The influence of multiple phase transformations on functional characteristics in TiNi alloys in various structural states

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Abstract. The article were discussed the effect of multiple martensitic transformations with a different number of cycles on the functional characteristics, microstructure and mechanical properties of the TiNi alloys in different structural states and chemical compositions. As a result of multiple martensitic transformations, the accumulation of defects and a decrease in the size of structural elements are observed. The most effective phase hardening is in an equiatomic alloy. The Ti49.8Ni50.2 alloy demonstrates stability to phase hardening in all studied states.

1. Introduction

Shape memory alloys (SMA) are often used as operating elements of actuators due to their unique ability to recover deformation and stress generation [1,2]. In actuators, the SMA elements are thermally cycled through the temperature range of martensitic transformations. Thus, the stability of the SMA properties under repeated cooling and heating is an important characteristic for applications [3-6]. Thermal stability of SMA properties depends on by chemical composition [7-9], yield point [6,10], the magnitude of the applied stress [2,11,12] and size of structural elements [10,13]. Thermal cycling of equiatomic NiTi alloys in a free state leads to a change in the temperatures of martensitic transformation and the change of theirs sequence [14-18]. This is most likely associated with an increase in the density of defects arising at cooling during forward martensitic transformation, which is accompanied by the formation of high internal stresses [19]. To accommodate this stress, the nucleation of dislocations and their sliding occurs, which in turn increases the density of dislocations [14,16,20]. An increase in the dislocation density leads to an increase in the elastic energy, which lowers the transformation temperature [21].

To change the grain size, the methods of severe plastic deformation (SPD) are used, which at the same time contribute to a change in the density of dislocations [22,23]. Thermal cycling of TiNi alloys in states obtained by SPD methods proceeds similarly to alloys in coarse-grained states after quenching [24,25,26]. One of the most important properties of alloys is their functional properties, which are evaluated using various experiments. But in some cases, it is difficult to conduct experiments to determine the functional characteristics. But the relationship between the yield stress and the phase yield stress is known, which determines the reactive stress (one of the characteristics of functional properties). The plateau size of the phase yield stress can be used to assess reversible deformation. In this work, the evaluation of functional characteristics was applied according to the data determined using mechanical tensile tests in alloys of different chemical composition and with different grain sizes.

2. Material and methods

The research materials were TiNi alloys of various chemical compositions with respect to stoichiometry – Ti50.0Ni50.0, having a B19’ crystalline lattice, Ti49.8Ni50.2 and Ti49.2Ni50.8, having a B2 crystalline lattice
in the initial state after quenching from a temperature of 800 °C in water. Thermal cycling of the samples was performed via a successive immersion of the samples into liquid nitrogen (-196 °C) followed by heating to a temperature of 150±5 °C, the temperatures which are known to be lower and higher than the temperature of the direct martensitic transformation, M_s and that of the reverse martensitic transformation, A_f in the all materials. The number of “heating – cooling” thermal cycles was from 0 to 100. The exposure time was \( t = 8 \text{ min} \) to ensure the complete heating/cooling of the samples. Tensile mechanical tests of small-sized flat samples were conducted at room temperature with a strain rate of \( 1 \times 10^{-3} \text{s}^{-1} \). The structure of the material was studied with a JEOL 2100 transmission electron microscope (TEM).

3. Results and discussions

The microstructure of B19'-martensite, shown in Figure 1, is generally typical for the Ti_{50.0}Ni_{50.0} binary alloys. Martensite B19' at room temperature has a predominantly packet morphology of pairwise twinned lamellar crystals. The width of twinned martensite plates (h_M) is 85 ± 15 nm. In the state after thermal cycling with the maximum number of thermal cycles (n = 100), the microstructure is also B19'-martensite containing I-type twins with a width of \( \sim 60 \pm 5 \text{ nm} \), within which compound nanotwins with a width of several nanometers (\( \sim 10 \pm 1 \text{ nm} \)) are observed, formed in the TC process. ECAP n = 8 at T = 400 °C leads to the formation of a complex martensitic structure in the material. The size of the initial austenite grain by the type of martensite packets is about 600 ± 30 nm, inside which there are twins with a plate width h_M = 79 ± 8 nm. TC with the maximum number of thermal cycles (100 cycles) leads to the formation of a predominantly martensitic structure containing twins 40 ± 7 nm wide; in addition, a noticeable increase in the dislocation density in the martensite matrix is observed. The size of B2-phase nanocrystallites is 34 ± 5 nm on average. It is known that with a decrease in the grain size to the NC range in TiNi alloys, the MT temperatures significantly decrease, which explains the austenitic nature of the Ti_{50.0}Ni_{50.0} alloy in the NC state [27-30]. During thermal cycling of the Ti_{50.0}Ni_{50.0} alloy in the temperature range of martensitic transformations with n = 100 cycles, the formation of composite nanotwins (001) B19' 3 ± 1 nm wide in B2 nanocrystallites 29 ± 3 nm in size was recorded.
Figure 1. TEM images of the microstructure of an Ti$_{50.0}$Ni$_{50.0}$ alloy in (a, b) in a coarse-grained state, (c, d) in an ultrafine-grained state, (e, f) in a nanocrystalline state. a, c, e – n=0; b, d, f – n=100.

