Functional properties and microstructure of TiNi alloy during multiple martensitic transformations

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Abstract. The influence of multiple martensitic transformations on the functional properties and microstructure of the equiatomic TiNi alloy is considered. An analysis of mechanical tests showed that in the CG and UFG state in the Ti50.0Ni50.0 alloy as a result of thermal cycling with an increase in the number of cycles, a monotonic increase in the yield strength is caused by phase hardening. Moreover, in the UFG state, the yield strength increases by 185 MPa, which is 67.5 MPa more than the increase in \( \sigma_{YS} \) in the CG state. In this case, ductility remains at the level of 40%, which is somewhat lower than ductility in the CG state (~ 60%). The phase yield stress and the estimated reactive stress of the CG and UFG states as a result of the TC also increase, with \( \sigma_{reac,UFG} \) reaching 830 MPa. The increase in the yield strength of the CG state in an overgrown alloy is 113 MPa, while in the UFG it is 155 MPa, in addition, an increase in the estimated reactive stress and the reversible deformation with an increase in the number of thermal cycling cycles.

1. Introduction
TiNi alloys with the shape-memory effect (SME) possess high functional characteristics, enhanced strength, ductility, corrosion resistance, biocompatibility, etc. [1-2]. They have a unique set of properties - high values of recoverable deformation and developed stresses, high corrosion resistance, due to which they are widely used in many industries and medicine [3-4].

At the same time, for many applications, especially in critical or small-sized products, the level of mechanical and functional properties possessed by TiNi alloys in the usual coarse-grained state is insufficient. Since physico-mechanical properties are structurally sensitive, methods of deformation-heat treatment are traditionally used to increase them, allowing to obtain various types of structures.

For these alloys, various metallurgical and metallurgical aspects are developed, new alloys and technologies for their processing are created, a systematic study of the structural and phase transformations in them, various properties, including the thermomechanical memory effects, unique in their temperature, deformation and power characteristics, is carried out.

In the development of products made of SMA (shape memory alloys), the following functional characteristics are most important: temperature interval of shape recovery, maximum reversible deformation, maximum fully reversible deformation, degree of shape recovery, similar characteristics of the reversible shape memory effect and superelasticity [1-10].

The heat treatment of this alloy requires high accuracy, as it greatly affects its properties. Heat treatment is the main means for finely controlling the temperature of the phase transformation. The duration and temperature of the heat treatment affect the deposition of various phases Ni-rich and thereby determine the amount of nickel deposited on the nickel-titanium crystal lattice; depleting the nickel matrix, heat treatment leads to an increase in the temperature of the phase transformation. The
A combination of heat and cold treatment is the main means of regulating the properties of this alloy. An effective method of hardening of structural elements and increasing strength and functional characteristics is heat treatment and thermal cycling. Thermal cyclic treatment (TCT) is accompanied by multiple phase transformations during heating and cooling with optimal speeds.

Shape memory alloys have a unique ability to restore shape upon heating, and it is known that multiple heat exchanges through the temperature range of martensitic transformations lead to a change in their functional properties [1,2].

During thermal cycling in a free state (without stress), a decrease in the temperature of phase transitions and a change in their sequence are observed [11]. If external stress acted upon the sample during thermal cycling, along with a change in the characteristics of martensitic transformations, the parameters of the shape memory effects change, and one-sided irreversible deformation accumulates.

Thermal cycling can have a beneficial effect on the formation of the structure and properties of metallic materials and alloys. In this regard, thermal cycling is included as one of the operations in the production technology of materials. It is important to determine the effect of multiple martensitic transformations on the functional properties and microstructure of TiNi alloy.

