STRUCTURE AND PROPERTIES OF AGEING AND NONAGEING ALLOYS Ti$_{49.4}$Ni$_{50.6}$ AND Ti$_{50.2}$Ni$_{49.8}$ SUBJECTED TO HIGH PRESSURE TORSION

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Abstract. Nanocrystalline (NC) samples of ageing and nonageing Ti$_{49.4}$Ni$_{50.6}$ and Ti$_{50.2}$Ni$_{49.8}$ alloys have been produced using high pressure torsion (HPT) by the technique that allows obtaining disc-shaped samples of 20 mm in diameter and 0.7 mm thick. It was revealed that in these Ti-Ni alloys a structure of a mix of amorphous phase and nanocrystalline B2 phase forms after HPT. Microstructure and mechanical properties of the Ti-Ni alloy after HPT and annealing with different temperatures and time (from 5 minutes to 6 days) were investigated. It was revealed that in Ti$_{49.4}$Ni$_{50.6}$ alloy after HPT and annealing at 400-500 °C for 1 h a nanostructure forms with the grain size of 30 and 50 nm respectively. In Ti$_{50.2}$Ni$_{49.8}$ alloy after HPT and annealing at 400 °C for 1 h a structure with a considerably larger grain size of about 150 nm forms.

1. INTRODUCTION

TiNi alloys are well-known as materials with the shape-memory effect. They are very promising for many structural and functional applications in engineering and medicine [1-3]. Fabrication of a nanostructured state by severe plastic deformation (SPD) techniques is a promising way to enhance the properties in various metals and alloys [4]. SPD can be applied to TiNi alloys as well.

The previous papers demonstrated that an amorphous phase [5-13] formed in TiNi alloys during high pressure torsion (HPT). Nanocrystalline states formed as a result of annealing of the TiNi samples after HPT [6-10]. Relatively “small” TiNi samples of 5-10 mm in diameter and about 0.1-0.2 mm in thickness were produced by HPT as a result of previous studies [6-13]. However, the small size of HPT samples (about 10 mm in diameter and 0.2 mm thick) used in Ref. [6-13] prevented from carrying out the comprehensive investigation of the mechanical properties. Special HPT equipment and techniques (using anvils with a groove) that allow producing relatively “big” HPT TiNi samples with a diameter of 20 mm and thickness up to 1 mm were used in [14-18]. The samples of these dimensions...
open new possibilities to investigate microstructure, mechanical and functional properties of TiNi alloys in the amorphous and nanocrystalline states. It is known that in the quenched coarse-grained TiNi alloys enriched with Ni with respect to the stoichiometry Tl49.4Ni50.6, including the Ti49.3Ni50.6 alloy, during annealing at 400-500 °C ageing processes take place accompanied with precipitation of Ni3Ti (X-phase), "Ni3Ti", Ni5Ti phase particles [1]. Such alloys are called "aging" ones. However, in HPT Ti49.4Ni50.6 samples after similar annealings no precipitates were observed [6-9,14-16]. But the composition of TiNi alloys significantly effects the structure formation processes during HPT. Thus, in the previous works [13], it was shown that in Ti50.1Ni49.8, Ti50.2Ni49.8 alloys the amorphous structure is formed at lower degrees of HPT, as compared to the ageing alloy Ti49.3Ni50.7 after similar HPT treatment. In [13] this difference in the deformation behavior of the alloys was explained by the fact that Ti49.3Ni50.7, Ti50.2Ni49.8 alloys have a considerably high temperature of martensitic transformation Ms (~80 °C) and possess a martensitic structure before HPT. Whereas Ti49.3Ni50.7 alloy possesses a considerably lower temperature of martensitic transformation Ms (~20 °C), and before HPT it has an austenitic structure [13]. It should be noted that during deformation the austenitic alloys Ti49.3Ni50.7, Ti49.4Ni50.6 suffer strain-induced martensitic transformation and transit into the martensitic state.

In this work the structure transformation and mechanical properties of TiNi alloys with different content (Ti50.2Ni49.8 and Ti49.4Ni50.6) after HPT and additional annealings with different temperature and time (from 5 minutes to 6 days) were studied.

