Microstructure and mechanical properties of the ultrafine-grained TiNi alloy after multiple martensitic transformations and subsequent aging

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Abstract. In this paper, we investigate the effect of preliminary thermal cycling in the temperature range of martensitic transformation on the aging processes in the ultrafine-grained Ti\(_{49.0}\)Ni\(_{51.0}\) alloy, using as an example the examination of the microstructure, mechanical properties and fractography. Our studies show that preliminary thermal cycling leads to a significant increase in the density of dislocations that promote the intensification of the aging process and thereby enhance the strength and functional characteristics of the TiNi alloy in the ultrafine-grained state.

1. Introduction

TiNi alloys with the shape-memory effect (SME) possess high functional characteristics, enhanced strength, ductility, corrosion resistance, biocompatibility, etc. [1-2]. It is known that a cycle of martensitic transformations (MTs) under cooling and heating leads to the generation of dislocations in the crystalline lattice. Understanding the effect 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 thereof [3-4]. Thermal cycling brings about changes in the structural and stress states, therefore it can be used to control the functional properties of shape-memory alloys (SMAs) [5-10]. For TiNi alloys, an important role is played by the aging processes – precipitation of the aging particles Ti\(_3\)Ni\(_4\), Ti\(_2\)Ni\(_3\) during the solid solution decomposition [11]. In [12], the authors proposed a method for improving the functional stability of NiTi alloys having a high content of Ni. The method consisted in combining two methods – multiple phase transformations and low-temperature aging. Grain size is of an important decisive significance for improving functional characteristics. The new approach stipulates that first the generation of dislocation occurs in the interior part of a grain through cyclic phase transformations, then the low-temperature treatment by aging is performed to introduce nanoparticles, and dislocations can act as heterogeneous centers for the nucleation of precipitates. As a result, the homogeneous distribution and improvement of functional characteristics due to particle precipitation [12].
However, in that paper only the material in the coarse-grained state was considered. Scientifically interesting is the combination of an ultrafine-grained structure and thermal cycling during subsequent aging and their role in producing a material with high functional and strength characteristics.

2. Material and methods
In this work, as the material for investigation we used a TiNi intermetallic – Ti$_{49.0}$Ni$_{51.0}$ (manufactured by MATEX, Russia), having a B2 crystalline lattice in the initial state after quenching from a temperature of 800 °C in water. To produce an ultrafine-grained structure, ECAP processing was conducted with the number of passes $n=6$ at a temperature of T=450 °C with an angle of 120°. 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 140±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, $A_f$. The number of “heating – cooling” thermal cycles was from 0 to 100 ($n=20$, $n=100$). The exposure time was $t=8$ min to ensure the complete heating/cooling of the samples. Heat treatment in the aging regime was performed in a Nabertherm furnace in a temperature range of 250-400 °C with exposure for 1 hour at each temperature. Tensile mechanical tests of small-sized flat samples with a gauge portion of $1\times0.25\times4$ mm were conducted at room temperature with a strain rate of $1\times10^{-3}$s$^{-1}$ on a Shimadzu AG-50kNXD machine.

3. Results and discussions
The structure of the Ti$_{49.0}$Ni$_{51.0}$ alloy produced by ECAP consists of grains-subgrains with a size of about 300±10 nm (Figure 1, a). The subsequent annealings at a temperature of T=400 °C do not result in a change in the grain size of the ECAP-sample. The structure after TC with $n=20$ in the UFG is martensitic; martensite packets with an average size of 300±15 nm can be observed (Figure 1, b). After $n=100$ cycles, martensite laths are also observed in the structure and the boundaries of the parent austenite phase are still preserved. The annealing at T=400 °C of the samples after $n=20$ and $n=100$ has produced similar structures with a size of the structural element of 250±10 nm (Figure 1, c).

![Figure 1. Structure of the Ti$_{49.0}$Ni$_{51.0}$ alloy: a) after ECAP, b) ECAP + TC (n = 20), c) ECAP + TC (n = 100) + annealing 400 °C.](image)

The mechanical tests were performed on the Ti$_{49}$Ni$_{51}$ alloy samples in the UFG state before and after TC, with subsequent aging in a temperature range of 250-400 °C (Table 1). The ECAP-processed samples have the ultimate tensile strength (UTS) of 1125 MPa; aging at T=400 °C raises the strength to 1185 MPa, which is related to the grain refinement accompanied by the precipitation hardening, the yield stress (YS) also increases from 960 to 1040 MPa, and the ductility slightly declines from 42 to 36.

In the condition after TC with $n=20$ and subsequent aging at T=400 °C, YS grows to 1220 MPa as compared to the condition before aging, which can be attributed to the homogeneous precipitation and distribution of aging particles on dislocation networks formed in the process of thermal cycling; UTS
also increases considerable, which is apparently related to the large quantity of strengthening $\text{Ti}_3\text{Ni}_4$ aging particles. The substantial increase in YS to 1300 MPa after TC with $n=100$ and aging at $T=400 \, ^\circ\text{C}$ can be related to the large density of defects accumulated during multiple martensitic transformations. Thus, preliminary thermal cycling before aging leads to a large increase in UTS and YS, as compared to the conditions after aging without thermal cycling.

A fractographic analysis was performed to evaluate fracture viscosity and to examine aging particles. Figure 2 (a) shows the fracture surface of the ECAP-processed alloy, the fracture is ductile, the dimple size is 20±2 μm. After aging at 400 $^\circ\text{C}$, the fracture is still ductile, and the dimple size is unchanged (figure 2, b).

