Effect of Manganese Addition on the Microstructure and Mechanical Properties of Ti-Nb Biomedical Alloys

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Effect of Manganese Addition on the Microstructure and Mechanical Properties of Ti-Nb Biomedical Alloys

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Abstract. A series of Ti-24Nb-xMn alloys were fabricated by no consumable electrode vacuum arc furnace, with the focus on the effect of Mn addition on the structure and mechanical properties of the alloys. Experimental results indicated that α" phase-dominated binary Ti-24Nb alloy exhibits a fine, acicular martensitic structure. When 1wt% Mn was added, equated β phase structure was retained. The M1 alloy with instability β phase exhibits the two-stage yielding from stress-strain curves due to the stress-induced martensite transformation from β to α" phase during tensile deformation. Addition of a small amount of Mn (1 and 3 wt %) improved the plasticity of alloys and the elongation increases from 33% to 41%. The strength of the alloy with Mn content of 3% is the highest, and the tensile strength is 893MPa. All the alloys with Mn exhibit the high micro hardness, the highest is 345HV， which is 1.13 times than binary Ti-24Nb alloy. The elastic modulus of M_1 is the highest of all alloys-172GPa. The elastic modulus of the other alloys with Mn are about 82-87GPa, close to those of human skeletons. These alloys seem to have a great potential for use as an implant material.

1. Introduction

Compared with other biomedical metal materials, titanium and titanium alloys had been widely used in orthopedics, bone replacement and joint repair because of their low density, high specific strength, good corrosion resistance and biocompatibility. At present, titanium alloys such as pure Ti (CP-Ti) and Ti-6Al-4V (TC4) alloys were used in clinical medicine, but higher elastic modulus (~110 GPa) is much higher than human bone (3-20 GPa). Implanted into the human body, it will be a "stress shielding" on the surrounding bones. It will lead to bone absorption around the implant, eventually cause aseptic loosening, shortening the life of the implant. In addition, a small amount of vanadium and aluminum ions precipitated in TC4 alloy reduce the adaptability of cells, and there is a potential safety hazard in long-term use [1]. The results show that the elastic modulus of β phase with body centered cubic structure is the lowest among titanium alloy [2]. Therefore, the research on novel biomedical β titanium alloys with non-toxic, lower elastic modulus and better biocompatibility has become one of the hot spots in recent years.

As stable element, Mn affected on theβ phase with strong solid solution strengthening effect. As one of the 14 essential trace elements confirmed by WHO, trace Mn plays an important role in maintaining normal metabolism. Recently, Santos et al. [3] showed that Ti-Mn alloy had excellent cell viability when Mn < 13%, which was similar to CP-Ti.

In this paper, it was undertaken to special research on the microstructure and mechanical properties of Ti-Nb [4] binary titanium alloy by Mn additions. The effects of Mn on the microstructure and mechanical properties of Ti-Nb binary titanium alloy Ti-24Nb [5] were studied on the basis of the designed low-niobium binary titanium alloy Ti-24Nb. Ti-Nb-Mn [6] ternary titanium alloy with β phase and multivariate biomedical Ti alloy with Mn were further discovered.

2. Experiment process

The master alloy is Ti-24Nb-xMn (abbreviated as TNM; x=0, 1, 3 and 5, mass fraction, abbreviated as M0, M_1, M_3 and M_5 respectively). Firstly pure titanium, niobium and manganese were melted in a non-consumable vacuum arc furnace with high purity argon protection and Ti absorption. In order to make the alloy ingot homogeneous, alloy was repeatedly smelted more than five times.

First, the master alloy ingots were heated toβphase region, then solid solution treated at 900°C for 30 min, and finally quenched by water to obtain theβphase. XRD, metallographic and tensile specimens were obtained after grinding and wire cutting. After grinding, electro polishing and etching, the specimens were observed by metallographic microscope. The corrosion agent was a mixture of hydrofluoric acid, nitric acid and water. The volume ratio was HF: HNO_3: H_2O=4:8:88. The phase structure of the alloy was analysed by D/max-2500X ray diffractometer. Tensile properties of the alloy were tested by CMT 5105 universal testing machine to obtain the tensile strength σ_b, yield strength σ_s, elongation δ, elastic modulus E .The test temperature was room temperature, and the samples of each alloy were repeated for 4 times.