2. EXPERIMENTAL PROCEDURE

The initial materials for the investigation were Ti50.2Ni49.8 alloy (made in China) and Ti49.4Ni50.6 alloy (supplied by Intrinsic Devices Inc. USA). Ti49.4Ni50.6 alloy has a certain excess of Ni with respect to stoichiometry of Ti50% - Ni 50%, and after solid solution quenching at 800 °C during the subsequent annealing the alloy ages [1-3]. The temperatures of martensitic transformations Ms of the quenched Ti49.4Ni50.6 alloy are 15 °C. The quenched alloy has B2-austenitic structure with a grain size of 30 µm at room temperature.

Ti50.2Ni49.8 alloy is a nonageing alloy. The temperature of martensitic transformations of the Ti50.2Ni49.8 alloy is about 75 °C. This alloy possesses a martensitic structure at room temperature.

After homogenization at 800 °C with subsequent water quenching, the TiNi alloys were subjected to HPT at a pressure of 6 GPa. The HPT die-set was equipped with the anvils of 20 mm in diameter with a groove 0.6 mm deep (HPT regimes are presented in more details in [14]). As it is known, the microstructure of the samples obtained by HPT can be non-homogeneous along the disc radius due to non-uniformity of deformation [4]. However, the previous investigations showed that in TiNi samples obtained by the applied HPT technique with the number of turns n=5 and over, the structure in the area from the half of the disk radius (S R) to the edge of the disk (R) can be considered as homogeneous [14-16].

Heat treatment was performed in the temperature range of 200-550 °C. Foils were prepared by twin jet polishing with the help of the 10%HClO4 +90%CH3(CHOH)2OH electrolyte to conduct electron microscopic analysis. The microstructure of the HPT samples was studied by TEM on the JEM-200CX and JEOL-2000EX microscopes. Selected area electron diffraction (SAED) patterns were taken from the areas of 0.5 µm² and 2.3 µm². The mean grain size was defined by dark-field images by averaging more than 300 grains. X-ray diffraction was measured on CoKα radiation (λ=1.78892A). X-ray diffraction (XRD) patterns were taken from an area from 1/2 R to R of the HPT disk.

The samples for mechanical tensile tests were cut out from the area ~ S R of the HPT disk. The tensile tests at room temperature were carried out on flat samples with a gage of 1×0.25×3 mm and a rate of extension 3×10⁻⁴ s⁻¹ using a specially designed tensile machine [15].

3. RESULTS AND DISCUSSIONS

X-ray diffraction (XRD) patterns of the Ti49.4Ni50.6 alloy in the initial quenched state, after HPT n=5, after HPT and annealing are represented in Fig. 1. The alloy in the initial quenched state has a B2- austenite structure (see Fig. 1). According to the XRD patterns, HPT with 5 turns leads to amorphization of the alloy. X-ray analysis displays a diffuse halo, the most intense of which is located near the 2θ of a reflection (110) B2 phase (Fig. 1). According to the XRD patterns, after HPT and annealing at 400 °C for 6 days the alloy possesses the austenitic B2 phase and martensitic B19' phase (Fig. 1). The martensitic phase can be explained by the ageing process that takes place during annealing. Due to ageing the temperature of start of the martensitic transformation B2-B19' becomes higher than room temperature [2], and as a result the martensitic phase B19' can be observed in the alloy. Probably, the reflec-
Fig. 1. X-Ray diffraction patterns of Ti$_{49.4}$Ni$_{50.6}$ alloy in initial coarse grain (CG) state after quenching; after HPT ($n=5$, $p=6$ GPa) and after HPT + annealing at 400 $^\circ$C 6 days.

The formation of ageing phases (X-phases) can also be observed on the XRD patterns after HPT and annealing. However, locations of reflections of B2, B19’ phases and X-phases coincide, which does not allow identifying the ageing phases (Fig. 1) more precisely.

TEM studies of the microstructure demonstrated the formation of an amorphous-nanocrystalline structure on the edge part of the sample Ti$_{49.4}$Ni$_{50.6}$ subjected to HPT $n=5$ (Fig. 2b). Along with separate areas of the amorphous phase, there are areas with nanocrystals in the amorphous phase. An average size of nanocrystals in the amorphous matrix was about 30 nm (in the edge part of the sample) by the dark field image (Fig. 2). A typical SAED, taken from the amorphous-crystalline part, is shown in Fig. 2b. It is observed that the intense halo of the amorphous phase overlaps the ring spots of the (110)$_{B2}$ planes. As our previous investigations showed, further increase of the strain rate of HPT up to 7 turns leads to insignificant enhancement of the volume fraction of the amorphous phase in Ti$_{49.4}$Ni$_{50.6}$ alloy [14].

