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Effect of HPT and accumulative HPT on structure formation and microhardness of the novel Ti18Zr15Nb alloy

D. Gunderov, S. Prokoshkin, A. Churakova, V. Sheremetyev, I. Ramazanov

Effect of HPT and accumulative HPT on the Ti18Zr15Nb biomedical alloy has been studied. According to the XRD and TEM data, the β-phase is a main phase in the alloy both in the initial state and after processing by HPT and accumulative HPT. The β-phase X-ray line width after HPT processing, and especially after ACC HPT processing has drastically increased as a result of an increase in defect concentration and grain refinement. According to TEM, the grains after HPT processing for n = 10 revolutions are refined in some regions down to 10–30 nm. As a result of HPT processing, the alloy’s microhardness has noticeably increased, which indicates an increase in strength and yield stress together with the preservation of the β-state.

1. Introduction

Titanium and its alloys are the most preferred materials for medical implants [1]. Especially promising are ternary and quaternary Ti-(Nb, Zr)-based shape-memory alloys (SMAs) [2–4]. These alloys, composed of non-toxic components, exhibit a unique combination of high biomechanical compatibility (low Young’s modulus and superelastic behavior) with excellent corrosion resistance. It is known that conventional thermomechanical treatment, due to the control of the structure of Ti-Zr-Nb SMAs, reduces Young’s modulus, functional fatigue resistance, and increases strength [5,6]. However, an additional increase in the strength characteristics of these alloys is necessary. It was demonstrated in [7,8] that the formation of the nanostructured state in pure titanium by means of severe plastic deformation (SPD) processing enables a considerable enhancement in its properties.

The SPD technique of high-pressure torsion (HPT) enables the strongest refinement of the material structure [9,10]. During the HPT processing of Ti-Ni shape-memory alloys, first, grain refinement to the nanocrystalline range is observed, followed by amorphization [11–13]. During the HPT processing of the low-modulus β-Ti alloy Ti-15Mo, a decrease in the size of β-grains/subgrains to 80 nm is observed, and the α′-phase appears at the early stages of HPT. In some β-Ti alloys of the Ti-Mo and Ti-Nb-Zr system grain refinement to 50 nm was revealed during HPT processing, while the alloys remained predominantly in the β-phase [13–16].

However, studies into the effect of HPT processing on the Ti-18Zr-15Nb alloys with improved superelastic properties have not been conducted yet. In addition, it has been demonstrated earlier that the HPT processing of high-strength materials actually produces a much smaller strain than expected, as a result of slippage [17,18]. In this context, an original “accumulative high-pressure torsion” (ACC HPT) procedure was proposed in [19] which enables producing much higher true strains in solid metallic materials than the regular HPT technique. In the present work, ACC HPT was first applied to the novel Ti18Zr15Nb SMA.

2. Experimental

A 15 kg ingot of the Ti-18Zr-15Nb (at.%) alloy produced by vacuum arc remelting was used. To eliminate the initial cast structure, the ingot was subjected to multi-axis forging at a billet heating temperature of 1050 °C.

The HPT die-set was equipped with anvils 20 mm in diameter with a 0.4 mm-deep groove. The HPT processing was conducted at a pressure of 6 GPa, and the number of revolutions was n = 1, 5 and 10. In the “accumulative HPT” procedure, at the first stage, a sample was subjected to HPT for n = 2. A disk with a thickness of h ≈ 0.6 mm © 20 mm was obtained. At the second stage, this HPT disk was cut into 4 segments, these segments were stacked on the HPT anvils on top of each other and HPT n = 2 was performed again and disk the same size was obtained again. Correspondingly,
the sample experienced large compressive strains in addition to torsional strains. The cycles of “accumulative HPT” $n = 2$ were repeated 3 times. At the 4th stage, the produced HPT disk was again cut into 4 parts, the segments were stacked the HPT cycle was repeated with $n = 4$, and a solid HPT disk was obtained. The total number of revolutions during “accumulative HPT” processing was $n_{\text{acc}} = 10$. It can be asserted that the total strain produced during “accumulative HPT” processing due to the summation of compressive and torsional strains was much larger than that during conventional HPT processing.

The structure and phase composition were studied using X-ray diffractometry (Rigaku Ultima IV) under Cu-Kα radiation. The microhardness measurements were performed using Durascal-50 (load 100 g, time 10 s). The fine structure of the samples was studied using a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV.

3. Results and discussion

The obtained X-ray diffractograms are presented in Fig. 1, while Table 1 contains some parameters extracted from the diffraction profiles.

Analysis of the XRD data shows that the BCC $\beta$ is a main phase constituent in the initial hot-forged condition. Very weak diffraction lines of the secondary $\alpha''$-martensite phase formed as a result of the cooling- or stress-induced $\beta \rightarrow \alpha''$ transformation are also visible (Fig. 1). The $\{110\}_\beta$ X-ray line width of about 0.3° is pronouncedly larger than that usually observed in analogous quenched alloys (about 0.2°) [20] indicating an increased dislocation density in the hot-deformed $\beta$-phase. The $\beta$-phase lattice parameter of 0.3341 nm (Table 1) correlates well with that regularly observed for this alloy [2]. The maximum transformation lattice strain $\varepsilon_{\text{max}}$ which is a theoretical (crystallographic) limit of recovery strain was calculated on the basis of the angular coordinates of $\{020\}_\alpha$ and $\{110\}_\beta$ in accordance with [4]. The obtained $\varepsilon_{\text{max}}$ value of 5.0% (Table 1) correlates well with that observed earlier in analogous alloys [4]. The phase composition after HPT processing is generally preserved up to the highest torsional strain (Fig. 1). The X-ray line width of the $\beta$-phase abruptly increases after HPT processing for $n = 1$ and then gradually grows with increasing strain (Table 1, Fig. 1) pointing to an increase in the dislocation density or/and grain refinement. The largest increase in the X-ray line width is observed after the ACC HPT which produces the largest strain (Table 1). The corresponding $B_{110\beta}$ of 1.12° is, however, much smaller than that in a Ti-Ni SMA (about 5°) after HPT processing via comparable regimes [21]. As the Ti-Ni SMAs undergo amorphization under HPT conditions [22], it is reasonable to assume that amorphization does not play a significant role for the Ti18Zr15Nb SMA under such conditions. Thus, the Ti18Zr15Nb SMA demonstrates an exceptional stability of the $\beta$-phase under enormous strains.