3. Discussion and analysis

3.1. Microstructures

Fig. 1 displayed XRD patterns of TNM alloys with different Mn content. Ti-24Nb binary alloy was consisted of hcp martensite α" phase, which was trapezoid lattice and precipitated rapidly by quenching. Other binary Ti alloys, such as Ti-Mo [5] and Ti-Fe [6], also occur when the content of Mo and Fe stabilizedβphase was relatively low.

The micro tissue of the alloys were remarkable changed onTi-24Nb alloys with Mn addition. The β phase with the body centered cubic lattice completely was retained to room temperature by addition of 1% Sn. The alloy increased of Mn content from 3% to 5% was still β phase, but the diffraction peak of β phase shifted to the left, which is the result of Mn solid solution in Ti matrix.

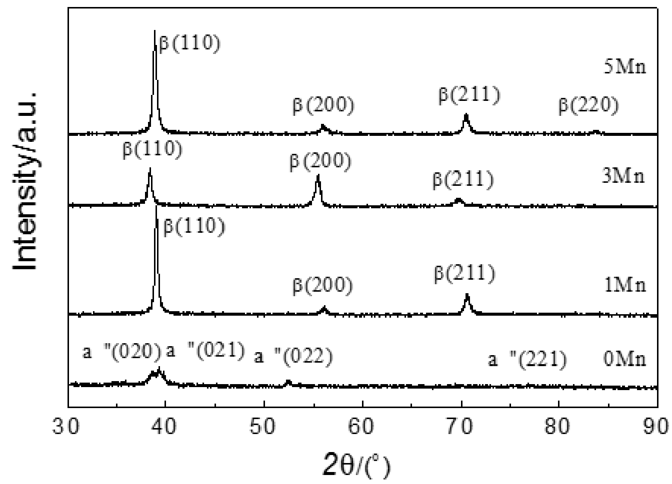

Figure 1. XRD patterns of TNM alloys with different Mn content

Mn had always been considered as a strong β phase stable element. In a series of studies on Ti-Mn alloys, Santos et al. [10] found that the β phase was completely retained at room temperature for Ti-Mn alloys, when the Mn content was higher than 9.0%.

Fig. 2 showed Optical micrographs of TNM alloys with different Mn content. In Fig.2a, Without Mn, the microstructure of M_0 binary alloy was fine needle like martensite (XRD was identified as α") However, after addition 1% Mn, the whole alloy is transformed into equated crystal phase and crystal, boundaries are clearly visible (Fig.2b). As Mn increased, the alloys are still composed of β phases of equiaxed grains (Fig. 2c, d).

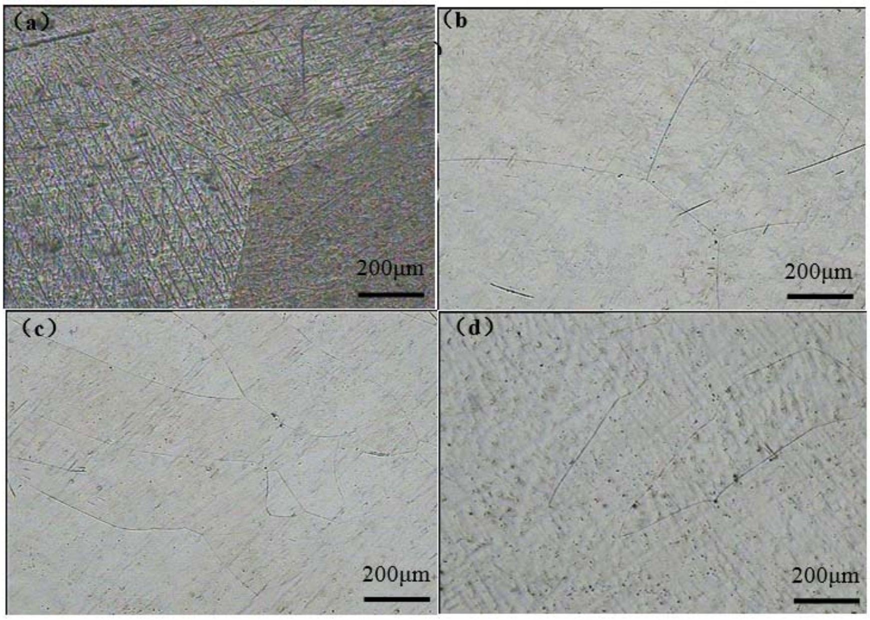

Figure 2. Optical micrographs of TNM alloys with different Mn content: (a) M_0, (b) M_1, (c) M_3, (d) M_5