Fig. 2. TEM image of the Ti$_{49.4}$Ni$_{50.6}$ alloy subjected to HPT $n=5$, $p=6$ GPa; a) centre part of the HPT sample; b) edge part of the HPT sample (dark field images and SAED).
In the central areas (where the strain degree is lower than at the edge) of the Ti$_{49.4}$Ni$_{50.6}$ samples a coarse band structure forms after HPT $n=5$, and the amorphous phase is not observed (Fig. 2a).

HPT with $n=5$ turns of Ti$_{50.2}$Ni$_{49.8}$ alloy results in the formation of an amorphous-nanocrystalline structure at the edge part and at S R (Fig. 3b). In the central parts of the HPT Ti$_{50.2}$Ni$_{49.8}$ samples a nanostructured state forms with some fraction of the amorphous phase, i.e. the structure is finer than that in HPT Ti$_{49.4}$Ni$_{50.6}$ alloy after similar deformation. Thus, it confirms the data [13] on faster amorphization during HPT of the alloy, the $M_s$ temperature of which is higher than room one (Ti$_{50.2}$Ni$_{49.8}$), as compared to the alloys with lower $M_s$ temperature (Ti$_{49.4}$Ni$_{50.6}$).

Annealing at 400 °C 5 min of the Ti$_{49.4}$Ni$_{50.6}$ alloy subjected to HPT $n=5$ results in full crystallization of amorphous phases and formation of an NC-structure with the grain size in the edge and S R parts of HPT samples of phase B2 about 15 nm. Annealing at 400 °C during 1 h leads to formation of an NC-structure B2 with an average grain size of 30 nm (Fig. 4a). The mean grain size in the HPT samples ($n=5$) at the edge and in the S R area increased up to 100-150 nm after annealing at a temperature of 400 °C during 6 days (Fig. 4b). In the SAED pattern (Fig. 4b), the B2, R and B19’ phase reflections are observed. Probably the reflections of ageing phases can also be observed on the SAED patterns. However, overlapping of the reflections of these phases and a small volume of the ageing phases do not allow identifying the ageing phases.

Fig. 3. TEM image of the microstructure of Ti$_{50.2}$Ni$_{49.8}$ alloy HPT ($n=5$, $p=6$ GPa), a) centre part of the HPT sample; b) edge part of the HPT sample; dark-field image, electron diffraction pattern.

Fig. 4. TEM structure of Ti$_{49.4}$Ni$_{50.6}$ alloy after HPT ($n=5$, $p=6$ GPa) and subsequent annealings 400 °C a) 1 hour and b) 6 days; edge parts of the HPT sample, bright field images and SAED.
The increase of 1-hour annealing temperature up to 500 °C for HPT samples Ti\textsubscript{49.4}Ni\textsubscript{50.6} leads to the grain size growth to approximately 50 nm (Fig. 5). In case of the annealing at temperature 550 °C (1 hour), a very intensive grain growth to 500 nm takes place (Fig. 6). Fig. 6b displays the SAED pattern after annealing at 550 °C (1 hour), numerous reflections are observed on it. These reflections belong to the B2 phase, martensitic B19' and R phases, and probably X-phase. The (hkl) indices of the reflections of these phases are shown in the scheme in Fig. 6b, but the closeness of the reflections of these phases does not allow univocally determining the ageing phases (Fig 6b).

Annealing at 400 °C for 1 hour of HPT Ti\textsubscript{50.2}Ni\textsubscript{49.8} alloys results in crystallization of the amorphous phase and formation of a structure with an average grain size of approximately 150 nm (Fig. 7). It should be noted that it is almost 5 times more than in case of a similar treatment of Ti\textsubscript{49.4}Ni\textsubscript{50.6} alloy. At room temperature the Ti\textsubscript{50.2}Ni\textsubscript{49.8} alloy after HPT and annealing 400 °C 1 hour is in the martensitic state (phase B19'), as it is testified by the SAED pattern and the presence of packs of nano-twins inside the grains. The length of twins is commensurable with the grain size, the width of martensitic twins is 9 nm. The formation of the martensitic structure in Ti\textsubscript{50.2}Ni\textsubscript{49.8} alloy after HPT and annealing is natural, because Ti\textsubscript{50.2}Ni\textsubscript{49.8} has a temperature of martensitic transformation of $M_s$ higher than the room temperature. It should be noted that, as it is shown in the previous works [11,19], in TiNi nanostructured alloys with a grain size less than 40 nm, the martensitic transformation B2 (austenite)→B19' is blocked. But in
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Fig. 7. TEM images of the microstructure of Ti$_{50.2}$Ni$_{49.8}$ alloy after HPT $n=5$, $P=6$ GPa and annealing at 400 °C for 1 hour; edge part of the HPT sample: bright-field image; dark-field image; SAED.

