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Microstructure and wear resistance of Ti-3Zr-2Sn-3Mo-15Nb (TLM) alloy

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Abstract: The effects of heat treatment on the microstructure and phase constitution of Ti-3Zr-2Sn-3Mo-15Nb (TLM) alloy were investigated by optical microscopy, X-ray diffractometry and transmission electron microscopy. The wear resistance of TLM alloy was tested by sliding wear in comparison with as-annealed Ti-6Al-4V and as-aged Ti-13Nb-13Zr. The results show that the specimen cooled from $\alpha+\beta$ dual phase region is mainly composed of β, α and α'' phases, while the specimen cooled from β single phase region is mainly composed of β and α phases, in which β phase is predominate. The coefficient of friction of TLM alloy treated at 680 ℃, 1 h, AC+510 ℃, 6 h, AC is smaller than that of others, thereby TLM alloy has a better wear resistance which is also proved by the surface topography after wear test.

Key words: Ti-3Zr-2Sn-3Mo-15Nb alloy; microstructure; wear resistance; phase constitution; β titanium alloy

1 Introduction

Titanium and its alloys have been widely used in many biomedical fields such as joint, dental implants and other orthopedic implants due to their excellent combination of biocompatibility, mechanical properties and corrosion resistance[1]. Pure titanium and $\alpha+\beta$ type titanium alloys such as Ti-6Al-4V were originally designed for that application. Unfortunately it was reported that the elements Al and V have the potential toxicity, potential inhibition of apatite formation and possible association with neurological disorders[2−4]. Thereafter, people developed Ti-5Al-2.5Fe and Ti-6Al-Nb, in which the V was replaced by Fe or Nb, but their modulus of elasticity are still greater compared with that of bone, which may lead to premature failure of the implant[5], and their comparatively lower strength and unfavorable wear properties compared with conventional 316L and CoCr alloy restricted its usage to certain applications such as pacemaker cases, heart valve cages and reconstruction devices[6]. Wear performance is also crucial for biomedical alloy material. Excessive wear of the components induces adverse cellular response, leading to inflammation, release of damaging enzymes, osteolysis, infection, implant loosening and pain[7].

Therefore, the designation and development on new biomedical titanium alloys with more biocompatibility (addition of Mo, Nb, Zr, Sn, Ta, etc) and also with higher strength (hardness) and improved wear resistance, lower modulus has been a promising research field. Recently, a great deal of efforts have been devoted to the study of beta and near-beta titanium alloys, such as Ti-35Nb-5Ta-7Zr, Ti-13Nb-13Zr, Ti-16Nb-10Hf, Ti-29Nb-13Ta-4.6Zr and Ti-15Mo-5Zr-3Al[8−9]. In these alloys, some have lower modulus (55 GPa) but the ultimate strength is lower than 600 MPa, such as Ti-35Nb-5Ta-7Zr, some have lower ductility and also have the toxicity element of aluminium, such as Ti-15Mo-5Zr-3Al. In addition, the cost of these alloys is a little higher because of the addition of more rare elements such as Hf and Ta.

Biomedical Ti alloys should meet better mechanical compatibility other than biocompatibility, namely the alloy simultaneously should possess lower E values,

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enough strength and toughness, better wear resistance and also fatigue properties etc, to ensure the safety and quality of implanting materials. So it is important to control alloying elements, microstructure, process and heat treatment. But strength, hardness, plasticity, wear properties, modulus of elasticity and so on are a complex contradiction[10]. Generally speaking, with increasing strength, the hardness and wear performance are improved, but the toughness and modulus of elasticity decrease a little accordingly. Thus, researchers sometimes have to lower some strength values to ensure higher plasticity, toughness and lower *E* values.

In order to develop higher performance β type biomedical Ti alloys with lower modulus of elasticity, higher strength and wear resistance, excellent plasticity and lower cost, a novel Ti-3Zr-2Sn-3Mo-15Nb(TLM in short) alloy was designed and developed by the present authors[11−13]. The purpose of this paper is to report in detail the influential effects of heat treatment on the microstructure, phase constitution and wear resistance of near β type Ti alloy Ti-3Zr-2Sn-3Mo-15Nb which meet the demands for surgical implants.