3.2. Mechanical property

Tensile stress-strain curves of TNM alloys at room temperature and variation of tensile properties with Mn content, respectively, were shown in Fig.3 and Fig. 4.It was showed on Fig. 3 that the tensile curves of all alloys undergo the process of elastic transformation yielding plasticity fracture. The difference was the phenomenon of double yielding on M1 alloy. The specimen first yielded at 425MPa and then yielded second times at 669MPa. As shown in Fig. 4, the δ value of alloy with Mn 1% was increased, and the values of σ_s and σ decrease. With the increase of Mn content to 3%, σ_s and σ_b_ increased and the value of_δ decreased, but value of_δ *was* still higher than the plastic value of Ti-24Nb binary alloy. Then, with the further increase of Mn, the values of δ, σ_s and σ_b decreased.

Fig. 5was the relationship between micro hardness, elastic modulus and Mn content of TNM alloy.

The micro hardness and elastic modulus had the same trend. The hardness of Ti-24Nb alloy was the lowest, only 302HV. After adding 1% Mn, the hardness increased to 354HV and increased by 17.2%.

When the Mn content increased to 3%, the hardness value decreased to 328HV. With the increase of Mn, the hardness value increased slightly. The highest elastic modulus of M1 is 172GPa, the lowest of M_3 is 82GPa, and the elastic modulus of M_5 is slightly larger than M_3, 87GPa.

The above mechanical properties are closely related to the type, quantity and size of phases in the alloy. The good plasticity of M_1 and M_3 alloys lies in their microstructure composed of ductile β phase. The β phase was a body centered cubic structure, which was more powerful than the trapezoid martensite α" phase in the binary M_0 alloy. The high strength of M_3 alloy is caused by the solid solution strengthening effect of Mn element. The solid solution strengthening effect of Mn on the β-Ti phase was very strong. When the content of Mn increases to 5%, the plasticity decreased greatly. It was worth noting that the hardness of M_1 alloy was the largest and the highest increase. The results showed that the hardness of_ω phase was the highest among all phases (α, α', α",β and ω phase), followed by α, α' and α" phase, β phase was lowest.

