order of 100 MPa for foils of the TNZ alloy is determined, which depends on the structure of the material and varies from -20 to -40°C, and the temperature of the end of the martensitic transformation is -60°C.

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