2. Material and methods

As the study material it chose a two-component alloy of the TiNi system - an alloy of the equiatomic composition Ti50Ni50, which has the structure of B19'-monoclinic martensite at room temperature, the transformation temperatures are Ms = 63 ºC, Mf = 40 ºC, As = 94 ºC, Af = 110 ºC. To form a solid solution the TiNi alloy were quenched from the homogeneity region (from 800 ºC) in water. Thermal cycling on the samples in different initial states is performed via consecutive dipping of samples in liquid nitrogen (-196 ºC) with subsequent heating to 150 ºC on the electric heater, which respectively is lower and higher than the temperatures of direct and reverse martensitic transformations. Samples with a section of less than 1 mm are subjected to thermal cycling, which ensures quick heating and cooling of samples. The number of thermocycles “heating-cooling” varies from 0 to 100. The dwell time for heating and cooling is 5 minutes. The fine structure of the material was studied with a JEM-2100 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. The foils for electron-microscopic studies were prepared on a TenuPol-5 twin jet electropolishing set according to the standard procedure with the help of the electrolyte 10%HClO4 + 90%CH3(CH2)3OH (90% butanol). Tensile mechanical tests of small-sized flat samples with a gauge portion of 1*0.25*4 mm were conducted at room temperature with a strain rate of 1*10^-3 s^-1 on a Shimadzu AG-50kNXD machine.

3. Results and discussions

First of all, consider the structure of the alloy in the coarse-grained state after quenching. In the initial quenched state in the equiatomic alloy Ti50Ni50, large austenitic grains with a size of about 200±10 microns with clear boundaries are observed (figure 1, a). According to the results of optical metallography, a surface relief in the form of a set of parallel strips from the plates of the martensitic phase is detected inside them (figure 1, b).
Figure 1. Microstructure of the alloy Ti$_{50}$Ni$_{50}$ in the quenched state (OM). Figure b shows a section with a large magnification and a martensitic relief.

The transmission electron microscopy analysis shows that the alloy has martensite microstructure at room temperature with mainly package morphology of paired twin plate crystals B19', which are twins (111) and (011) B19' of the I type (on the whole it is typical of binary TiNi alloys). The width of twin martensite plates $h_M$ is 85±15 nm, the boundaries between martensite crystals are clear and free of defects, Figure 2.

Figure 2. Typical TEM images of the microstructure of B19'-martensite of Ti$_{50}$Ni$_{50}$ alloy in the coarse-grained state.

Thermal cycling with consecutive increase of the number of cycles results in enhancement of the dislocation density and successive decrease of the martensite plate width. After thermal cycling in the temperature range MT B2 $\rightarrow$ B19' with a number of cycles equal to 20 in a microstructure consisting mainly of plate martensite, a complex dislocation substructure arises in some regions. With an increase in the number of thermal cycles from 20 to 50, developed dislocation clusters are observed in this state, forming the so-called “dislocation forest”. Filming from various sections of the foil revealed the first composite nanotwins and stacking faults formed inside the martensite twins ($h$ (001)$_{B19'}$ = 12 ± 3 nm). The width of the martensite plates decreases to $h_M = 65 \pm 10$ nm. In the state after thermal cycling with the maximum number of thermocycles, the microstructure is B19'-martensite with twins (011)$_{B19'}$ of I type 60±5 nm wide, inside which composite nanotwins (001)$_{B19'}$ several nanometers wide (~10±1 nm) and formed during thermal cycling are observed, Figure 3.
Figure 3. Typical microstructure of coarse-grained Ti₅₀Ni₅₀ alloy after 100 thermocycles (a), (b) displays composite nanotwins (001)_{B19'}

The ECAP n=8 at T=400°C leads to the formation of a complex martensitic structure in the material. The size of the initial austenitic grain in the form of martensite packets is about 600±30 nm, inside which there are twins with a plate width h_M=79±8 nm (Figure 4, a). Microdifraction has a close to annular distribution of reflexes, which indicates high-angle disorientation of grain boundaries in the deformed structure. In addition, there is an azimuthal blur of individual reflexes, indicating the presence of small-angle disorientation in the structure (Figure 4, b).

Figure 4. TEM image of microstructure of alloy Ti₅₀Ni₅₀ in UFG state: bright-field (a, b) images corresponding to UFG structure microdifraction (b).

