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Effects of Element (Al, Mo, Sn and Fe) Doping on Phase Structure and Mechanical Properties of the Ti-Nb-Based Alloys

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Abstract: In the paper, Ti-18Nb-5X (X = Mo and Sn) and Ti-33Nb-2X (X = Al, Sn, Fe and Mo) alloys were investigated to evaluate the effects of Al, Mo, Sn and Fe doping and different heat treatments on the properties and microstructures of the Ti-Nb-based alloys. The results show that Al decreased the volume of β_M in the water-quenched Ti-33Nb-2Al alloy and promoted the formation of β phase in the furnace-cooled Ti-33Nb-2Al alloy. Fe-doping was proven to stabilize the β phase. Sn-doping plays a complicated role to promote the formation of α'' phase in the water-quenched Ti-33Nb-2Sn alloys but increases the β phase in the furnace-cooled Ti-33Nb-2Sn alloys and Ti-18Nb-5Mo-5Sn. The alloys containing α'' and β_M phases show larger superelastic strains and lower Young's moduli. In the water-quenched Ti-based alloys, the Young's modulus decreases, and the superelastic strain is enhanced with the increasing volume of α''.

Keywords: Ti-Nb alloys; phase constitutions; mechanical properties; Young's modulus; superelastic strain

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1. Introduction

Ti-based alloys have been widely used in a variety of medical applications, due to their excellent bio-compatibility, corrosion resistance and non-toxicity [1–5]. For joint implants, β-type Ti alloys gained great attention due to their low elastic modulus [6]. The β-type Ti alloys with body-centered cubic structures exhibit a lower Young's modulus than do α and α + β types [7]. However, at present, the wide-application Ti alloys are usually composed of α and α + β structures. Compared with the elastic modulus of human bones, α- and α + β-type Ti alloys show high elastic moduli [7]. Therefore, the demand for new Ti-based alloys with a low elastic modulus, high strength, significant work hardening and good wear resistance is ascending.

Several β-type Ti alloys, such as Ti-15Mo, Ti-15Mo-5Zr-3Al, Ti-35Nb-5Ta-7Zr-0.40 and Ti-16Nb-10Hf [8–11], have been widely developed for medical applications. However, their elastic moduli are higher than that of human bones. The elastic modulus of Ti-based alloys can be controlled by the addition of alloying elements [12,13], heat treatment [14] or an additive manufacturing process [15].

To improve β-type Ti alloys for implant applications, additional decreases of the elastic modulus can be achieved from Ti-Nb-based alloys that undergo solid-state phase transitions during heat treatment. When the Nb contents is up to 12% in weight with quenched alloys in the Ti-Nb system, a metastable hexagonal closed-packed (HCP) α' martensitic phase occurs [16]. At above 12% Nb, BCC β and hexagonal lattice ω phase are also formed in Ti alloys. Between 32% and 42% Nb, the elastic modulus decreases to its lowest value with the increasing of relatively proportion of β phase [16]. By adding alloying elements, such as Mo, Al, Zr, Si and O, in Ti-Nb alloys, one can adjust the martensite phase transformation temperature [17].

Some research indicated that a small addition of Zr to β-type Ti alloys shifts the β and β + ω (or α″) grain boundary to the poorer β-stabilizing elements region [18]. The β stabilizing effect of Zr increased with increasing content of the other β-stabilizing element in the alloy [19]. Although Al, Sn and O are called α-stabilizing elements, the synergetic effects of Al, O and Sn are complex in modifying the phase structures [17]. For instance, above 5% Al, metastable β phase is formed and eventually predominates [20]. Sn can suppress the formation of ω phase and increase the stability of the β phase [19]. The β-stabilizing abilities of Mo and Fe are stronger than those of Nb [21].

The Ti-33Nb alloy showed two phases of α + β for the furnace-cooled state or α″ + β_M for the water-quenched specimen [19,22] and was also used to investigate the effects of third elements on the phase constitutions of Ti-33Nb alloy. Fe also can form a eutectic phase and compounds and reduce the β volume during slow cooling [22]. Therefore, the previous research results have dispersibility and uncertainty with respect to the effect of the α and β stabilizing elements on the phase constitutions of Ti-Nb alloys. Thus, further investigation should study the effects of the elements on the phase constitutes and microstructures and mechanical properties in Ti-based alloys in order to clarify the relevant mechanisms.