2 Experimental

A new near β alloy Ti-3Zr-2Sn-3Mo-15Nb was designed whose Mo equivalence (Mo_{eq}) was 9.9. The 0 grade Ti sponge, pure Zr bar (4 mm×2 mm, 99.7%), pure Sn bar (5 mm×2mm, 99.9%), pure Mo powder and Nb53Ti47 intermediate alloy were used as raw materials. The alloy ingot of 5 kg was melted by VAR, then hot rolled to the plates of 1.1 mm in thickness.

The specimens for microstructure observation, phase analysis and wear resistance test were prepared by electro-discharge machining on the hot-rolled plates. To investigate the effects of heat treatment on microstructure, phase constitution and wear resistance, the specimens were heat treated at 680, 750 and 820 ℃ for 1 h. The β phase transformation temperature is 700−710 ℃. Some of the specimens treated at 680 ℃, AC were then aged at 510 ℃ for 4 to 6 h. Some of TLM alloy specimens treated as hot-rolled were directly aged at 510 ℃ for 4 to 6 h. All specimens were cooled in air. The specimens were wet ground with water-proof silicon carbide papers to 2000 grit, and then buff polished. Finally they were cleaned by using acetone, ethanol and de-ionized water in an ultrasonic bath and then dried in air.

X-ray diffraction (XRD) for phase analysis was conducted by using a D8 Advance X-ray diffractometer (Germany, Bruker) operated at 40 kV and 40 mA. A Ni-filtered Cu K_α radiation (λ=1.540 6 nm) was used. The phases were identified by matching their characteristic peaks with those in the files of the Joint Committee on Power Diffraction Standards (JCPDS).

Transmission electron microscopy (TEM) was performed by using a H500 operated at 200 kV. The thin foil specimens were prepared by using a twin jet polisher in an electrolyte with 30 mL perchloric acid, 175 mL n-butyl alcohol and 300 mL methanol at −30 ℃ with a voltage ranging in 15−20 V.

The sliding wear test of the TLM alloy was performed on a block-on-ring type wear tester, using TLM alloy specimens as block and SiC as the slider ring. All tests were carried out at ambient temperature. A load of 36 g was applied to the specimens and the slider rotated at a constant velocity of 200 r/min. As a comparison, the annealed Ti-6Al-4V and aged Ti-13Nb-13Zr specimens were used. The wear resistance of TLM alloys was characterized by the coefficient of friction. The surface topography of the specimens after a test time of 12 min was examined by the optical microscope.

3 Results and discussion

3.1 XRD analysis

Fig.1 shows the XRD patterns of the TLM alloy specimens under different heat treatment conditions. Metastable β phase as a predominant phase (bcc structure) was detected whether the specimens were cooled from $\alpha+\beta$ dual phase region or β single phase region, which suggested that the solution treated TLM alloy is mainly in a matrix phase state. The lattice parameters of bcc β phase are summarized in Table 1. The XRD patterns in Fig.1 (a) shows the coexistence of α and β phases because of the precipitation of second α phase when TLM alloy specimen was aged at 750 ℃, AC+610 ℃ for 1 h.

3.2 TEM analysis

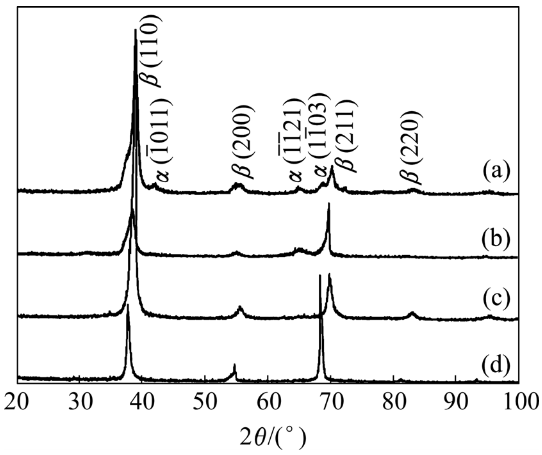

Fig.1 XRD patterns for TLM alloy specimens under different treatment conditions: (a) 750 ℃, AC+610 ℃, 1 h, AC; (b) 680 ℃, AC; (c) 750 ℃, AC; (d) 820 ℃, AC