Table 1. Results of mechanical tensile tests.

| State                         | UTS, MPa | $\sigma_{\text{ms}}$, MPa | YS, MPa | $\sigma_{\text{r}}$, MPa | $\delta$, % |
|-------------------------------|----------|---------------------------|---------|--------------------------|------------|
| CG initial                    | 840±30   | 255±15                    | 460±20  | 205±15                   | 33±5       |
| ECAPed                        | 1125±20  | 275±15                    | 960±20  | 685±10                   | 42±5       |
| ECAP + annealing 250 $^\circ\text{C}$ | 1120±15  | 260±15                    | 980±20  | 720±15                   | 35±5       |
| ECAP + annealing 400 $^\circ\text{C}$ | 1185±20  | 265±15                    | 1040±20 | 775±10                   | 36±5       |
| ECAP + TC ($n=20$)            | 1180±25  | 342±15                    | 950±20  | 608±15                   | 20±5       |
| ECAP + TC ($n=100$)           | 1365±25  | 420±15                    | 1170±20 | 750±15                   | 20±5       |
| ECAP + TC ($n=20$) + annealing 250 $^\circ\text{C}$ | 1242±25  | 365±15                    | 1036±20 | 671±10                   | 22±5       |
| ECAP + TC ($n=100$) + anneal. 250 $^\circ\text{C}$ | 1318±25  | 411±15                    | 1160±25 | 749±10                   | 24±5       |
| ECAP + TC ($n=20$) + anneal.400 $^\circ\text{C}$ | 1220±25  | 400±15                    | 1040±25 | 640±10                   | 20±5       |
| ECAP + TC ($n=100$) + anneal.400 $^\circ\text{C}$ | 1300±25  | 421±15                    | 1165±25 | 742±15                   | 20±5       |

Figure 2. The fracture surface of sample: after ECAP (a); after ECAP and aging at T= 400 $^\circ\text{C}$ (b).

Figure 3, a shows the fracture surface of the alloy after TC with $n=20$ at T=400 $^\circ\text{C}$; the fracture is ductile, the dimple size is 20±3 μm. The fracture surface of the alloy after TC with $n=100$ at T=400 $^\circ\text{C}$ is also ductile, the dimple size is 22±3 μm, but the dimples appear to be more elongated, presumably (Fig. 3, b) Ti$_3$Ni$_4$ aging particles are observed inside the dimples [13].

It can be noted that the dimple size (20 μm) on the fracture surface of the sample after ECAP is significantly larger than the grain / subgrain size, which indicates the intercrystalline propagation of the crack upon fracture.
Figure 3. Fractography of the Ti$_{49}$Ni$_{51}$ alloy sample in the UFG+TC condition: a) n=20 T=400 °C, b) n=100 T=400 °C (SEM).

4. Conclusions
The structure of the Ti$_{49}$Ni$_{51}$ alloy produced by ECAP consists of martensite laths with the size of the austenite grains-subgrains with a size of about 300 nm. TC and subsequent annealings at a temperature of T=400 °C do not result in a change of the grain size. According to TEM, the size of martensite packets is 300±15 nm. The results of tensile mechanical tests show that preliminary TC (n=20 and n=100) during subsequent aging promotes to an increase in the ultimate tensile strength and yield stress in the UFG state. Fractographic analysis reveals that in the Ti$_{49}$Ni$_{51}$ alloy in the UFG state there is a pronounced ductile fracture, the dimple size is on average 20±5 µm, and the dimples have inclusions in individual regions. The fracture behavior does not change as a result of thermal cycling and subsequent aging, the dimple size varies within the measurement error, but in separate regions in the condition TC n=100 T=400 °C aging presumably Ti$_3$Ni$_4$ particles are observed inside the dimples.

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References
[1] Khachin V N 1992 Titanium Nickelide: Structure and Properties (Moscow: Nauka) [in Russian]
[2] Brailovski V, Prokoshkin S, Terriault P and Trochu F 2003 Shape Memory Alloys: Fundamentals, Modeling, Applications (Montreal: ETS Publ.)
[3] Otsuka K 1999 Shape Memory Materials (Cambridge: Cambridge University Press)
[4] Gunther V E et al. 1998 Medical Materials and Implants with Shape Memory, ed V E Gunther (Tomsk: TSU) [in Russian]
[5] Miyazaki M, Igo Y and Otsuka K 1986 Acta Metall. 34 2045
[6] Erofeev V Y, Monasevich L A, Pavskaya V A, Paskal Y I 1982 Fiz. Met. Metalloved. 53 963 [in Russian]
[7] Mironov Yu P, Erokhin P G and Kul'kov S N 1997 Russian Physics Journal 40 210
[8] Furuya Y, Park Y C 1992 Nondestructive Testing and Evaluation 8-9 541
[9] Lin G M, Lai J K L, Chung C Y 1995 Scripta Metall. Mater. 32 1865
[10] Belyaev S, Resnina N 2013 Int. J. Mater. Res. 104 11
[11] Kustov S, Mas B, Salas D, Cesari E, Raufov S, Nikolaev V, Van Humbeeck J 2015 Scripta Mater. 103 10
[12] Wang X, Pu Z, Yang Q, Huang S, Wang Z, Kustov S, Humbeeck J V 2019 Scripta Mater. 163 57
[13] Xu G X, Zheng L J, Zhang F X, Zhang H 2019 Journal of Alloys and Compounds 775 698