The effect of combined thermomechanical treatment on the structure, phases and hardness of a superelastic Ti-Zr-Nb bar stock

V Sheremetyev¹, A Kudryashova¹, M Derkach¹, K Lukashevich¹, V Andreev², S Galkin¹, S Prokoshkin¹ and V Brailovski³

¹National University of Science and Technology “MISiS”, Moscow, Russia
²Baikov Institute of Metallurgy and Materials Science, RAS, Moscow, Russia
³Ecole de technologie superieure, Montreal, QC, Canada

E-mail: sheremetyev@misis.ru

Abstract. The superelastic Ti-19Zr-14Nb (at.%) alloy was subjected to a novel sequence of thermomechanical treatment, including radial shear rolling, rotary forging and post-deformation annealing. The features of the grain structure, phase composition and hardness of a long-length bar stock for fabrication of bone implants were analyzed. It was shown that after the aforementioned combined thermomechanical treatment followed by annealing in the 550-750 °C temperature range, the produced bar stock demonstrates uniformly distributed grains of β-phase and uniform hardness across its section.

1. Introduction

An increasing interest in metastable β-Ti alloys as promising materials for load-bearing implants, is caused by two main features: superelasticity and the absence of toxic elements in their composition [1, 2]. The superelasticity of these alloys is due to stress-induced reversible martensitic transformation from body center cubic β-phase to orthorhombic α′-phase [1]. These alloys exhibit high strength, good corrosion resistance, a relatively low Young’s modulus, and excellent biocompatibility [1-3]. Ti-Zr-Nb alloys have been particularly investigated due to their large (up to 7%) transformation strain and, therefore, outstanding superelasticity [4].

It is known that thermomechanical treatment (TMT) is an effective technique to improve the mechanical and functional properties of shape memory alloys via the control of their microstructure and phase composition [5]. For example, traditional TMT including cold rolling (ε=0.3) and post-deformation annealing (PDA) led to the formation in Ti-Zr-Nb alloys of a polygonized dislocation substructure of β-phase with nano- to submicrometer-sized subgrains and to stable functional fatigue behavior with a Young’s modulus as low as 30-40 GPa [6]. It was also shown that combining hot radial shear rolling (RSR) and hot and cold rotary forging (RF) allows manufacturing bar stocks with a dynamically polygonized substructure of β-phase, homogeneous across-the-section grain size distribution and superior functional fatigue behavior [7]. Thus, the consistent application of the RSR, RF, and PDA operations to Ti-Zr-Nb alloys looks like a promising way to produce long-length bar stock with an optimal combination of phase composition, microstructure and functional properties. In
this study, the effect of such a combined TMT on the phase composition, structure and mechanical properties of a Ti-19Zr-14Nb bar stock is investigated.

2. Experimental procedure
A 20 kg-weight, 55 mm-diameter Ti-19Zr-14Nb (at.%) ingot was produced by vacuum arc remelting and isostatically-pressed (900 °C, 100 MPa, 2 h). The ingot was cut and subjected to hot radial melting at 900 °C using “14-40” and “10-30” rolling mills to form a 11.5 mm-diameter bar stock (an accumulated true strain of \( e=3.2 \)). The bar was then subjected to hot rotary forging at 600 °C using an RKM-2 forging machine to form a 7.8 mm-diameter bar (\( e=0.8 \)). After both the RSR and RF operations, the bars were air-cooled. The hot-forged bar was then subjected to room temperature RF to form a 6.6 mm-diameter bar stock (\( e=0.3 \)). Next, the bar was straightened and ground to obtain a 6.0 mm-diameter bar stock. Samples for structural characterization and hardness measurements were cut from the bar stock and annealed for 0.5 h in argon atmosphere in the 500 to 750 °C temperature range, and then water-quenched. The cross-section surfaces of the RF and RF+PDA samples were prepared using an ATM Saphir 560 grinding and polishing machine. Specimens for optical microscopy and X-ray diffractometry were mechanically polished and then etched in 1HF:3HNO\(_3\):6H\(_2\)O solution to remove a damaged surface layer.

The microstructure of the alloy and its phase composition before and after TMT were studied using a Union Versamet-2 Union optical microscope equipped with a Nikon D90 camera and a PANalytical X’pert Pro X-ray diffractometer. The lattice parameters of the studied phases were calculated from the angular coordinates of the \( \beta \) and \( \alpha'' \)-phase XRD peaks. The maximum \( \beta\rightleftharpoons\alpha'' \) transformation lattice strain (\( e_{\text{max}} \)), which corresponds to a theoretical recovery strain limit, was calculated from the lattice parameters of the \( \beta \) and \( \alpha'' \)-phases, using the methodology described in [7]. Hardness was measured using a Metkon microhardness tester with an applied load of 1 kg and a loading time of 10 sec.