Table 1 Lattice parameters of metastable β phase of TLM alloy

Heat treatment	a/nm	b/nm	c/nm
680 ℃, AC	0.335 1	0.335 1	0.335 1
750 ℃, AC	0.329 4	0.329 4	0.329 4
820 ℃, AC	0.332 6	0.332 6	0.332 6
610 ℃, AC	0.332 0	0.332 0	0.332 0

In order to investigate the difference of microstructures when the specimens were cooled from $\alpha+\beta$ dual phase region and β single phase region, TEM observation were performed. Although the orthorhombic martensite was not detected by XRD analysis, but it was actually confirmed by TEM observation in the specimen treated at 680 ℃, AC. Fig.2 (a) shows a TEM bright field image revealing the needle-like martensite formed in the β-Ti matrix. Some martensites are indicated in position A. Fig.2 (b) shows the corresponding selected-area electron diffraction (SAED) with the diffraction spots from the $[100]_{\beta}$ zone axis and the$[321]_{\alpha''}$ zone axis. The following orientation relationship can be obtained from the above SAED pattern: $[321]_{\alpha''}//[100]_{\beta}$, $(01\bar{1})_{\beta}//(1\bar{1}\bar{1})_{\alpha''}$. The α phase was also observed in the specimen treated at 680 ℃, AC. Some plate-like α phase is indicated in the area marked by B. Fig.2 (c) shows the corresponding selected-area electron diffraction (SAED) with the diffraction spots from the $[\bar{1}00]_{\beta}$ zone axis and the $[000\bar{1}]_{\alpha}$ zone axis. The following orientation relationship can be obtained from the above SAED pattern: $[000\bar{1}]_{\alpha}//[\bar{1}00]_{\beta}$, $(01\bar{1})_{\beta}//(10\bar{1}0)_{\alpha}$.

Fig.3 shows the detailed analysis of the α'' martensite in matrix. Fig.3 (a) shows a TEM bright image in the specimen treated at 680 ℃, AC. Fig.3 (b) shows the dark image at the same place in Fig.3 (a). The SAED pattern is given in Fig.3 (c). It is clearly shown that the needle-like α'' martensite appears in the plate-like β phase.

Fig.4 shows the detailed analysis of microstructure in 820 ℃, AC specimen. The SAED pattern of Fig.4 (c) was taken from one α plate in bright field image (Fig.4 (a)) with the diffraction spots from the $[000\bar{1}]_{\alpha}$ zone axis. A dark field image (Fig.4 (b)) was taken at the same place as Fig.4 (a) using an α spot indicated $[000\bar{1}]_{\alpha}$. Combined with the result of XRD, we can draw a conclusion that the TLM alloy cooled from β single phase region is mainly composed of much more β phases and some α phases but without α'.

3.3 Wear resistance

Fig.5 shows the curves of friction coefficient versus time. When the curves are stable, the friction coefficients are recorded, as summarized in Table 2. The coefficient of friction of TLM alloy specimen treated at 680 ℃, AC+510 ℃, 6 h, AC is smaller than that of others, even smaller than that of the annealed Ti-6Al-4V and aged Ti-13Nb-13Zr, whereas the specimen treated at 510 ℃, 6 h, AC exhibits the highest value. So, heat treatment and alloy composition have a great influence on the wear resistance for Ti alloys. This is also proved by the surface topography before and after wear test.

Fig.6 shows the typical optical micrographs of the specimen surface of TLM alloy after wear test. In Fig.6 (a), there are many adhesions on the specimen surface Fig.6 (a) is more severe than those in Fig.6 (b)−(d). The