The present study aims to investigate the effect of the ternary elements, Al, Fe, Sn and Mo, on the phase transformation and mechanical properties of the Ti-Nb-based alloys.

2. Materials and Methods

Ti-Nb-based alloys were fabricated by direct combination of the pure metallic constituents: Ti (99.99%), Mo (99.9%), Nb (99.9%), Al (99.999%), Fe (99.99%) and Sn (99.9%). The alloys with normal chemical compositions (wt.%) of Ti-18Nb-5Mo, Ti-18Nb-5Mo-5Sn and Ti-33Nb-2X (X = Al, Sn, Fe and Mo) were prepared by arc melting the pure elements in an Ar atmosphere. The alloy ingots with 80 g were obtained. The ingots were rolled and cut into round bars with a thickness of about 10 mm. The specimens were heated up to 950 °C for 30 min in the Ar atmosphere and then were furnace-cooled and water-quenched. The chemical compositions and heat treatments can be seen in Table 1.

Table 1. The nominal chemical compositions and heat treatments.

Nominal Chemical Compositions (wt.%)	Heat Treatments (950 °C, 30 min)	
Ti-18Nb-5Mo Ti-18Nb-5Mo-5Sn Ti-33Nb-2X (X = Al, Sn, Fe and Mo)	Furnace-cooled	Water-quenched

Phase constitutions in furnace-cooled and water-quenched specimens with different compositions were determined using a Bruker D8 ADVANCE-type X-ray diffraction apparatus (Bruker Inc., Karlsruhe, Germany) with Cu K_α radiation of λ = 0.154 nm, diffraction angle 2θ = 20~80°, and scanning rate of 0.02 °/s. The compression properties of the specimens were detected using an E/A-QT-01 mechanical testing instrument (Shanghai, China). The specimen dimensions for testing the compression properties were 5 × 5 × 10 mm^3.

3. Results and Discussion

3.1. The Phase Constitutions of Ti-Nb-Based Alloys

Figures 1 and 2 show the X-ray diffraction results of the furnace-cooled and water-quenched Ti-33Nb-2X (X = Al, Fe, Mo and Sn) alloys, respectively. It can be seen that, when the Sn is added, the relative diffraction intensity of the β phase increases and of the α phase decreases in the furnace-cooled specimens. On the phase constitutions of the furnace-cooled Ti-33Nb-2Sn, the volume fraction of the α phase is the lowest.

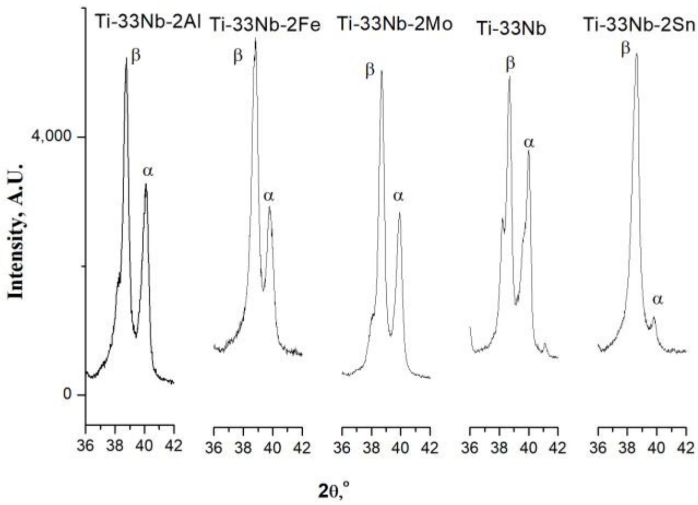

Figure 1. X-ray diffraction profiles of the furnace-cooled Ti-33Nb-2X (X = Al, Fe, Mo and Sn) alloys.

