Original Article

The Effect of Heat Treatment on the Properties of Titanium-50 Zirconium Alloy

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Abstract

Due to their excellent mechanical properties and biocompatibility, pure titanium and titanium alloys are widely used for clinical purposes. Zirconium, the biocompatible β-stabilizing element of titanium, can be added to titanium to provide a stable β-phase to improve the clinical applicability of titanium. Thereby, β-titanium alloy with a lower Young's modulus can be obtained. However, limited data is currently available on titanium-zirconium alloys. Therefore, in this study, we focused on how heat treatment influences the properties of titanium-50 zirconium alloys. The microstructure of the alloy was analyzed by X-Ray diffraction (XRD) and scanning electron microscopy (SEM), and the Young's modulus was measured. Under the as-cast state, the alloy can obtain a structure as the α'-phase acicular martensite. After high-temperature heat treatment, the alloy becomes wider and plate-like. The XRD data showed that, after long-term heat treatment at 800 °C, β-phase formation could be observed, with the lowest detected Young's modulus of 63.2 GPa. Therefore, compared to commercial materials, titanium-50 zirconium alloy displays less stress shielding effect after the heat treatment, ensuring its high application potential in implantable medical materials.

Key words: Titanium-50 Zirconium, Heat treatment; Young's modulus, Microstructure analysis

Introduction

Various types of metals are used in designing medical devices, with common biomedical materials, including stainless steel, cobalt-chromium alloy, precious metals, or nickel-titanium memory alloy, selected for multi-site applications[1]. Among biomedical metals, titanium and titanium alloys exhibit high specific strength, light weight, good corrosion resistance, and biocompatibility, making them widely popular for various applications in multiple fields. For their use as medical equipment, these characteristics facilitate their use as bone screw nails in orthopedics and metal implants or titanium meshes in dentistry[1–5].

The commonly used titanium variants comprise pure titanium and the alloy titanium-6 aluminum-4 vanadium. However, as the vanadium and aluminum ions released from titanium-6 and aluminum-4 vanadium are reportedly toxic in recent studies, these materials could have adverse effects on human tissues[2,4,5,6]. In addition, the Young's modulus of titanium alloy is significantly higher than that of human bones, potentially resulting in stress shielding and uneven stress distribution of implanted materials on the bone, potentially causing bone atrophy adjacent to the implantation and even operation failure[6–8]. Therefore, to design implantable biomedical titanium alloys that are harmless to the human body, the Young's modulus is reduced by adding β-stabilizing elements, such as niobium, tantalum, molybdenum, and zirconium[7–10]. Binary β-titanium alloy systems, such as titanium-molybdenum, titanium-niobium, and titanium-tantalum alloys, have been extensively studied, although limited research data is available on titanium-zirconium binary alloys.

Y. D. Shi et al[11]. supplemented titanium alloy with a high content of zirconium and water-quenched it after hot rolling treatment above the β transition temperature (735 °C) to obtain a new alloy with a mixed-phase structure of β with a body-centered cubic structure and orthorhombic crystals α": titanium-50 zirconium-5 aluminum-4 vanadium. This alloy exhibits ultra-low Young's modulus (45 GPa), ultra-high tensile strength (1185 MPa), and high elastic strain (2.2 %); this alloy is thus considered to be of particular significance among the implantable materials. When Y. Murayama et al[12]. investigated titanium-chromium-tin-zirconium alloys, alloys of different compositions were quenched, with the microstructure changed from martensite to the β-phase. After these treatments, titanium-5 chromium-9 tin-5 zirconium and titanium-2 chromium-6 tin-45 zirconium alloys adopted an unstable β-phase and generated a two-step yield phenomenon in the stress-strain curve, through the induced transformation of martensite, with the lowest registered Young's modulus of ~41 GPa, measured in the titanium-2 chromium-6 tin-45 zirconium alloy. For instance, compared with multi-element alloys, binary alloys are relatively easy to control the composition and temperature based on the phase stability. Our current focus is on the addition of Zr to obtain Ti-Zr binary alloy, which are the most fundamental to analyze the variation of additional elements.

In this study, based on the premise of obtaining a low Young's modulus and biological safety, we aimed at designing a titanium-50 (wt%) zirconium binary alloy using high zirconium content and pure binary alloy to measure the changes in the Young's modulus through nanoindentation under different heat treatment parameters, with microstructure analysis for structural observation. Based on these results, we investigated the correlation between the change in phase structure and heat treatment temperatures to serve as the process basis for the future development of novel β-titanium alloys.

Methodology

Material preparation

The titanium-50 (wt%) zirconium binary alloy was prepared through a vacuum melting furnace, then hot forged at 1000 °C and cast into a 20 mm thick sheet. After cutting, it was hot forged at 830 °C to form a 3-mm thin plate and finally cut into 10 × 10 × 2 mm test pieces. The material was heat-treated in a small vacuum heat treatment furnace, and solid solution annealing was performed at 800 °C on α+β area for 1, 4, and 16 hours. The same alloy with "as-cast state" was used for comparison.