3. Results and discussion
The metallography images obtained after different RF+PDA combinations and the corresponding average grain size values \( d \) are shown in figure 1. It can be seen that immediately after RSR+RF, microstructure formed in the bar stock is heterogeneous across the section. It is well known, that during RSR, metal flows helicoidally, thus forming a very peculiar deformed state with a characteristic inhomogeneity [7-9]. In this case, the microstructure of the peripheral zone is composed of grains with an average size of \( d=6 \) \( \mu \)m (figure 1a). When moving to the center, in the intermediate zone, the average grain size increases to \( d=9 \) \( \mu \)m (figure 1b), and finally, in the central zone, to \( d=13 \) \( \mu \)m (figure 1c). After PDA at 550 °C, a significant amount of small statically recrystallized grains can be observed on the local scale, but the initially heterogeneous microstructure is preserved (figure 1d-f).

With an increase of the PDA temperature to 600 °C, the recrystallization process extends over the entire cross-section of the bar stock (figure 1g-i). PDA at 750 °C leads to an intensive grain growth, and the grain distribution across the section line becomes uniform (figure 1j-l).
The X-ray diffractograms obtained directly after RF, and then after RF+PDA at different temperatures, are shown in figure 2a. The main phase constituent in all the cases is BCC $\beta$-phase. After PDA in the 500-525 °C range, a certain amount of cooling- or annealing-induced $\alpha$-phase is also observed. After cold RF and PDA in the 525-600 °C range, $\alpha''$-martensite lines are observed. The lattice parameters of the $\beta$- and $\alpha''$-phases, as well as the crystallographic limit of the recovery strain, are presented in table 1. The recovery strain value is limited to $\sim$5.9% irrespective of the TMT route. The evolution of the level of lattice defects after various treatments was evaluated from the changes in the $\beta$-phase half-width X-ray lines (figure 2b). Immediately after cold RF, the $\beta$-phase X-ray diffraction lines are strongly broadened, thus reflecting significant lattice defectness and substructural hardening of the material. With an increase of the PDA temperature from 500 to 750 °C, the width of the $\beta$-phase lines first decreased rapidly from RT to 525 °C, and then monotonically, from 550 to 750 °C.
These observations can be interpreted as the results of polygonization (500-550 °C), and recrystallization (550-750 °C) processes occurring in Ti-Nb-Zr SMA during post deformation annealing after cold rotary forging [6], which correlate well with the results of optical microscopy. Note that directly after RF, the {200}β X-ray line is not narrower than the {211}β X-ray line, whereas after PDA at 500 °C, the width of the former drops far below the width of the latter. These observations correlate with a transition from a highly dislocated work-hardened substructure to a polygonized (subgrained) dislocation substructure of β-phase during the polygonization process, like it was observed in Ti-Ni SMA earlier [9].

The results of hardness measurements are presented in figure 3. After RF, the alloy exhibits the most hardened state. Additional PDA in the 500-550 °C range leads to rapid alloy softening and then in the 600-750 °C range, to stabilization of HV values (figure 3a). These hardness behavior correlates well with changes in the β-phase line widths related to the polygonization and recrystallization processes. Figure 3b demonstrate heterogeneous distribution of hardness across the section of bar stock after RF and RF+PDA (500-525 °C), which can be explained by different structure states at different points of the cross-section line (see figure 1a, b, c). After PDA at 550-750 °C, the formation of a homogeneous grain structure due to the process of recrystallization results in the leveling of the mechanical properties along the cross-section (figure 3b).
Figure 3. Results of hardness measurements of Ti-Zr-Nb alloy after RF and RF+PDA: HV vs PDA temperature (a), HV measured at different radial positions along the bar stock cross-section (b).

4. Summary
As a result of applying combined thermomechanical treatment, which comprises hot radial shear rolling and hot and cold rotary forging operations, to the superelastic Ti-19Zr-14Nb alloy, a strongly non-uniform microstructure was formed across the bar stock section with a subsequent non-uniform distribution of the mechanical properties. After post deformation annealing of the deformed alloy in the 550-750 °C temperature range, the cross-section β-phase grain and hardness distributions become uniform, and the bar stock semi-product becomes acceptable for implant manufacturing.

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