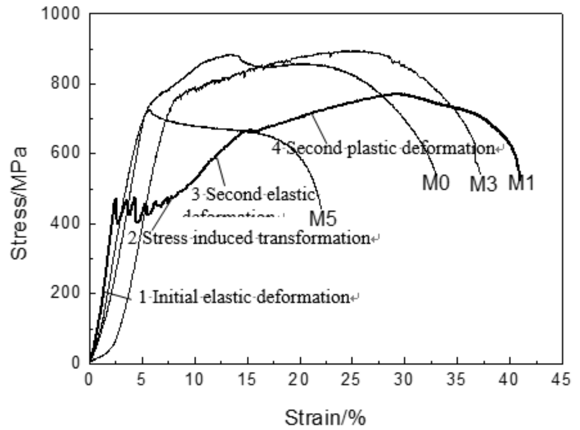

Figure 3. The stress-strain curves of TNM alloys

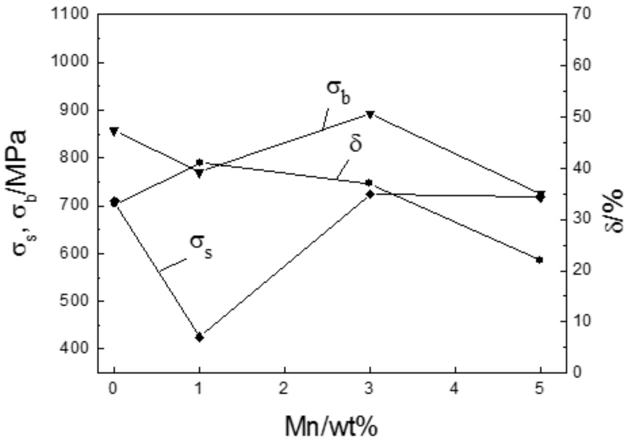

Figure 4. Variation of tensile properties with Mn content

The amount of stable element Mn in the β phase in M_1 alloy was small, so the precipitation of_ω phase may not be completely inhibited during quenching from high temperature beta phase region to room temperature, and the very fast cooling rate could not inhibit the precipitation. The amount of ω phase precipitated was not detected and observed in XRD (Fig. 1) and metallographic structure (Fig. 2). Although the amount of ω phase precipitation was very small, it had a great influence on the mechanical properties, especially the hardness and modulus of elasticity of Ti alloy, which may be the reason for the high hardness of M_1 alloy. When the content of Mn increases to 3%, the ω phase disappears and the hardness decreases due to the strong stabilization of β phase by Mn. After that, a slight increase in hardness was due to the strengthening effect of Mn on Ti matrix.

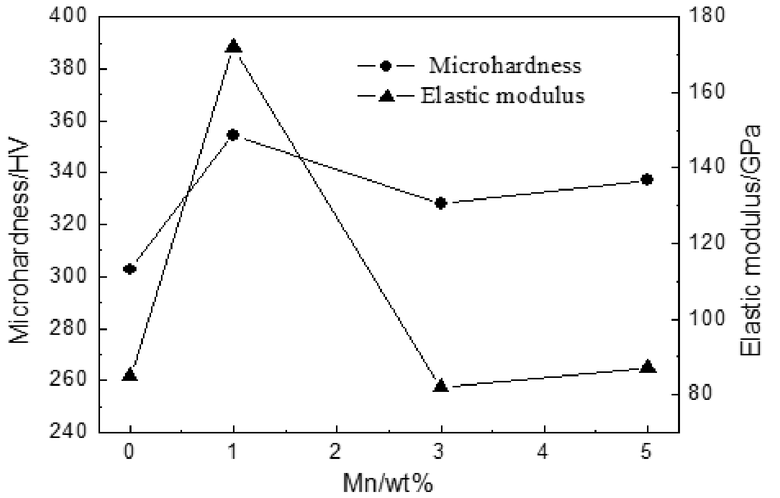

Figure 5. Variation of microhardness and elastic modulus with Mn

As we all know, elastic modulus was the essential property of materials, and depended on the binding force between atoms [7]. This binding force was related to the crystal structure and atomic spacing of the material. Many studies had shown that the order of modulus of elasticity in various phases of Ti alloy was ω>α'>α">β, the highest of ω phase and the lowest of β [8]. As mentioned earlier, M_1 alloy may contain ω phase, so the high modulus of elasticity of M1 alloy might be caused by ω phase precipitated during quenching. When the content of Mn increased to 3%, the ω phase disappeared. Although the content of Mn increased and the solid solution effect of Mn increased, the effect on the relative elastic modulus was much smaller than that of ω phase[9] [10], so the elastic modulus of M3 alloy with only β phase decreased greatly. With the increase of Mn content, the solid solution effect of Mn and the interatomic binding force increased, and the E value of M_5 alloy increased slightly.

4. Conclusion

1) The binary Ti-24Nb alloy consisted of fine needle likeα" martensite phases. The addition of strong β phase stabilizing element Mn inhibited the precipitation of α" phase during quenching, and the β phase of equated crystals was retained at room temperature with addition1% Mn.

2) Stress induction occurred in the tensile process of M_1 alloy with unstable β phase, and the martensite transformation from β phase to α" phase presented a "double yield" phenomenon. With the increase of Mn content, it disappeared and transformed into a single yield.

3) A small amount of Mn (1, 3%) was added to improve the plasticity of the alloy, and the elongation increased from 33% to 41%. The alloy with Mn content of 3% had the highest strength and tensile strength of 893MPa. The micro hardness of all alloy containing Mn was very high, the highest was 345HV, which was 1.13 times of that of Ti-24Nb alloy. The elastic modulus of M_1 alloy was the highest, reaching 172GPa. The modulus of elasticity of other alloys containing Mn was between 82-87GPa and it closed to that of human bone.

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