Fig. 8. TEM image of the microstructure of the quenched coarse-grained Ti$_{49.4}$Ni$_{50.6}$ alloy after annealing at 400 °C, for 1 h.

Ti$_{50.2}$Ni$_{49.8}$ alloy a considerably larger grains (about 150 nm) is formed after HPT and annealing at 400 °C. One can note that in Ti$_{50.2}$Ni$_{49.8}$ alloy with the grain (size of) ~150 nm martensitic transformation follows the mechanism of one-pack martensite formation within the boundaries of every submicron grain. Previously formation of such a structure of one-pack martensite within the boundaries of the grains of B2 phase with the size of about 100 nm was observed in [19].

As it has been observed in [13] the difference in amorphization rate during HPT of TiNi alloy of a different content (in [13] - Ti$_{50}$Ni$_{50}$ and Ti$_{49.3}$Ni$_{50.7}$) was explained by the difference of their $M_f$ and different (martensitic or austenitic) alloy state before deformation. But it is more difficult to explain the different behavior of HPT alloys Ti$_{49.4}$Ni$_{50.6}$ and Ti$_{50.2}$Ni$_{49.8}$ during annealings by different states (martensitic or austenitic) of these alloys before the deformation.

The following assumption can be made. Ti$_{49.4}$Ni$_{50.6}$ is an ageing alloy [1-3]. In the initial coarse-grained (CG) quenched Ti$_{49.4}$Ni$_{50.6}$ samples after annealing at 400 °C for 1 hour ageing particles of Ti$_{5}$Ni$_{1}$ phase of 40-50 nm are clearly observed (Fig. 8). One can suppose that precipitations of the ageing phase (Ni$_{4}$Ti$_{3}$, Ni$_{3}$Ti$_{2}$, Ni$_{3}$Ti) are also formed during low-temperature annealing and during crystallization of the amorphous phase of HPT Ti$_{49.4}$Ni$_{50.6}$ alloy. In these studies TEM did not reveal any particles of the ageing phase in the HPT samples after annealing at 400 °C or 500 °C. Probably this is caused by strong dispersability of ageing particles in HPT TiNi, which...
Fig. 9. Stress-strain curves Ti$_{49.4}$Ni$_{50.6}$ alloy after HPT ($n=5$) and subsequent annealing: 1) HPT 2) HPT + annealing at 400 °C during 5 min, 3) HPT + annealing at 400 °C, 20 min, 4) HPT + annealing at 400 °C, 60 min, 5) HPT + annealing at 400 °C during 6 days.

are apparently precipitated and distributed along the nanograin boundaries. Probably, the presence of very fine particles of Ti$_3$Ni$_4$ ageing phases on the boundaries of B2 grains restrains the grains growth during annealing at 400 and 500 °C of HPT Ti$_{49.4}$Ni$_{50.6}$ samples.

Ti$_{50.2}$Ni$_{49.8}$ alloy is a nonageing alloy. Accordingly, the ageing phase does not precipitate in HPT Ti$_{50.2}$Ni$_{49.8}$ samples during annealing, and accordingly in HPT Ti$_{50.2}$Ni$_{49.8}$ alloy the grain grows considerably (5 times) faster during applied annealings at 400 °C for 1 hour as compared to the HPT Ti$_{49.4}$Ni$_{50.6}$ samples.

Tensile tests demonstrated that formation in alloy Ti$_{49.4}$Ni$_{50.6}$ of the amorphous-nanocrystalline structure as a result of HPT $n=5$ increases ultimate tensile strength (UTS) from 1050 MPa up to 2250 MPa (Fig. 9, curve 1).

Annealing of the HPT samples $n=5$ at 400 °C for 5 min and formation of an NC structure with the grain size of about 15 nm do not decrease the UTS significantly, that is 2200 MPa, and yield stress (YS) = 2050 (Fig. 9, curve 2). Herewith, a pseudo yield plateau where deformation takes place due to deformation-induced phase transformation austenite-martensite, can be observed, when the stress achieves $\sigma_m=460$ MPa. The mechanical properties of the sample did not change considerably after annealing at 400 °C for 20 min (Fig. 9, curve 3).

