Study of the deformation behavior and structure formation of Ti-Zr-Nb shape memory alloy

V A Sheremetyev¹, O Akhmadkulov¹, V S Komarov¹, A V Korotitsky¹, S P Galkin¹, V A Andreev²,³ and S D Prokoshkin¹

¹National University of Science and Technology “MISiS”, Moscow, Russia
²Baikov Institute of Metallurgy and Materials Science, RAS, Moscow, Russia
³MATEK-SMA Ltd., Moscow, Russia

E-mail: sheremetyev@misis.ru

Abstract. The deformation behavior and structure formation of the Ti-19Zr-14Nb (in at. %) shape memory alloy have been studied. The as-cast ingot was subjected to multi-axis forging at a billet heating temperature of 1050 °C and then to rotary forging at 600 °C. Plastometric compression tests of the forged alloy were carried out at a strain rate 0.1 s⁻¹ at temperatures of 600-1000 °C, the strain degree is not more than 0.7. The obtained flow curves and the results of studying the grain structure and hardness were used to determine the features of the thermomechanical behavior of the material. The study of the microstructure showed that under these processing conditions, the processes of dynamic polygonization and dynamic recrystallization occur simultaneously. According to the obtained hardness measurement results, it can be assumed that in order to achieve a low Young's modulus and perfect superelastic behavior, deformation must be carried out at temperatures of 700-800 °C.

1. Introduction

Currently, one of the most intensively developing areas of scientific and technical activity is the development of technologies for the manufacturing of metallic materials for medical application. The need for biomaterials with high strength, low elastic modulus of elasticity and high biocompatibility has led to the development of new titanium-based alloys. Shape memory alloys (SMA) based on Ti-Zr-Nb system are promising materials for the bone implants fabrication due to their high biomechanical compatibility, which is due to the low Young's modulus and superelastic behavior similar to the mechanical behavior of bone tissue [1-4].

Thermomechanical treatment (TMT) of these alloys is a key tool for control the structural-phase state and thus improves the functional properties of these alloys [3, 5-7]. It was shown that the low-temperature TMT of the Ti-18Zr-14Nb alloy results in the formation of polygonized substructure of β-phase with an average subgrain size of 100-300 nm. The alloy in this structural state shows an improved combination of static functional properties, including a low Young's modulus (37 GPA) and a large difference between dislocation and transformation yield stresses [8]. On the other hand, this alloy with a mixed dynamically polygonized and dynamically recrystallized structure induced by hot deformation, demonstrates a 1.5-times or more increased functional fatigue resistance compared to the structure formed as a result of static processes during low-temperature TMT [9].
The TMT technology of Ti-Zr-Nb alloys which makes it possible to obtain semi-products suitable for the manufacturing of bone implants, needs to be developed and optimized. This can be most effectively implemented by using a combination of physical and mathematical modeling of the TMT processes [10-12]. Physical modeling makes it possible to obtain rheological models of material deformation behavior under various temperature and strain rate conditions, while mathematical modeling is very effective for studying the features of plastic deformation using a specific method of [11-13]. The study of the processes of structure formation in the course of physical modeling provides additional information that allows predicting the structural-phase state of the material.

The purpose of this work was to study the deformation behavior and structure formation of the Ti-Zr-Nb alloy under various temperatures simulating metal forming processes to identify favorable TMT conditions.

2. Experimental

A 30 kg ingot of the Ti-19Zr-14Nb (in at. %) alloy produced by vacuum arc remelting was used. The melting of the alloy provided low amount of impurities (O < 0.05, C < 0.01, N < 0.01, H < 0.01 in wt. %). To eliminate the initial cast structure, the ingot was subjected to multi-axis forging at a billet heating temperature of 1050 °C. Then a 6 mm bar stock was fabricated by multi-pass rotary forging at 600 °C with a total cumulative strain $\varepsilon \approx 2.5$ using an “RKM-2” forging machine. Samples with a diameter of 5 mm and a height of 10 mm were cut from the bar stock.

