

Hot deformation processing of Ti–Zr–Nb biomedical alloys

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Abstract: Hot deformation is a promising approach for modification the microstructure of metallic materials, as it combines the simultaneous action of elevated temperature and mechanical loading. Under these conditions, intense plastic flow increases the density of crystal lattice defects and promotes dynamic recrystallization, resulting in grain refinement and a corresponding increase in the grain boundary density. Since grain boundaries serve as effective vacancy sinks, the formation of such deformed and recrystallized microstructures enhances vacancy diffusion and activates pore elimination, thereby promoting densification and the formation of low-porosity or nearly fully dense materials.

Keywords: TITANIUM ALLOY, POWDER METALLURGY, HOT DEFORMATION

1. Introduction

Ti-Nb-Zr alloys have attracted considerable attention for biomedical applications, including orthodontic archwires, bone fixation plates, and vascular stents, owing to their excellent corrosion resistance, high strength, and favorable elastic properties [1-3]. The addition of zirconium to titanium enhances the mechanical performance of these alloys while maintaining excellent corrosion resistance and biocompatibility [4, 5]. A key requirement for metallic implant materials is a low Young's modulus, ideally approaching that of human cortical bone (approximately 30 GPa), in order to minimize the stress shielding effect and promote long-term implant performance [6-7]. Previous studies have demonstrated that alloying Ti-Zr alloys with a sufficient amount of the β -stabilizing element niobium significantly reduces the Young's modulus to approximately 50-60 GPa. This reduction is primarily attributed to the formation and stabilization of the β body-centered cubic (BCC) Ti-Zr-Nb phase [8-10].

It is well known that in powder metallurgy production pore elimination gradually slows during the final stage of sintering and eventually ceases because pore coalescence becomes the prevailing process without reducing the total pore volume. This behavior is explained by the Slyozov mechanism [20]. According to this mechanism, the vacancy flux from the pore system to vacancy sinks is redirected from smaller to larger pores within the same grain. As a result, larger pores grow at the expense of smaller ones, leading to pore coarsening rather than further densification. Therefore, enhancing pore elimination requires increasing the density of effective vacancy sinks, such as grain boundaries and dislocations, which promote vacancy migration and facilitate continued densification.

Thermomechanical processing is one of the most effective approaches for tailoring the microstructure of metallic materials and enhancing their mechanical and physical properties. This approach is also applicable to alloys produced by the powder metallurgy route employed in the present study. Accordingly, additional deformation processing at room and elevated temperatures offers a promising strategy for reducing the residual porosity of the synthesized Ti-Zr-Nb alloys while improving their mechanical performance. Therefore, this section examines the effect of cold and hot deformation on the microstructural evolution, densification, and resulting mechanical properties of the synthesized alloys.

2. Materials and methods

Due to promising mechanical properties there were investigated two biomedical materials: 59Zr-19Ti-22Nb and 35Zr-39.5Ti-25.5Nb. They were manufactured using powder metallurgy methods. The starting materials were zirconium hydride powders ZrH_2 and titanium TiH_2 with a size of less than 100 microns and niobium metal powder with a size of less than 63 microns. The mixing process of the corresponding elements took place for six hours. The compaction of the mixtures was carried out by cold pressing in steel molds. The pressing pressure was 650 MPa. The resulting compacts were sintered at a temperature of 1250°C with a

subsequent holding time of 4 hours, after which they were cooled together with the furnace.

There were used sintered samples of parallelepiped shape with a length of ~ 60 mm, a width of ~ 20 mm and a thickness of ~ 9 mm for hot pressing. Pressing was carried out at a temperature of 900°C and a pressure of 780 MPa.

3. Results

The microstructure shown in Fig. 1 indicates that the investigated materials are characterized by a significant level of porosity. Therefore, hot deformation was employed as an additional processing method to modify the microstructure and reduce the residual porosity of the materials. The material is simultaneously exposed to mechanical stresses and high temperature with intense metal flow and an increase in the defectivity of its crystal structure, which causes the development of recrystallization processes with a decrease in grain size and a corresponding increase in the density of grain boundaries. Since grain boundaries are sinks for vacancies, the creation of such deformed and recrystallized structural states activates the processes of pore healing, contributing to the achievement of low-porosity or practically non-porous structures.