HPT samples $n=5$ after annealing $T=400$ °C for 1 hour suffer brittle failure during tensile tests. Perhaps such a brittle behavior of the samples was caused by initiation of ageing processes and precipitation of embrittlement particles or segregations along nano-grain boundaries during annealing at 400 °C for 1 h (Fig. 9, curve 4). In case of short-term annealings at 400 °C (5 and 20 min) such particles or segregations, which embrittle the material, do not have time to form. During long-term annealings the particles enlarge, coagulate, and this also leads to appearance of ductility in the material.

The UTS decreased insignificantly down to 1850 MPa, YS comprised 1620 MPa after annealing at $T=400$ °C for 6 days and grain growth up to about 100 nm. The material demonstrated ductility of $\delta=28\%$, which is a high value for such a high-strength state (Fig. 9, curve 5).

In the initial quenched coarse-grained state the stress-strain curves for the Ti$_{50.2}$Ni$_{49.8}$ and Ti$_{49.4}$Ni$_{50.6}$ alloys are rather similar. As a result of HPT $n=5$ annealing at 400 °C for 1 hour and formation of a structure with the grain size of approximately 150 nm, the ultimate tensile strength of Ti$_{50.2}$Ni$_{49.8}$ alloy reaches 1660 MPa, and yield stress $\sigma_m=1550$ MPa (Fig. 10). The stress of deformation-induced martensitic transformation $\sigma_m$ reaches 300 MPa (Fig. 10). The specified mechanical properties are close to the mechanical properties of the HPT Ti$_{49.4}$Ni$_{50.6}$
alloy after annealing at $T=400$ °C for 6 days, in which the grain size is also about 100 nm.

4. CONCLUSIONS

Thus, as a result of the performed investigations, the following conclusions can be made:

1. It was revealed that in the nonageing Ti$_{50.2}$Ni$_{49.8}$ and ageing Ti$_{49.4}$Ni$_{50.6}$ alloys after HPT, an amorphous-nanocrystalline structure forms along the applied regimes. But the intensity of grain growth in Ti$_{50.2}$Ni$_{49.8}$ and Ti$_{49.4}$Ni$_{50.6}$ alloy after HPT differs during subsequent annealings. In the Ti$_{50.2}$Ni$_{49.8}$ alloy a considerably larger grain (up to 150 nm) forms after HPT and annealing at 400 °C for 1 hour than after treatment of the Ti$_{49.4}$Ni$_{50.6}$ alloy via similar regimes. The observed phenomena can be explained as well by ageing processes during HPT of Ti$_{49.4}$Ni$_{50.6}$ samples, though the ageing particles were not observed after annealing at 400-500 °C.

2. In the HPT Ti$_{49.4}$Ni$_{50.6}$ alloys after HPT and annealing at 400 °C and 500 °C for 1 hour a nanocrystalline structure with the grain size of 30 and 50 nm correspondingly forms. An unusual grain growth up to 600 nm in the HPT Ti$_{49.4}$Ni$_{50.6}$ samples was observed during annealing and 550 °C for 1 hour.

3. Tensile tests demonstrated that formation of the amorphized (amorphous-nanocrystalline with the grain size of 30 nm) structure as a result of HPT TiNi alloy increases ultimate tensile strength UTS from ~1050 MPa up to 2000 MPa. Annealing of the HPT Ti$_{49.4}$Ni$_{50.6}$ samples at 400 °C for 5 min and 20 min and formation of the nanocrystalline state with D< 20 nm do not decrease the UTS significantly. A pseudo yield plateau ($\sigma_y$) can be observed on the strain curves after these annealings. HPT Ti$_{49.4}$Ni$_{50.6}$ samples after annealing $T=400$ °C for 1 hour suffer brittle failure during tensile tests. HPT Ti$_{49.4}$Ni$_{50.6}$ samples after annealing $T=400$ °C for 6 days demonstrate ductility of $\delta = 28\%$, which is a high value for such a high strength (up to 1800 MPa). HPT Ti$_{50.2}$Ni$_{49.8}$ samples after annealing $T=400$ °C for 1 hour demonstrate the mechanical properties that are similar to the properties of the Ti$_{49.4}$Ni$_{50.6}$ alloy after HPT and annealing at 400 °C for 6 days.

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