Thermal cycling (n=20) leads to dislocations in martensitic plates. The width of the B19'-martensite twins is 70±5 nm. After 50 thermocycles, the density of dislocations and defects in the structure increases markedly, but it is difficult to make numerical estimates of changes in structural parameters from TEM images. Dislocation walls and thick extinction contours at the grain boundary also confirm that the accumulation of defects occurs in the alloy during multiple heat changes. Although this makes it difficult to quantify the structural elements, the average width of the measured plates is 55±9 nm. TC with the maximum number of thermal cycles (100 cycles) leads to the formation of a predominantly martensitic structure containing twins with a width of 40±7 nm (Figure 5, a), in addition, there is a noticeable increase in the density of dislocations in the martensite matrix (Figure 5, b). The increase in the individual grain allows to detect in the structure of composite nanowires (001)_{B19'} (Figure 5, c). The width of the nanowires is about 7±4 nm, and the length is equal to the width of the martensite twins. Azimuthal diffusion of reflexes indicates high internal stresses.
Figure 5. Typical TEM images of the microstructure of Ti50Ni50 alloy with UFG structure and maximum number (n=100) of cycles: bright-field (a,b,c) images: dislocation cluster (b), grain containing compound nanotwins (c)

In the initial coarse-grained state, the yield strength of the alloy is 430 MPa, with an increase in the number of thermal cycles, the yield strength of the alloy nonlinearly changes with the achievement of a maximum at 100 cycles and becomes equal to 547.5 MPa. The increase in the phase yield limit indicates that with the increase of thermal cycles, the phase transformation under load becomes more difficult, and a greater stress is necessary for its implementation, in this case it is caused by an increase in the density of defects accumulated at the TC. The estimated reactive stress, defined as the difference between the dislocation and phase yields, increases with the number of thermal cycles. Therefore, thermal cycling increases the functional properties of the alloy. The length of the phase flow plateau, which determines the possible resource of reversible deformation, increases from 5.1 to 5.45 % (figure 6, a). In the UFG state, the yield strength increases to 935 MPa. TC alloy in the UFG state with an increase in the number of thermal cycles leads to an increase in the yield strength to 1120 MPa at the maximum number of cycles. Thus, the yield strength increase in the UFG state is greater than in the CG (185 MPa - in the UFG, 117.5 MPa - CG). In the UFG state, there is an increase in the tensile strength by 110 MPa. The plasticity remains at an acceptable level of ~ 40 %, which, however, is slightly lower than the plasticity in the CG state (~ 60%). For the UFG state, along with the increase in the tensile strength and yield strength, a monotonic increase in the phase yield strength and the estimated reactive stress, up to 290 and 830 MPa, respectively, is also characteristic (figure 6, b).
Figure 6. Dependences of estimated reactive stress and reversible deformation in CG (a) and UFG (b) states of Ti$_{50}$Ni$_{50}$ alloy on the number of thermal cycles

4. Conclusions
Under the influence of multiple martensitic transformation in the structure of the alloy Ti$_{50}$Ni$_{50}$ there is a decrease in the width of martensitic plates in both coarse-grained and ultrafine-grained states. In addition, it was found that at the maximum number of cycles in the martensite twins, composite nanowires $(001)_{B19}^*$, several nanometers in size, are formed to reduce the level of internal stresses. Analysis of the results of mechanical tests showed that as a result of thermal cycling in the CG and UFG states there is an increase in the yield strength associated with the accumulation of defects in the alloy. At the same time, in the UFG state, there is a noticeable increase in the yield strength by 185 MPa, which is 67.5 MPa more than the increase in the CG state. The plasticity remains at the level of 40 %, which is slightly lower than the plasticity in the coarse-grained state (~60%). The ultrafine-grained state is characterized by a monotonic increase in the phase yield strength and estimated reactive stress to 290 and 830 MPa, respectively. The dependence of microhardness on the number of thermal cycles is similar to the behavior of the alloy under tension: with an increase in the number of cycles, an increase in the values of microhardness is observed.

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