Plastometric tests with a true strain of $\varepsilon = 0.7$ were performed in the temperature range of 600-1000 °C at strain rate of 0.1 s$^{-1}$ using the complex of physical modeling of plastic deformation. To reduce the influence of surface friction forces, a lubricant based on graphite and boron nitride was used. To ensure deformation under isothermal conditions, samples were heated and deformed in steel cups with tungsten carbide strikers and a hole for a thermocouple. Following the deformation, samples were immediately cooled in water. Processing of obtained data, building of flow curves and their adjustment for friction, temperature and strain rate was carried out using the AUK specialized software.

The deformed samples were cut along the axis of the load direction, mechanically polished, and then etched in a Kroll etching solution with 10% HF, 30% HNO$_3$, and 60% H$_2$O$_2$ and were prepared for metallographic analysis. The microstructure was studied using a Versamet-2 Union light microscope in different deformation zones. The obtained images were used to calculate the average grain size by the linear intercept method. The hardness of the samples was measured using a Metkon Metallography hardness tester for at least 5 measurements per each deformation zone under a load of 1 kg and holding time 10 s.

3. Results and discussion

3.1. Plastometric tests

The flow curves of the Ti-Nb-Zr alloy at a strain rate of 0.1 s$^{-1}$ and in the temperature range under study are shown in figure 1a. At these temperatures, the alloy is located in a single $\beta$-phase region before compression deformation. The shape of the flow curve can be used to define the process of dynamic softening. At temperature of 600 °C, the curves show an unclear smooth maximum. An increase in temperature in the 700 to 900 °C range leads to an early achievement of the critical deformation $\varepsilon_{\text{max}}$ which corresponds to the maximum flow stress (figure 1b). It can be assumed, that the recovery and/or polygonization processes predominantly occur at 600 °C, and the recrystallization process at 700-900 °C. In this context, the recovery is regarded as a combination of point defect redistribution and annihilation, and redistribution of dislocations without formation of new subboundaries; the polygonization is regarded as a formation of new perfect subboundaries, subgrains, and subgrain growth. During deformation at 1000 °C the $\varepsilon_{\text{max}}$ increase. It should be noted, however, that in all cases except 1000 °C a barrel-shaped specimen is formed as a result of deformation (figure 1b). As a result of deformation at 1000 °C, a specimen is formed with broadenings closer to the
ends and a thick white-gray oxide layer. These circumstances prevent direct comparison of the flow curve with the curves obtained at other temperatures. Note that according to the flow curves, in all cases, no distinct steady-state stage was revealed. This thermomechanical behavior of the alloy may indicate its tendency to localize deformation during TMT.

![Graph](image1)

**Figure 1.** Flow curves at different temperatures at the strain rate of 0.1 s\(^{-1}\) (a); the dependence of the maximum deformation stress \(\sigma_{\text{max}}\) and the critical strain degree \(e_{\text{max}}\) on the deformation temperature (b).

### 3.2. Microstructure examination

The microstructure of the initial (as-forged) and deformed Ti-Zr-Nb alloy according to three different zones of the sample is presented on figure 2. In initial state, a mixed dynamically polygonized and dynamically recrystallized structure with the average grain size about 15 μm is observed (Figure. 2a), which correlates well with the data of [9]. The plastometric tests lead to a monotonic increase in the average grain size from 15-20 to 175-260 μm and from 10-15 to 70-85 μm perpendicular to the compression direction and along the compression direction, respectively, with increasing temperature from 600 to 1000 °C (figures 2 and 3). The elongated and equiaxed grains are observed in the structure of central part of the localized deformation zone after tests at all temperatures. It can be assumed that the process of dynamic polygonization in the alloy during deformation proceeds up to high temperatures. It also should be noted that at these temperatures, static recrystallization and grain growth can occur during heating.