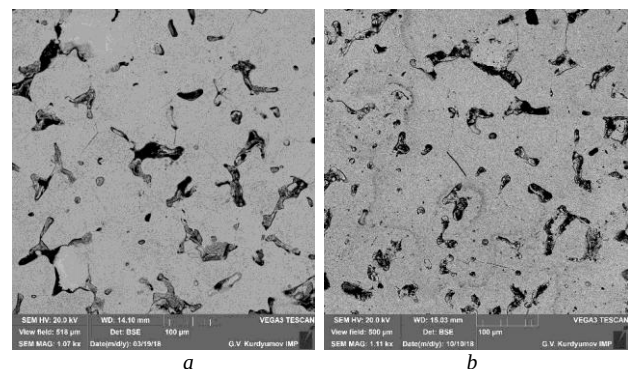


Fig.1. As-sintered microstructures of 59Zr-19Ti-22Nb (a) and 35Zr-39.5Ti-25.5Nb (b) alloys.

For these alloys, deformation values of the order of 55-65% can be achieved in one cycle of heating to 900 °C with a load. Fig.2 shows that already at deformation levels of about 30%, porosity is significantly reduced, individual, significantly deformed grains are visible in the microstructure and signs of recrystallization processes appear. Thus, along with relatively large grains (of the order of 100-140 µm), which were formed during the synthesis of alloys, there are smaller grains (40-50 µm), formed as a result of recrystallization. In addition, it was recorded that, in addition to a decrease in the volume fraction of pores (up to 2%), their size also decreases (up to 10-20 µm).

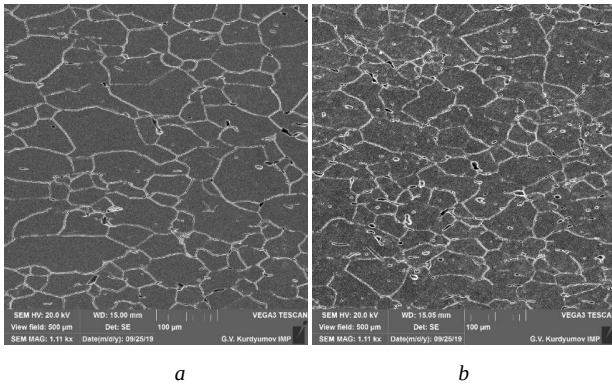


Fig.2 Microstructures of the 59Zr–19Ti–22Nb (a) and 35Zr–39.5Ti–25.5Nb (b) alloys after hot pressing at 900 °C with a deformation degree of 30%.

At deformation levels of 40–55% (fig.3), the volume fraction of pores decreases to approximately 1–1.5%. At the same time, a substantial increase in the fraction of recrystallized grains is observed compared with deformation levels of up to 30% (fig.2). It should be noted that the evolution of deformation and recrystallization processes is strongly dependent on the chemical composition of the alloys. Consequently, the investigated alloys exhibit some differences in both the residual pore fraction and the proportion of recrystallized grains.

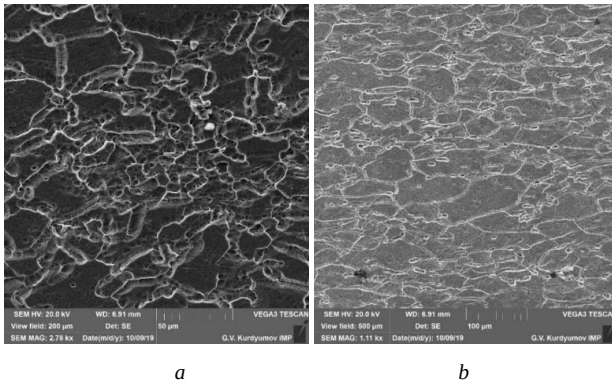


Fig.3 Microstructures of the 59Zr–19Ti–22Nb (a) and 35Zr–39.5Ti–25.5Nb (b) alloys after hot pressing at 900 °C with a deformation degree of 40–45%.

When alloy deformation degrees of about 60% are reached (fig.4), a practically non-porous recrystallized structure is observed, which is anisotropic due to the elongated shape of the grains.

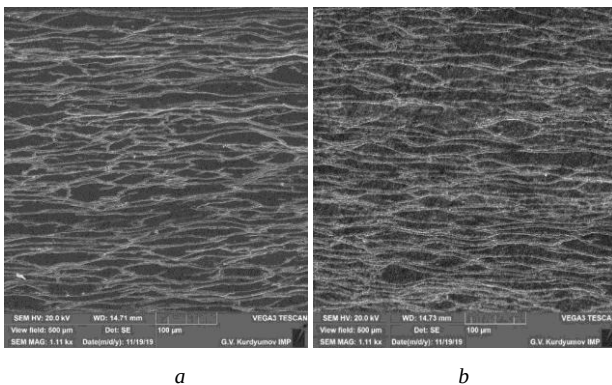


Fig.4 Microstructures of the 59Zr–19Ti–22Nb (a) and 35Zr–39.5Ti–25.5Nb (b) alloys after hot pressing at 900 °C with a deformation degree of 60%.