The bright-field (BF) and dark-field (DF) images, as well as the SAED patterns of the Ti-Zr-Nb SMA observed after the initial treatment are presented in Fig. 2a, b. Analysis of the TEM images reveals a recrystallized grain structure of the $\beta$-phase (Fig. 2a) with a grain size of about 5–10 μm. The grains contain an increased dislocation density obviously preserved during cooling after hot deformation. This correlates with the above-mentioned increased X-ray line width. A slight azimuthal broadening of the reflexes in the SAED patterns also indicates the increased dislocation density which is the reason for the appearance of the imperfect orientation of the crystal lattice in the selected area. Rare plate-like crystals surrounded by the $\beta$-phase matrix (Fig. 2b) represent $\alpha''$-martensite whose very weak X-ray lines are present in the X-ray diffraction pattern as well (see Fig. 1).
The main structure constituent after HPT processing is a nanocrystalline structure (Fig. 2c). The nanocrystalline structure represents wide fields of a nanograined structure (NGS) consisting of grains 10–30 nm in diameter surrounded by high-angle boundaries. The NGS fields contain rare inclusions (about 100 nm in size) of a nanosubgrained structure (NSS) which consists of several closely oriented (i.e. separated by low-angle subboundaries) subgrains (Fig. 2c). Typical NGS and NSS features are described in detail elsewhere [23]. The corresponding SAED pattern consists of only β-phase diffraction rings formed by strongly overlapped individual reflexes from individual grains of the NGS with superimposed arc-wise reflexes from the NSS. Another structure constituent is the NSS mixed with the highly dislocated substructure from which it cannot be distinguished visually (Fig. 2d). The corresponding SAED pattern consists mainly of only β-phase arc-wise reflexes where the maximum azimuthal broadening is low-angle (<15°). The presence of α″-martensite is demonstrated in Fig. 2e which shows that the α″-martensite is present in two structure 

Table 1
Results of the XRD study and microhardness of Ti-Zr-Nb alloy at different conditions.

| Treatment          | X-ray line width B110°*, deg. | β-phase lattice parameter a₀*, nm | Maximum transformation lattice strain e max, % | Microhardness, HV [±8] |
|--------------------|--------------------------------|---------------------------------|---------------------------------------------|------------------------|
| Initial            | 0.31 ± 0.02                    | 0.3341 ± 0.0002                 | 5.0 ± 0.2                                   | 265                    |
| HPT, n = 1         | 0.84 ± 0.05                    | –                               | –                                           | 325 365 360            |
| HPT, n = 5         | 0.93 ± 0.06                    | –                               | –                                           | 333 385 390            |
| HPT, n = 10        | 0.98 ± 0.06                    | –                               | –                                           | 300 345 355            |
| ACC HPT, n = 10    | 1.12 ± 0.05                    | –                               | –                                           | 315 330 330            |

*In the case of HPT, any acceptable extrapolation is impossible for methodological reasons.

**The line width B110° of β-phase is somewhat overestimated in most cases due to superimposition of secondary phase lines.

![Fig. 2. Structure of the Ti-18Zr-15Nb alloy after the initial hot forging (a, b) and HPT for n = 5 (c-e). Transmission electron microscopy.](image-url)
modifications (NGS and NSS), as well as the β-phase. The TEM studies of the structure after ACC HPT processing will be performed in the future (they have been suspended due to COVID-19).

As a result of HPT processing, the microhardness grows noticeably (Table 1). In the center of the samples processed by HPT for \( n = 1 \) revolution, the microhardness is considerably lower than in the region \( \frac{1}{2}R \) and at the sample edge. After HPT processing for \( n = 5 \), HV somewhat increases both in the center and at the edge. However, as the number of revolutions increases above \( n > 5 \), HV does not increase further and even slightly declines after ACC HPT processing for \( n = 10 \). This result is unusual and calls for additional investigations and analysis. The increment in the microhardness after HPT processing indicates an increase in strength and yield stress together with the preservation of the β-state, and opens up prospects for improving functional properties of the alloy.

4. Conclusions

According to the XRD and TEM data, the β-phase is a main phase in the Ti-18Zr-15Nb alloy both in an initial state and after processing by HPT and accumulative HPT, and the β-phase in the Ti-18Zr-15Nb alloy is stable under large strains. The width of the β-phase X-ray lines after HPT processing, and especially after ACC HPT processing has drastically increased as a result of an increase in defect concentration and grain refinement. According to TEM, the grains after HPT processing for \( n = 10 \) are refined in some regions down to 10–30 nm. As a result of HPT processing, the microhardness has noticeably increased, which indicates an increase in strength and yield stress together with the preservation of the β-state.

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CRediT authorship contribution statement

D. Ganderov: Methodology, Writing - original draft. S. Prokoshkin: Methodology, Writing - original draft. A. Churakova: Investigation, Writing - review & editing. V. Sheremetyev: Investigation. I. Ramazanov: Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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