In the initial Ti$_{49.8}$Ni$_{50.2}$ alloy in coarse-grained state, grain boundaries free from dislocation accumulations are visible, the structure mainly contains equiaxed grains (Figure 2, a). During thermal cycling, an increase in internal stresses and distortion of the crystal lattice are observed. The average grain size at the maximum number of heat cycles, compared to the initial values, monotonically decreases to 28 ± 2 microns (Figure 2, b). ECAP treatment in the Ti$_{49.8}$Ni$_{50.2}$ alloy leads to the transformation of the initial coarse-grained structure into an ultrafine-grained (UFG) structure with an average size of structural elements of 220 ± 15 nm (Figure 2, c). The grains are elongated. As a result of thermal cycling of the UFG Ti$_{49.8}$Ni$_{50.2}$ alloy, the dislocation density at the grain boundaries increases, and the average size of structural elements decreases to 200 ± 15 nm. This can be seen in the TEM analysis results. Cold upsetting of the sample by 30% after ECAP treatment led to an increase in the dislocation density and the formation of deformation bands (Figure 2, e). The width of the bands and the size of the structural elements are within 175 ± 20 nm. Thermal cycling of the sample after additional upsetting led to an insignificant change in grain size 165 ± 15 nm (Figure 2, f). After the maximum number of thermal cycling cycles, grains are observed in the structure with both equilibrium boundaries and nonequilibrium ones - with a high dislocation density and internal stresses.
According to the obtained TEM data in the CG state in Ti$_{49.8}$Ni$_{50.2}$ without thermal cycling, triple joints with clear equilibrium boundaries are observed in the microstructure of the alloy (Figure 3, a). In the coarse-grained state with the number of thermal cycles ($n = 100$), the first composite nanotwins (001) B19' and stacking faults formed in the TC process were found (Figure 3, b). The width of the martensite bands is $h_M \approx 250 \pm 30$ nm, while the twins have a width of $\sim 6 \pm 3$ nm. According to the TEM analysis in UFG state (Figure 3, c) structure with nonequilibrium grain boundaries with insignificant dislocation accumulations in the grain body. In the state after thermal cycling with the number of thermal cycles ($n = 100$), an inhomogeneous structure is observed, part of the structure is a deformed structure in the ultrafine-grained range, and a part of the structure has a larger grain size (which may indicate the inhomogeneity of deformation processes) separated by stripes (Figure 3, d). An increase in the number of thermal cycles led to an even greater accumulation of dislocations both in the grain boundaries and in the body of the stripes. The width of the martensite bands is $h_M = 320 \pm 30$ nm. The size of the dislocation cells is $\sim 0.8 \mu$m.

**Figure 2.** TEM images of the microstructure of an Ti$_{49.8}$Ni$_{50.2}$ alloy in (a, b) in a coarse-grained state, (c, d) in an ultrafine-grained state, (e, f) in the UFG + cold upsetting (nanocrystalline) state. a, c, e – $n=0$; b, d, f – $n=100$. 
Figure 3. Microstructure of the Ti$_{49.2}$Ni$_{50.8}$ alloy in coarse-grained (a, b), ultrafine-grained (c, d) states.

The dependences of changes in mechanical and functional characteristics are shown in Figures 4 and 5. So the greatest increase in the yield stress in the coarse-grained state is observed in the Ti$_{49.2}$Ni$_{50.8}$ alloy, and in the Ti$_{50.0}$Ni$_{50.0}$ alloy - in the ultrafine-grained state. It is worth noting that the Ti$_{49.8}$Ni$_{50.2}$ alloy demonstrates approximately the same increase in the yield stress (about 15%) in all studied states, thus, the phase hardening in it does not depend on the initial size of the structural elements. According to the change in functional characteristics (calculated from the data of mechanical tests), the greatest change in reactive stress is observed in an equiatomic alloy in both coarse-grained and ultrafine-grained states. The rest of the alloys show a slight increase in reactive stress. At the same time, the most significant increase in reversible deformation is observed in the Ti$_{50.0}$Ni$_{50.0}$ alloy in the ultrafine-grained state, and in the Ti$_{49.2}$Ni$_{50.8}$ alloy in the coarse-grained state, in other states the changes are in the range of 0.5-0.8%.
Figure 4. Graphs of the dependence of the yield stress on the number of cycles for TiNi alloys of various chemical compositions: a - coarse-grained, b - ultrafine-grained, c – nanocrystalline states.

Figure 5. Graphs of the dependence of reactive stress (a) and reversible deformation (b) for alloys of various compositions in the coarse-grained, ultrafine-grained states.

4. Conclusions
As a result of multiple martensitic transformations in alloys of various chemical compositions, a decrease in the size of structural elements is observed due to the accumulation of dislocations and the formation of subboundaries. The formation of I nanotwins of type (001) B19' is observed. Structural changes are related to mechanical and functional characteristics. The greatest change in properties is
demonstrated by an equiatomic alloy in both coarse-grained and ultrafine-grained states. The Ti_{49.8}Ni_{50.2} alloy demonstrates the independence of phase hardening from the initial grain size. In the Ti_{49.2}Ni_{50.8} alloy with a high nickel content, the greatest changes are observed in the coarse-grained state (this feature requires additional research).

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