### 3.3. Hardness measurements

Figure 4 represents the results of hardness measurements of samples in the initial forged state and after plastometric tests. In the initial as-forged state, the alloy hardness is around 210 HV. After compression tests at 600 °C, the hardness does not change. An increase in the deformation temperature has led to reduction of hardness down to about 195 HV in the 700-900 °C temperature range. It is associated with dynamic softening processes (recovery, polygonization and recrystallization) with an increase in the deformation temperature. Another reason for the HV reduction can be related with the \(\alpha''\leftrightarrow\beta\) transformation phenomena and the corresponding softening of the crystal lattice which contributes to a decrease in Young's modulus and improvement of superelastic behavior [5, 9]. The transformation behavior requires additional study of the alloy after treatments at these temperatures. After deformation at 1000 °C, the hardness tends to increase in two zones of the samples located close to the surface (figure 4a,c). This tendency is explained by saturation with gas-forming impurities in near-surface layer, which can lead to embrittlement.
Figure 2. Microstructure of samples initial state (a) and after deformation in 3 zones: zone of annular tangential tensile stresses (b, e, h, k, n), central part of the localized deformation zone (d, g, j, m, p), localized deformation zone (c, f, i, l, o).
4. Conclusion
The deformation behavior and structure formation of the Ti-19Zr-14Nb (at.%) alloy have been studied in the compression temperature range of 600 to 1000 °C at strain rate of 0.1 s⁻¹. It is shown that the process of dynamic polygonization occurs in the entire deformation temperature range. In the temperature range of 800-1000 °C, dynamic recrystallization is a main mechanism of microstructural evolution, accompanied by dynamic polygonization. Based on the hardness measurements, it can be assumed that to get a low Young's modulus and perfect superelastic behavior, deformation should be carried out at temperatures of 700-800 °C.

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References
[1] Geetha M, Singh A K, Asokamani R and Gogia A K 2009 Progress in Materials Science 54(3) 397
[2] Kim H Y, Fu J, Tobe H, Kim J I and Miyazaki S 2015 Shape Memory and Superelasticity 1 107
[3] Sheremetyev V A, Kudryashova A A, Dinh S T, Galkin S P, Prokoshkin S D and Brailovsky V 2019 *Metallurg* **1** 45 (in Russian)

[4] Laheurte P, Prima F, Eberhardt A, Gloriant T, Wary M and Patoor E 2010 *Journal of the Mechanical Behavior of Biomedical Materials* **3**(8) 565

[5] Prokoshkin S, Brailovski V, Dubinskiy S, Zhukova Y, Sheremetyev V, Konopatsky A and Inaekyan K 2016 *Shape Memory and Superelasticity* **2**(2) 130

[6] Nunes A R V, Borborema S, Araújo L S, Malet L, Dille J, and de Almeida L H 2020 *Journal of Alloys and Compounds* **820** 153078

[7] Hao Y L, Niinomi M, Kuroda D, Fukunaga K, Zhou Y L, Yang R and Suzuki A 2003 *Metallurgical Materials Transactions A* **34**(4) 1007

[8] Sheremetyev V, Kudryashova A, Dubinskiy S, Galkin S, Prokoshkin S and Brailovski V 2018 *Journal of Alloys and Compounds* **737** 678

[9] Kudryashova A, Sheremetyev V, Lukashevich K, Cheverikin V, Inaekyan K, Galkin S, Prokoshkin S and Brailovski V 2020 *Journal of Alloys and Compounds* **843** 156066

[10] Akopyan T K, Gamin Y V, Galkin S P, Prosviryakov A S, Aleshchenko A S, Noshin M A, Koshmin A N and Fomin A V 2020 *Materials Science and Engineering A* **786** 139424

[11] Hadasik E, Kuziak R, Kawalla R, Adamczyk M, Pietrzyk M 2006 *Steel Research International* **77** 927

[12] Gamin Y, Akopyan T, Koshmin A, Dolbachev A, Aleshchenko A, Galkin S P and Romantsev B A 2020 *International Journal of Advanced Manufacturing Technology* **108**(3) 695

[13] Xuan T D, Sheremetyev V A, Kudryashova A A, Galkin S P, Andreev V A, Prokoshkin S D and Brailovski V 2020 *Izvestiya vuzov. Non-ferrous metallurgy* **2** 22 (in Russian)