The increased stability of a coarse-grained and ultrafine-grained Ti$_{49.15}$Ni$_{50.85}$ shape memory alloy achieved with multiple martensitic transformations

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Abstract. The influence of thermal cycling in the temperature range of B2-B19' martensitic transformations on the TiNi alloy structure and properties are studied. The level of properties, obtained as a result of mechanical tests and measurements of microhardness, obtained in the process of thermal cycling, remains stable during soaking at room temperature in the TiNi alloy.

1. Introduction

Titanium nickelide-based alloys (TiNi) belong to the class of functional materials with shape memory effects (SME), caused by the B2-B19’ thermoelastic martensitic transformations occurring in the temperature range close to room temperature [1-4]. These alloys are widely used in medicine and technology. It is known that the cycle of martensitic transformations (MT) during cooling and heating leads to the generation of dislocations in the crystal lattice. Understanding the nature of the influence of multiple “cooling and heating” cycles below and above the martensitic transformation points - thermal cycling (TC) - on the structure and properties of materials is of great importance for TiNi alloys and products made from them. The phenomenon of phase hardening - the accumulation of dislocations during martensitic transformations - does not seem trivial in the case of MTs with reversible motion of martensitic boundaries. The term "thermoelastic transformation" in the strict sense does not imply irreversible changes in the structure.

At the same time, in real metallic materials, including TiNi alloys, during multiple MT cycles, there is some increase in the dislocation density, which, in turn, is accompanied by a change in the martensitic transformation temperatures and a certain increase in the dislocation yield strength of the alloys under mechanical loading [5-7]. However, for TiNi alloys, thermal cycling is not used to increase the yield strength as such, but with the use of thermal and mechanical cycling, it is possible for TiNi to have a multiple shape memory effect for special applications. The influence of thermal cycling on the structure and properties of TiNi alloys is a fairly large number of works [8-10].

But at the same time, studies of the impact on the UFG and NC alloys were carried out in limited quantities and, mainly, were devoted to changing the temperature of martensitic transformations and shape memory effects in TC [11-16], whereas the evolution of mechanical properties and structure was practically not studied. Unlike most other known materials with martensitic transformations, in
particular steels, the temperatures of martensitic transformations to TiNi are close to room temperature, therefore thermal cycling does not lead to noticeable thermal relaxation of the pre-formed UFG and NC structures. In this regard, the alloys under consideration are a unique object for studying the effect of intergranular boundaries on the generation of dislocations during martensitic transformations in the UFG and NC states.

Quite important is the question of how stable the formed structure and the level of properties are at aging at room temperature (soaking at room temperature). The paper [17] considered the aging at room temperature of the alloy after thermal cycling.

2. Material and methods

The Ti$_{49.15}$Ni$_{50.85}$ with a large atomic content of Ni with regard to stoichiometry is chosen as research material. The Ti$_{49.15}$Ni$_{50.85}$ alloy after quenching is in the austenite state at room temperature, and during heating to 500 °C ageing processes take place in it, and the martensitic transformations temperature increases.

In order to form ultrafine-grained structure, quenched TiNi samples with a cylinder shape (Ø20 mm, 100 mm long) are subjected to 8 equal cannel angular pressure (ECAP) cycles on a die-set with the angle of channels intersection of 120° at 450 °C.

Thermal cycling on the samples in different initial states is performed via consecutive dipping of samples in liquid nitrogen (-196 °C) with subsequent heating to 150 °C 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 1mm 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 microstructure analysis of alloys in the initial coarse-grained (CG) state is performed on the optical microscope OLYMPUS GX51. The thin structure is studied by transmission electron microscopy (TEM) on the JEOL-2100. X-ray studies are performed on the diffractometers Rigaku Ultima IV in Cu-Kα radiation with a wavelength $\lambda=1.54418$ Å, the photography is performed at room temperatures.

The mechanical tensile tests of small flat samples with a gauge part 1*0.25*4 mm are performed at room temperature with a strain rate of 1*10$^{-3}$ s$^{-1}$ on the Shimadzu AG-50kNXD.

3. Results and discussions

The stability study was carried out on samples, on which results were obtained on the transformation of the microstructure and mechanical properties of TiNi stoichiometric alloys, presented in [18]. In the initial short-circuit state after quenching, the Ti$_{49.15}$Ni$_{50.85}$ alloy at room temperature has a predominantly equiaxed B2-austenite structure with a grain size of about 20 ± 5 μm (Figure 1 a,b). The structure of the alloy is single-phase; in this case, globular inclusions 0.5–1 μm in size were found inside and at the grain boundaries, the fraction of which can take up to 5%.

![Figure 1. Optical image of the microstructure of the alloy Ti$_{49.15}$Ni$_{50.85}$ in CG state after quenching (a) and after thermal cycling (b).](image-url)
According to the TEM data obtained in the CG state without thermal cycling, the grain microstructure and the triple grain junctions free from dislocations are observed in the alloy microstructure (Figure 2 a,b). The type of extinction thickness contours is characteristic of materials in the annealed state and confirms the low density of dislocations and internal stresses. The microdiffraction pattern corresponds to the B2-austenite structure (Figure 2 a, diffraction).

![Figure 2. TEM images of the microstructure of the alloy Ti49.15Ni50.85 in CG state.](image)

Studies of the microstructure after soaking at room temperature (t = 2 years) showed that no change in structure was observed (Figure 3 a-b).