Microstructure analysis

After grinding and polishing, the test piece was etched in a mixed solution of 15 % nitric acid (HNO_3) + 5 % hydrochloric acid (HCl) + 80 % alcohol for approximately 3 minutes. The test piece was cleaned with ultrasonication and dried. A scanning electron microscope (JEOL JSM-6380, Tokyo, Japan), with an operating voltage of 15kV, was used to observe the microstructure of the material. To explore the structural composition of the different groups, we used an XRD analyzer (Bruker D8, Billerica, MA, USA), with Cu-$K_{\alpha1}$ rays, a working voltage of 45 kV, and a 2θ range of 20–80°.

The measurement of the Young's Modulus

In this study, we used a nanoindentation measurement system to measure imprints. The principle of the nanoindentation experiment with MTS Nano indenter XP is driving the movement of the indenting probe by a machine, with contact between the probe tip and test material during the probe movement. Throughout the experiment, the machine records the load, displacement, and indentation area on the test material. The downward displacement of the center point of the probe tip is calculated by considering the surface of the test material as the origin. After the experiment, the machine calculated the final Young's modulus of the material based on the input formula.

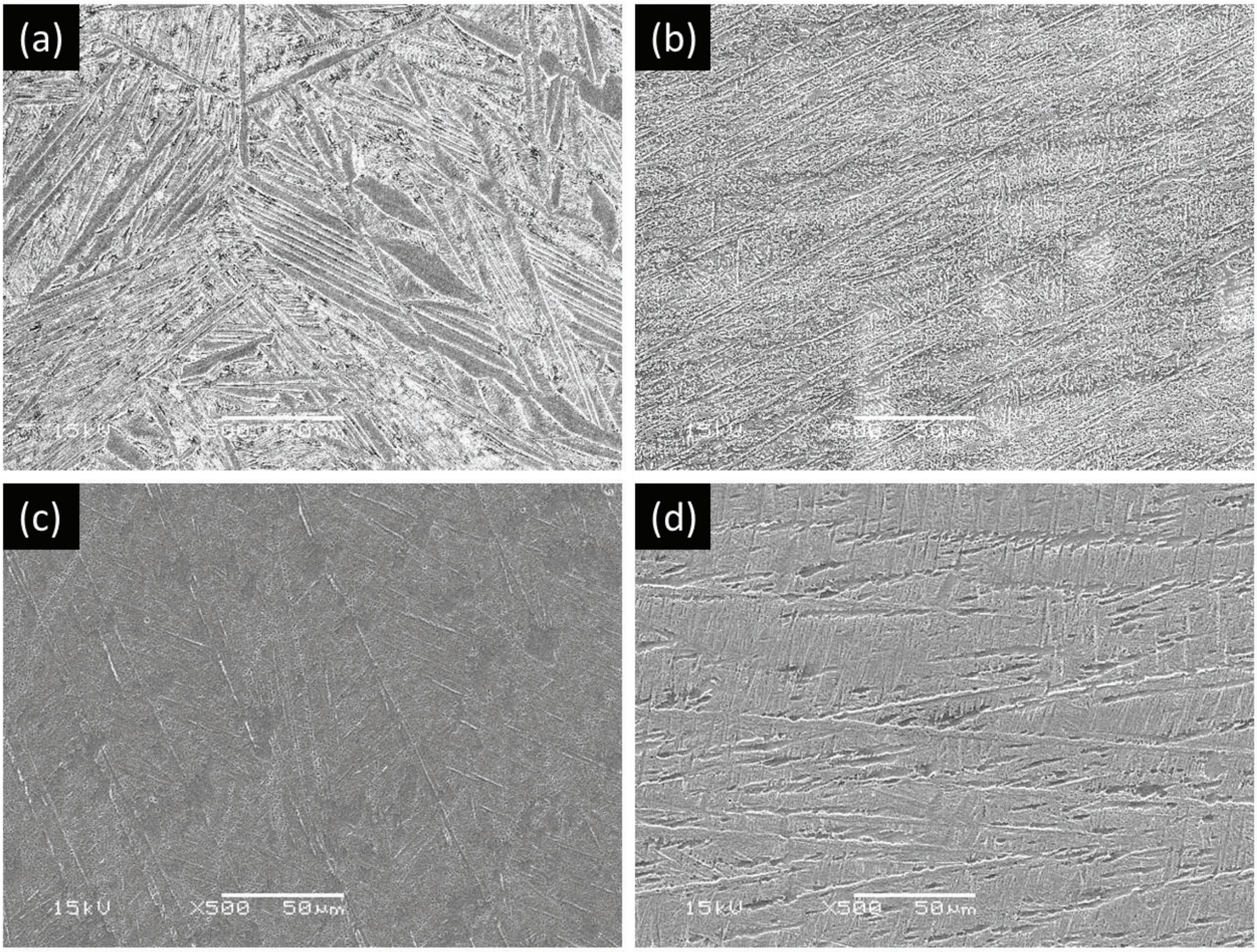

Figure 1. SEM pictures of different titanium-50 zirconium alloy microstructures after different heat treatments
(a) As-cast state (b) 800 °C , 1 h (c) 800 °C , 4 h (d) 800 °C , 16 h