To evaluate the influence of microstructural changes obtained under the action of hot pressing on the mechanical characteristics of alloys of the Zr–Ti–Nb system, their hardness and Young's modulus were measured. Given the difference in the shape and size of the samples required for conducting different types of mechanical tests, materials hot pressed with a deformation value of up to 60% were

investigated to measure hardness, and 40–45% to measure Young's modulus. The results are given in Table 1.

Table 1: The effect of hot deformation on changes in hardness and Young's modulus.

Alloy composition	Hot-deformed state		Hot-deformed state	
	Young's modulus, GPa	Hardness HV	Модуль Юнга, ГПа (deform. 40–45%)	Hardness HV (deform. 60%)
59Zr–19Ti–22Nb	56.3	185	71.3	298
35Zr–39.5Ti–25.5Nb	55	159	62.6	291

X-ray diffraction analysis performed for the 39Zr–36.1Ti–24.9Nb alloy revealed no changes in the phase composition following deformation. The material retained its single-phase β -BCC structure (fig.5), indicating that the applied deformation treatment does not induce phase transformations. The preservation of the β phase is particularly beneficial for the intended biomedical application, as stabilization of the β -BCC structure is essential for achieving a reduced Young's modulus and, consequently, improving the mechanical compatibility of the alloy with bone tissue.

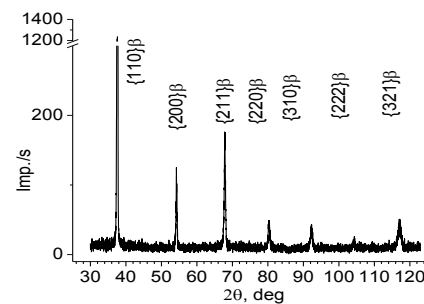


Fig.5 X-ray diffraction analysis of 39Zr–36.1Ti–24.9Nb alloy

As shown in Table 1, hot pressing with deformation levels of up to 60%, resulting in a practically pore-free microstructure, leads to an increase in the hardness of all investigated Zr–Ti–Nb alloys. It is also noteworthy that deformation substantially reduces the differences in hardness among the studied compositions. This behavior can be attributed to the initially different porosity levels of the synthesized alloys, which means that their hardness is governed by two main factors: the pore volume fraction and the chemical composition of the β -BCC phase. Following deformation, the formation of a nearly pore-free structure eliminates the contribution of porosity to the measured hardness, making the effect of the β -phase composition the dominant factor determining the hardness of the alloys.

Considering the critical importance of Young's modulus for biomedical alloys, its value was measured for the 59Zr–19Ti–22Nb and 35Zr–39.5Ti–25.5Nb alloys in both the as-synthesized and deformed states to evaluate the effect of hot pressing. In the as-synthesized state, both compositions exhibited relatively low Young's modulus values of 55–56 GPa (Table 1). As expected, deformation treatment resulted in an increase in Young's modulus, which reached 63–71 GPa in the nearly pore-free states (Table 1). According to [21], this increase can be attributed to the approximately linear dependence of Young's modulus on the porosity of the material. Thus, the substantial reduction in the pore

volume fraction during hot pressing leads to a corresponding increase in the effective elastic modulus (Fig. 6).

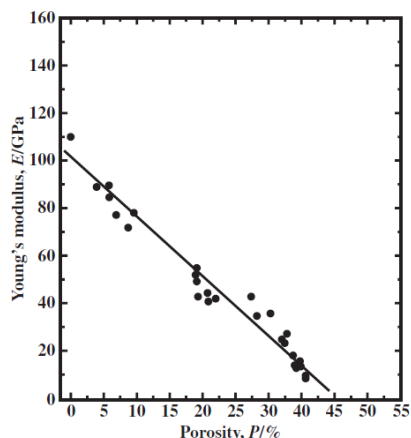


Fig.6. Young's modulus dependence on the titanium alloys porosity [21].

4. Conclusions

Hot pressing effectively reduced the residual porosity of the synthesized alloys. At deformation levels of 40–55%, the pore fraction decreased to 1–1.5%, while deformation up to 60% resulted in nearly pore-free structures. Increasing deformation also promoted recrystallization.

The Young's modulus of the investigated alloys increased from 55–56 GPa in the as-synthesized state to 63–71 GPa after hot deformation. This increase is mainly attributed to pore elimination, as the effective elastic modulus of porous materials strongly depends on their porosity.

Hot deformation is an effective way to influence the microstructure of synthesized Zr-Ti-Nb alloys. The hot-pressing method achieved practically pore-free states, which made it possible to significantly regulate the complex of physical and mechanical characteristics of the material, which was confirmed by an increase in the values of their hardness and Young's modulus.

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