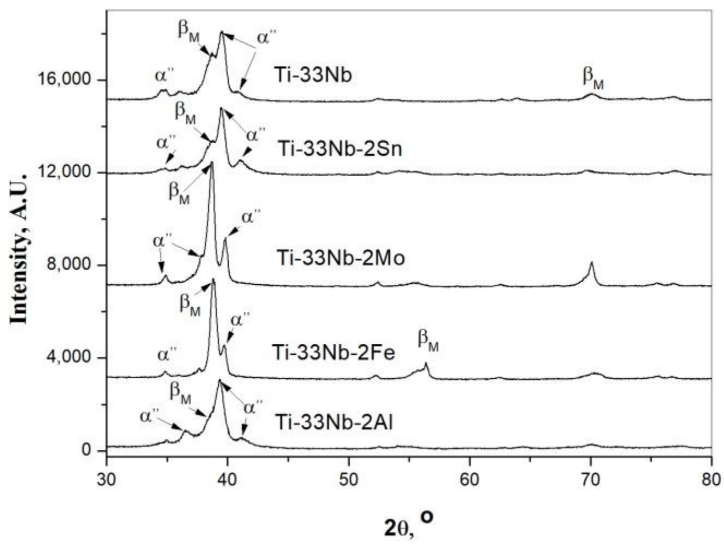

Figure 2. X-ray diffraction profiles of the water-quenched Ti-33Nb-2X (X = Al, Fe, Mo and Sn) alloys.

The Sn addition inhibits the formation of ω phase although it is an α-stabilizer and, therefore, can promote the formation of β phase, increasing the volume of the β phase [23]. In addition, the effect of β-stabilizing of Fe and Mo can be presented in the furnace-cooled Ti-33Nb alloy, and the former is stronger than the latter in the effect of β-stabilizing. Al is an α-stabilizer, and generally, it can increase the peak height of the α peak. Al appears to have a tendency to increase the β phase as shown in Figure 1. Some research indicated that Al may become a β-phase stabilizer since it limits the transformation of β→ω during aging [20,24,25].

A possible mechanism is that Al hinders the distribution of Ti atom in β phase. Another reason is that Al makes the formation of ω phase difficult in rich-Ti regions. The β phase will not be seriously reduced due to the addition of Al in Ti-Nb alloys [24,25]. In Figure 2, it can be observed that the phase constitutions are mainly β_M and α'' phases in the water-quenched Ti-33Nb and Ti-33Nb-2X (X = Al, Fe, Mo and Sn) alloys. In the water-quenched Ti-33Nb, Ti-33Nb-2Sn and Ti-33Nb-2Al, the volume fraction of α'' phase was more than that of Ti-33Nb-2Mo and Ti-33Nb-2Fe.

Ti-33Nb-2Sn possessed a greater volume fraction of the α'' phase. The β_M phases were significantly increased in the water-quenched Ti-33Nb-2Fe and Ti-33Nb-2Mo alloys. Fe and Mo also exhibited β stabilizing in the water-quenched Ti-33Nb alloy. Figures 3 and 4 show the X-ray diffraction results of furnace-cooled and water-quenched Ti-18Nb-5Mo and Ti-18Nb-5Mo-5Sn alloys. It can be seen that Sn acts as a β phase stabilizer in the alloys.

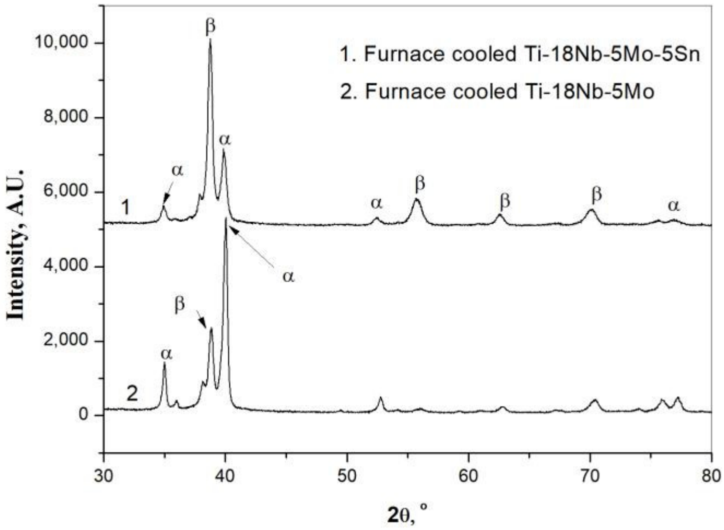

Figure 3. X-ray diffraction profiles of the furnace-cooled Ti-18Nb-5Mo and Ti-18Nb-5Mo-5Sn alloys.

