The microstructure and mechanical characteristics of the alloy Ti-50.7 at.%Ni with different deformation processing during multiple martensitic transformations

A A Churakova1,2,* and D V Gunderov1,2

1 Institute of Molecule and Crystal Physics - Subdivision of the Ufa Federal Research Centre of the Russian Academy of Sciences, 151 pr. Oktyabrya, 450075, Ufa, Russia
2 Ufa State Aviation Technical University, 12 K. Marx str., 450008, Ufa, Russia

* churakovaa_a@mail.ru

Abstract. The influence of thermal cycling in the temperature range of B2-B19’ martensitic transformations on the TiNi alloy structure and properties are studied. Different states are considered, namely the initial coarse-grained (CG) state, the ultrafine-grained (UFG) state after ECAP, the state after ECAP and cold upsetting by 30%. It is shown that, as a result of thermal cycling, microhardness and strength grow in all the three states. According to the data from TEM analysis, the increment of the dislocation density is observed, resulting from thermal cycling.

1. Introduction

TiNi-based alloys belong to the class of functional materials with a shape memory effect (SME) caused by thermoelastic martensitic transformations [1-4]. These alloys are widely used as structural functional materials in engineering and medicine. Processing of ultrafine-grained (UFG) and nanocrystalline (NC) states by severe plastic deformation techniques allows increasing service properties of different metals and alloys, including TiNi-based alloys [5, 6]. The two most popular SPD techniques are high-pressure torsion (HPT) and equal-channel angular pressing (ECAP) [5]. The ECAP technique enables producing large-sized samples with a grain size of about 300 nm and enhanced strength and shape memory effect properties. The HPT technique enables producing TiNi samples in the amorphized state, and their subsequent annealing may result in the formation of an NC structure with a grain size starting from 20 nm [6]. Studies have shown that TiNi alloys in the NC state with a grain size of about 50 nm demonstrate the highest service properties [6]. UFG and NC TiNi are of great interest for practical applications [5, 7-8].

Thermal cycling (TC) is a technique used for additional enhancement of strength properties in some alloys. The term “thermoelastic transformation” in the strict sense excludes any noticeable irreversible changes. However, in the case of coarse-grained (CG) TiNi, some increase of the dislocation density takes place during multiple cycles of martensitic transformations, which is accompanied by a slight change of the martensitic transformation temperature and some enhancement of the yield stress during mechanical loading [9].

The influence of grain boundaries on defect generation during cyclic martensitic transformations is poorly studied at present. It is of special interest to establish the influence of the UFG state of TiNi
alloys on the structural changes during thermal cycling through martensitic transformation temperatures, to determine the role of grain boundaries in dislocation generation at phase martensitic transformations. There are a limited number of publications reporting on the studies of the effect of thermal cycling on UFG TiNi alloys [10-13]. However, the paper [11] is devoted mainly to the effect of mechanocycling on the superelastic deformation of ECAP-processed TiNi. The papers [12-14] mainly deal with the issues of dilatation in UFG TiNi alloys during thermal cycling.

2. Material and methods
The studies were carried out on Ti$_{49.3}$Ni$_{50.7}$ (at.%) alloy (manufactured by «Industrial Center MATEX», Moscow) subjected to homogenizing water quenching from 800 ºC. The alloy is in the austenite state with a B2 structure (CzCl-type) at room temperature.

In order to form a UFG state, quenched cylinder samples were subjected to 8 passes of ECAP using a die-set with the angle of channels intersection of 120º at 450 ºC.

Separate samples after ECAP were subjected to additional deformation by cold upsetting by 30% to produce a UFG state with enhanced dislocation density and shear bands.

Thermal cycling treatment of samples in different initial states was carried out by cooling to the temperature of liquid nitrogen (-196 ºC) and heating to 150 ºC. The number of “heating – cooling” thermocycles was from 0 to 100. The characteristic temperatures of martensitic transformations for this alloy in the quenched state are $M_s$=-32 ºC, $M_f$=-62 ºC, $A_s$=-29 ºC, $A_f$=-5 ºC.

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%HClO$_4$ + 90%CH$_3$(CH$_2$)$_3$OH (90% butanol). The voltage was 50 V. Tensile mechanical tests were performed at room temperature with a test speed of 10$^{-3}$ s$^{-1}$ on a tensile machine at USATU.

3. Results and discussions
In the initial CG state at room temperature the Ti$_{49.3}$Ni$_{50.7}$ alloy has an austenitic structure with a grain size of about 50±5 µm according to optical metallography analysis (Figure 1a). Optical metallography does not allow performing precision estimation of the structural changes after thermal cycling (Figure 1b). According to the TEM data, dislocation-free grain boundaries are observed in the CG state (Figure 1c). After thermal cycling with a number of cycles equal to 20, dislocations pile up near the grain boundaries due to phase hardening (Figure 1d). The subsequent increase in the number of thermal cycles to 100 has apparently resulted in an additional increase of the dislocation density in grain bodies, near grain boundaries and triple joints (Figure 1 e, f).

After ECAP processing, a UFG structure with a grain size of about 200 nm is formed in TiNi (Figure 2a). As a result of thermal cycling (n=20), a complex diffraction contrast appears, which testifies to an increase of the dislocation density. Extinction contours appear in grain boundaries, which indirectly proves the dislocation density increase in grain boundaries (Figure 2b). The analysis of TEM images enables assuming that thermal cycling with the number of cycles n=50 and n=100 has resulted in an additional enhancement of the dislocation density (Figure 2 c,d).