![Figure 3. TEM images of the Ti49.15Ni50.85 microstructure in CG condition and soaking at room temperature.](image)

As a result of thermal cycling with the maximum number of cycles (n = 100), a large number of dislocations accumulate in the structure in the form of clusters and disordered walls and tangles of dislocations (Figure 4). Figure 4 shows the typical microstructure observed in the Ti49.15Ni50.85 alloy after thermal cycling.
Figure 4. Typical microstructures of the alloy Ti$_{49.15}$Ni$_{50.85}$ in CG condition and after multiple thermal cycles (n=100): bright field image (a), microelectron diffraction pattern (b).

After this state is maintained at room temperature, a decrease in the density of dislocations is observed in the microstructure, separate dislocations are observed instead of significant accumulations after thermal cycling (Figure 5). Figure 5 shows a TEM photograph of a part of the structure with a particle Ti$_4$Ni$_2$O, which is confirmed by microdiffraction analysis.

Figure 5. Typical microstructures of the alloy Ti$_{49.15}$Ni$_{50.85}$ in CG condition, after multiple thermal cycles (n = 100) and subsequent soaking at room temperature: bright field images (a, b, d), microelectron diffraction pattern (c).

ECAP leads to the transformation of the original CG structure into a grain-subgrain UFG structure with a higher dislocation density (Figure 6). The average size of the structural elements is $300 \pm 20$
nm. Figure 6, c shows an enlarged image of a single grain, in which the dislocations accumulated during deformation are clearly visible. The diffraction pattern has the form of concentric rings with point reflections distributed over them from individual planes. This type of microdiffraction confirms the presence of grains with high-angle misorientations. Studies on the stability of the structure of the UFG state showed that there was a slight decrease in the density of dislocations, the grain size was within $310 \pm 10$ nm (Figure 6 e-f).

![Image of TEM micrographs](image-url)

**Figure 6.** TEM images of the Ti$_{49.15}$Ni$_{50.85}$ alloy microstructure in UFG: bright (a, c) and dark field (b) images, microelectron diffraction pattern (d); UFG condition and subsequent soaking at room temperature (e-f).

After the maximum number of heat cycles, grains with both equilibrium boundaries and non-equilibrium ones are observed in the structure - with a high dislocation density and internal stresses.
The average size of the structural elements is $240 \pm 15$ nm. This state is characterized by the presence of reflexes blurred in the azimuthal direction (Figure 7).

![Figure 7](image)

**Figure 7.** TEM images of the microstructure in the UFG state with the maximum number of cycles $n = 100$: bright field (a, b), microelectron diffraction pattern (a).

In the UFG state after thermal cycling and soaking at room temperature, the microstructure exhibits relaxation of the dislocation structure; however, in some grains one can observe a rather high defect density and clearly distinguishable fragments separated by dislocation boundaries (Figure 8b). In addition, the microstructure contains grains with distinguishable nanotwins (001) or stacking fault (highlighted area in figure c). The average size of the structural elements is $250 \pm 20$ nm, i.e. this state is characterized by some increase in the average size of structural elements.

![Figure 8](image)

**Figure 8.** Typical microstructures of the alloy Ti$_{49.15}$Ni$_{50.85}$ in the UFG state, after multiple thermal cycles ($n = 100$) and subsequent soaking at room temperature: bright field images (a-c), microelectron diffraction pattern (d).
According to the XRD analysis, in all studied states, a decrease in CSR values, an increase in internal microdistortions and an increase in the dislocation density associated with them after thermal cycling are observed. Subsequent soaking at room temperature leads to relaxation of the level of internal stresses and dislocation density. XRD data confirm the observed changes in the microstructure.

It can be noted that for the coarse-grained state, the stress of the strain-induced martensitic transformation $\sigma_m$ as a result of the TC increases from 365 to 390 MPa. But the most sensitive characteristic for thermal cycling is the yield strength of the alloy (a consistent increase from 495 to 610 MPa). The ductility as a result of thermal cycling decreased from 46 to 43%. For the UFG state higher strength values (1045 MPa) of the yield strength due to the contribution of grain-boundary hardening are characteristic. In the case of the UFG condition, an increase in the ultimate strength is observed at TCs up to 1195 MPa with $n = 100$, the yield and phase yield limits also increase with increasing number of heat cycles.

After soaking at room temperature, there is a fluctuation in the level of properties within the error in the CG state and a small decrease in the level of properties in the UFG condition. Increasing the ultimate strength in the state of the TC $n = 100$ is most likely an artifact and requires additional research. In general, changes in the level of properties are not more than 10%.

4. Conclusions

1. As a result of thermal cycling in the alloy, an increase in the density of dislocations occurs, internal stresses in the coarse-grained and ultrafine-grained states increase, the size of the structural components decreases slightly, which is associated with the formation of dislocation walls and sub-boundaries.

2. Studies of the stability of properties have shown that in a coarse-grained state, a slight increase in the parameter is observed - the tensile strength is up to 10%, and the yield strength decreases to 5%, the strength and yield stress decreases to 10% in some ultrafine-grained states too. In general, it can be said that according to the results of mechanical tests and measurement of microhardness, the level of properties obtained in the process of thermal cycling remains stable with long exposure in the TiNi alloy.

Acknowledgment

This work was supported by the Grant of the Bashkortostan Republic of Russian Federation to young scientists (№28 GR from 07.03.2019).

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