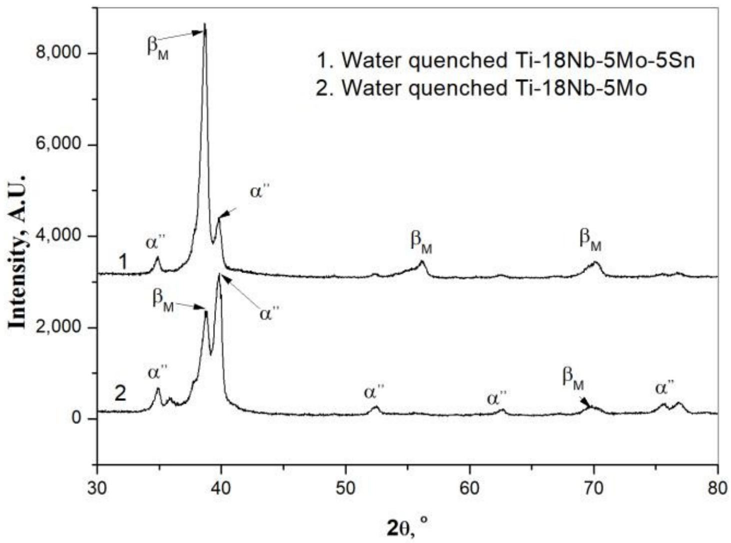

Figure 4. X-ray diffraction profiles of the water-quenched Ti-18Nb-5Mo and Ti-18Nb-5Mo-5Sn alloys.

3.2. The Young's Modulus and Yield Strength of the Ti-33Nb-2X (X = Al, Sn, Fe and Mo) Alloys

3.2.1. The Young's Modulus, Yield Strength and the Superelastic Strain of the Water-Quenched Ti-33Nb-2X (X = Al, Sn, Fe and Mo) Alloys

Figure 5 shows the stress–strain curves of the water-quenched Ti-33Nb-2X (X = Al, Sn, Fe and Mo) alloys. Among the Ti-18Nb-2X (X = Al, Sn, Fe and Nb) alloys, the Young's modulus of Ti-18Nb-2Mo was the highest, and the Ti-18Nb-2Sn alloy possessed the lowest Young's modulus. Ti-18Nb-2Sn had the highest superelastic strain; however, Ti-18Nb-2Mo had the highest yield strength among the Ti-18Nb-2X alloys. The water-quenched Ti-33Nb-2Sn possessed the lowest Young's modulus and the largest superelastic strain and yield strength.

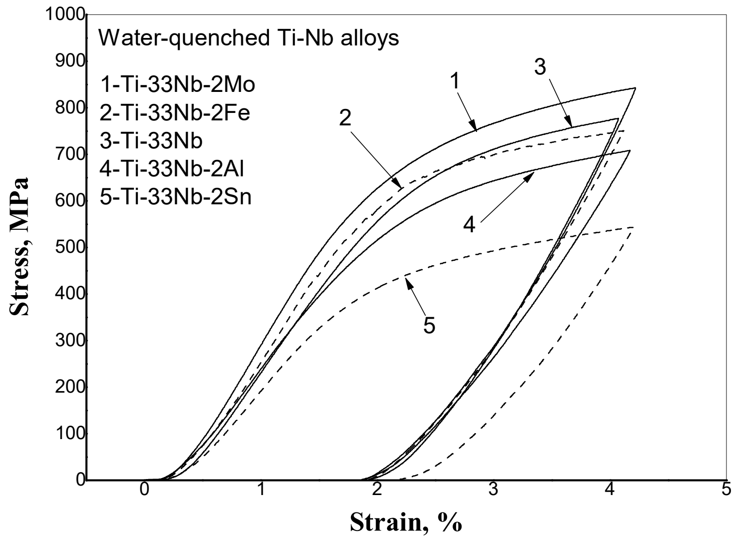

Figure 5. The stress–strain curves of the water-quenched Ti-33Nb-2X (X = Al, Sn, Fe and Mo) alloys.

From Table 2, we can see that the addition of 2 wt.% Sn in Ti-33Nb alloy led to a subtle decrease in the Young's modulus from 41.54 to 40.00 GPa, which is closer to that that of bone. However, the addition of 2 wt.% Mo, Fe and Al led to a noticeable increase in the Young's modulus. From Figure 2, it can be observed that the water-quenched Ti-33Nb-2Sn possessed a greater volume fraction of the α'' phase, resulting in an increase in the superelastic strain and decrease in the Young's modulus. The superelastic strain was approximately increased, and the Young's modulus decreased with the increasing volume of the α'' phase. The yield strength of the Ti-18Nb-2X alloys was also related to the phase constitutions since the α'' phase had low strength.