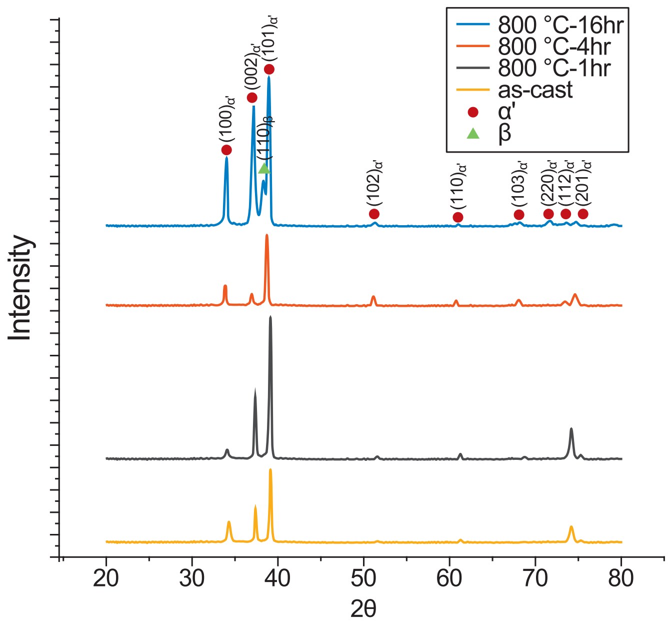

Figure 2. XRD analysis of different titanium-50 zirconium alloy compositions after different heat treatments
(a) As-cast state
(b) 800 °C , 1 h
(c) 800 °C , 4 h
(d) 800 °C , 16 h

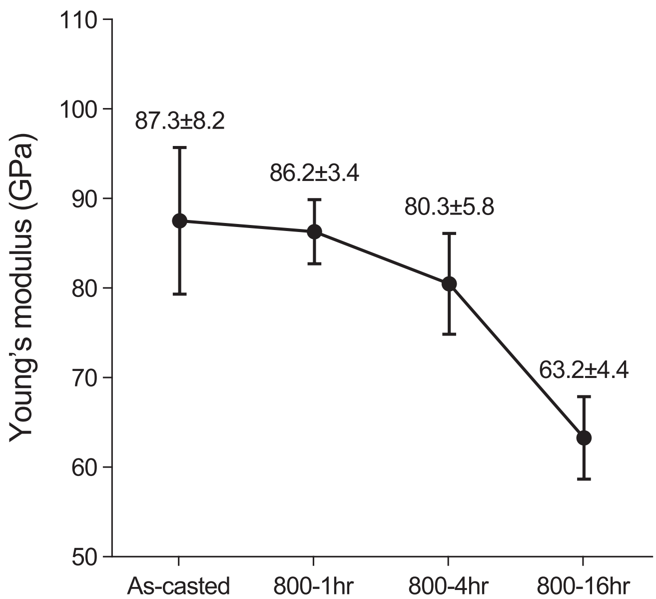

Figure 3. Young's modulus after different heat treatments

Results and Discussion

Microstructure

Under SEM, we could observe that the titanium-50 zirconium alloy is an acicular structure under the as-cast condition, as shown in Figure 1(a). After the high-temperature heat treatment at 800 °C for 1 and 4 hours, the acicular structure began to grow thicker, as shown in Figure 1(b) and (c). As the heat treatment time reached 16 hours, the acicular structure changed to a coarse lath shape, as shown in Figure 1 (d). In addition, the XRD analysis showed that the alloy was in α′ phase after the heat treatment at 800 °C for 1 and 4 hours, while the α′ phase and β-phase peak value were both detected upon heat treatment at 800 °C for 16 hours, as shown in Figure 2.

Young's modulus

The typical values of the Young's modulus for titanium-50 zirconium alloy with different heat treatment are shown in Figure 3. In the as-cast state, the Young's modulus of the titanium-50 zirconium alloy was 87.3 GPa. After heat treatment at 800 °C for 1 hour and 4 hours, the Young's modulus reached 86.2 and 80.3 GPa, respectively. The reason for obtaining a lower Young's modulus of 63.2 GPa at 16 hours could be the appearance of the β-phase in the alloy after the heat treatment at 800 °C for 16 hours, as shown in Figure 1(d); this phenomenon has been reported previously[13]. Different studies reported that a lower Young's modulus would be obtained when the alloy microstructure displays a β-phase, showing that the existence of the β-phase could reduce the overall Young's modulus of the material[7].

Conclusion

On adding high zirconium content (50 wt%), the structure of the titanium-50 zirconium alloy was acicular martensite α′ phase in the as-cast state. After the heat treatment at 800 °C, the alloy adapted a wider and larger lath shape. The Young's modulus of the titanium-50 zirconium alloy decreased to 63.2 GPa from 87.3 GPa as the time of heat treatment increased. The underlying reason for this result is that a small amount of β-phase was formed in the titanium-50 zirconium alloy under the conditions of 800 °C treatment for 16 hours.

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