Cold upsetting by 30% of an ECAP-processed sample usually leads to the formation of deformation bands and a significant increase of the dislocation density in the structure. The band width and the size of structural elements are about 50 nm (Figure 3a). Thermal cycling leads to some increase of the dislocation density in separate structure areas (Figure 3b-d).
Figure 1. Structure of Ti$_{49.3}$Ni$_{50.7}$ in different states: a – CG, b – CG+TC (OM), c – CG (TEM), d – CG+TC (n=20), e – CG+TC (n=50), f – CG+TC (n=100)

Figure 2. Microstructure of Ti$_{49.3}$Ni$_{50.7}$ in the UFG state: a – UFG, b – UFG + TC (n=20), c – UFG + TC (n=50), d – UFG + TC (n=100)
The ultimate tensile strength $\sigma_{UTS}$ of Ti$_{49.3}$Ni$_{50.7}$ in the CG state is 820 MPa and increases to 900 MPa as a result of thermal cycling due to phase hardening. Deformation-induced martensitic transformation as a phase pseudo-yield plateau typical of the CG state is observed on the plots. The values of the stress of deformation-induced martensitic transformation (phase yield stress $\sigma_m$) also grow as a result of thermal cycling, from 440 to 620 MPa. This is accounted by the fact that the dislocations in the austenite phase, that formed as a result of thermal cycling, hamper deformation-induced martensitic transformation. Note should be made that the stress of dislocation flow (YS) of the CG alloy is very close to the value of $\sigma_m$. However, the YS of the CG alloy, has increased by 100 MPa as a result of TC. The ductility of the CG alloy was reduced from 36 to 31% as a result of thermal cycling.

The strength stress value (1300 MPa) and the yield stress value (1150 MPa) of the UFG alloy are significantly higher than those of the CG alloy (820 and 500 MPa, respectively). At the same time, the phase yield stress values of the UFG alloy and the CG alloy are almost identical (about 450 MPa). Thus, the formation of a UFG structure with an increased density of grain boundaries efficiently increases the yield stress of the alloy, but has little effect on the phase yield stress values. Thermal cycling insignificantly increases the strength and YS of the UFG alloy to 1370 MPa and 1200 MPa. The increment in the strength and YS of the UFG alloy, resulting from thermal cycling, is even somewhat smaller than in the CG alloy. At the same time, in the UFG alloy the dislocation density grows more significantly as a result of thermal cycling, than in CG TiNi. Perhaps, the small increment in the UTS and YS of the UFG alloy, resulting from thermal cycling, can be accounted for by the fact that the UFG alloy is already in a strengthened state. The phase yield stress values of the UFG alloy also grow as a result of thermal cycling.

In the UFG+upsetting state, the ultimate tensile strength was about 1770 MPa, which is markedly higher than in the UFG state. It should be noted that the curve rate for the state with a high density of defects differs from that for the CG and UFG states. There is no phase pseudo-yield plateau on the curves for the UFG+upsetting alloy, which testifies to the blocking of deformation-induced martensitic transformation. But it is more probable that in the UFG+upsetting alloy, martensitic transformations occur at different loads, and as a consequence, a pseudo-yield plateau is not observed on the tensile
curve. The thermal cycling enabled achieving an increase in the ultimate tensile strength by 100 MPa, up to 1880 MPa.

Hence, the treatment by thermal cycling of the UFG+upsetting alloy has allowed to achieve the highest values of YS, UTS, microhardness in the Ti_{49.3}Ni_{50.7} alloy. Here, the elongation in this state remains rather good.

4. Conclusions
1. The highest dislocation density increment is observed as a result of thermal cycling in the UFG+upsetting state – a state with the most refined structure. The grain boundaries, the density of which is higher in UFG materials, are additional dislocation generation areas at diffusionless martensitic phase transformations.
2. A set of enhanced mechanical properties, namely strength, yield stress, ductility, is achieved as a result of the combined treatment that includes ECAP, upsetting and thermal cycling.

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

References
[1] V N Khachin 1992 Titanium nickelide: structure and properties (Moscow)
[2] V Brailovski, S Prokoshkin, P Teriaultet and F Trochu 2003 Shape memory alloys: fundamentals, modeling, applications, (ETS) Publ. (Canada: Montreal)
[3] K Otsuka 1999 Shape Memory Materials (UK Cambridge: Cambridge University Press)
[4] S Miyazaki, T Imai, Y Igo and K Otsuka 1986 Metall. Trans. 17A pp 115–20
[5] R Z Valiev 2000 Progr. Mater. Sci. 45 pp 103–89
[6] D V Gunderov, A V Lukyanov, E A Prokofiev, A R Kilmametov, V G Pushin and R Z Valiev 2009 Mater. Sci. Eng. A 503 pp 75-77.
[7] R Z Valiev, D V Gunderov, E A Prokofiev, V G Pushin and Yu Zhu 2008 Materials Transactions 49 (1) pp 97–101
[8] D Gunderov, A Lukyanov, E Prokofiev, A Churakova, V Pushin, S Prokoshkin, V Stolyarov and R Valiev 2013 Materials Science Forum 738-739 pp 486–490
[9] Y Liu and P G McCormick 1990 Acta Metall. Mater. 38 pp 1321–1326
[10] A A Churakova, D V Gunderov, A V Lukyanov and N Nollmann 2015 Acta Metallurgica Sinica (English Letters) 28 (10) pp 1230-1237
[11] Y X Tong, F Chen, B Guo, B Tian, L Li, Y F Zheng, D V Gunderov and R Z Valiev 2013 Mat. Sci. and Eng. A 587 pp 61–64
[12] R I Babicheva and Kh Ya Mulyukov 2011 Letters on materials 1 pp 156–161
[13] R I Babicheva and Kh Ya Mulyukov 2014 Applied Physics A 116 (4) pp 1857–1865
[14] W Tang and R Sandström 1993 Mater. Des. 14 (2) pp 103–113