Table 2. The Young's modulus of water-quenched Ti-33Nb-2X (X=Al, Sn, Fe and Mo) alloys obtained from the compression test.

Nominal Chemical Compositions (wt.%)	Young's Modulus (GPa)
Ti-33Nb	41.54
Ti-33Nb-2Mo	54.32
Ti-33Nb-2Al	46.25
Ti-33Nb-2Sn	40.00
Ti-33Nb-2Fe	48.24

3.2.2. The Young's Modulus, Yield Strength and the Superelastic Strain of the Water-Quenched Ti-18Nb-5Mo and Ti-18Nb-5Mo-5Sn Alloys

Figure 6 shows the Young's modulus, yield strength and the superelastic strain of the water-quenched Ti-18Nb-5Mo and Ti-18Nb-5Mo-5Sn alloys. It can be seen that the water-quenched Ti-18Nb-5Mo alloy had a smaller elastic modulus and larger superelastic strain compared with the water-quenched Ti-18Nb-5Mo-5Sn alloy, which is attributed to a greater α'' phase in the water-quenched Ti-18Nb-5Mo alloy. However, the water-quenched Ti-18Nb-5Mo-5Sn alloy had a larger yield strength compared with the water-quenched Ti-18Nb-5Mo alloy, which is not in accordance with the above results. The detail mechanisms cannot be elucidated in the present experiments. In addition, according to Refs. [17,26], the Young's modulus decreases with increasing both the bond order (Bo) and the metal d-orbital energy level (Md).

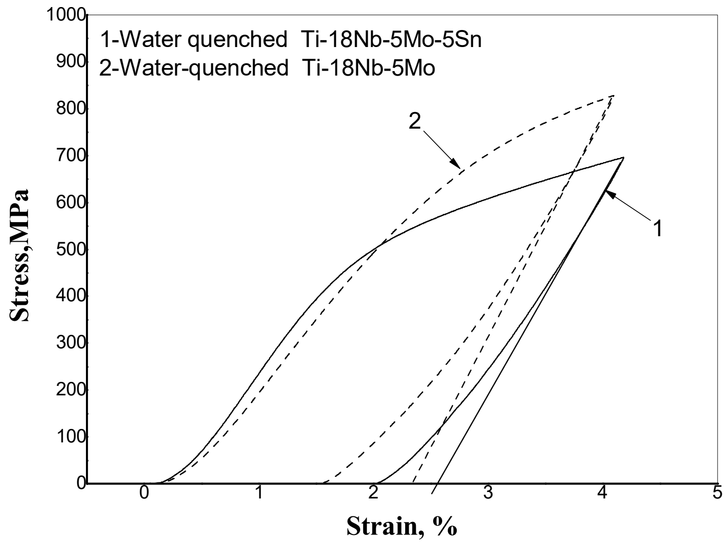

Figure 6. The stress–strain curves of the water-quenched Ti-18Nb-5Mo and Ti-18Nb-5Mo-5Sn alloys.

4. Conclusions

(1) Al increased the volume of the α'' phase and reduce the volume of the β_M phase in the water-quenched Ti-33Nb-2Al alloy.

(2) The volume fraction of the β phase increased in the furnace-cooled Ti-33Nb-2Fe alloy when compared with the furnace-cooled Ti-33Nb alloys. Similarly, the volume of β_M also increased in the water-quenched Ti-33Nb-2Fe alloy when compared with Ti-33Nb with the same heat treatment. Fe may form compounds under the condition of a low cooling rate to reduce the volume fraction of the β phase.

(3) The β-stabilizing effect of Mo was present in both furnace-cooled and water-quenched Ti-33Nb-2Mo alloys.

(4) Sn-doping played a complicated role to promote the formation of the α'' phase in the water-quenched Ti-33Nb-2Sn alloys but increased the volume fraction of the β phase in the furnace-cooled Ti-33Nb-2Sn alloys and Ti-18Nb-5Mo-5Sn. Sn may impede β to ω phase transition and depresses the transition temperature of the β phase.

(5) The water-quenched alloys with α'' and β_M phases possessed a better superelastic strain and smaller Young's modulus. The water-quenched Ti-33Nb-2Sn possessed the least Young's modulus and the largest superelastic strain and yield strength. For the present water-quenched Ti-based alloys, the Young's modulus decreased and the superelastic strain was raised when increasing the volume of α''.

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