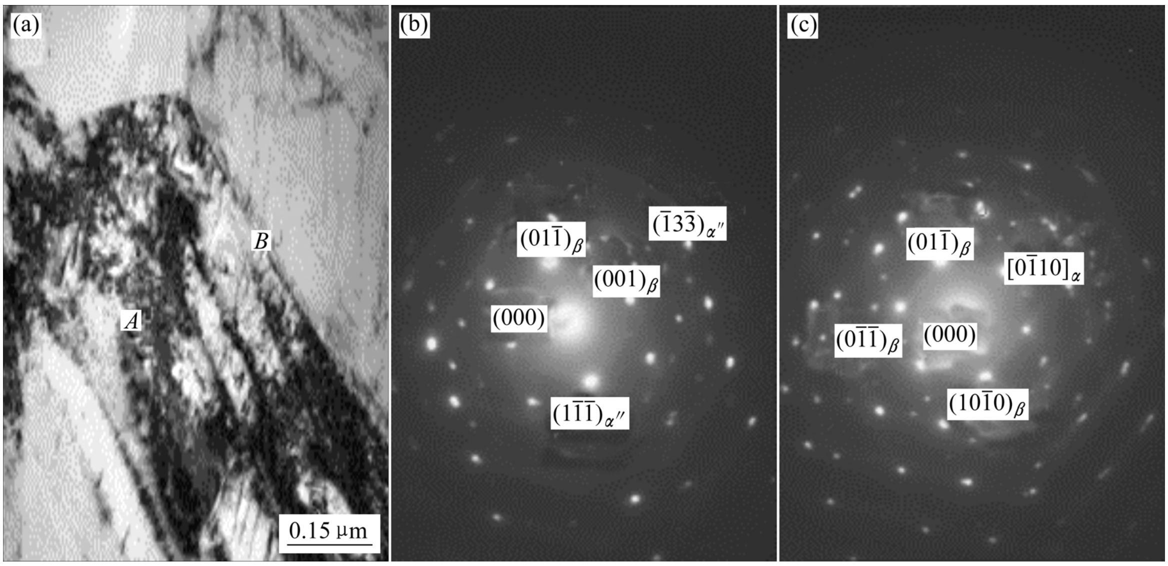

Fig.2 TEM bright field micrograph showing α''-Ti and α-Ti in β-Ti phase (a), SAED pattern taken from area marked by position A revealing orientation relationship ($[321]_{\alpha''}//[100]_{\beta}$, $(01\bar{1})_{\beta}//(1\bar{1}\bar{1})_{\alpha''}$) between matrix and martensite in specimen treated at 680 ℃, AC (b), SAED pattern taken from area marked by position B revealing orientation relationship ($[000\bar{1}]_{\alpha}//[\bar{1}00]_{\beta}$, $(01\bar{1})_{\beta}//(10\bar{1}0)_{\alpha}$) between matrix and martensite in specimen treated at 680 ℃, AC (c)

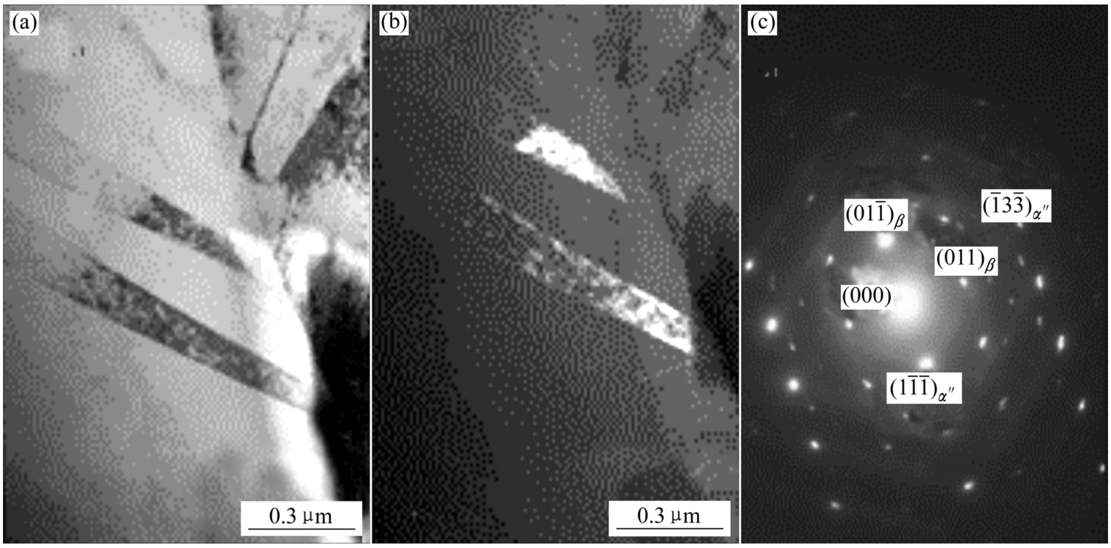

Fig.3 TEM bright field micrograph (a), TEM dark field micrograph (b) and SAED pattern (c) of specimen treated at 680 ℃, AC

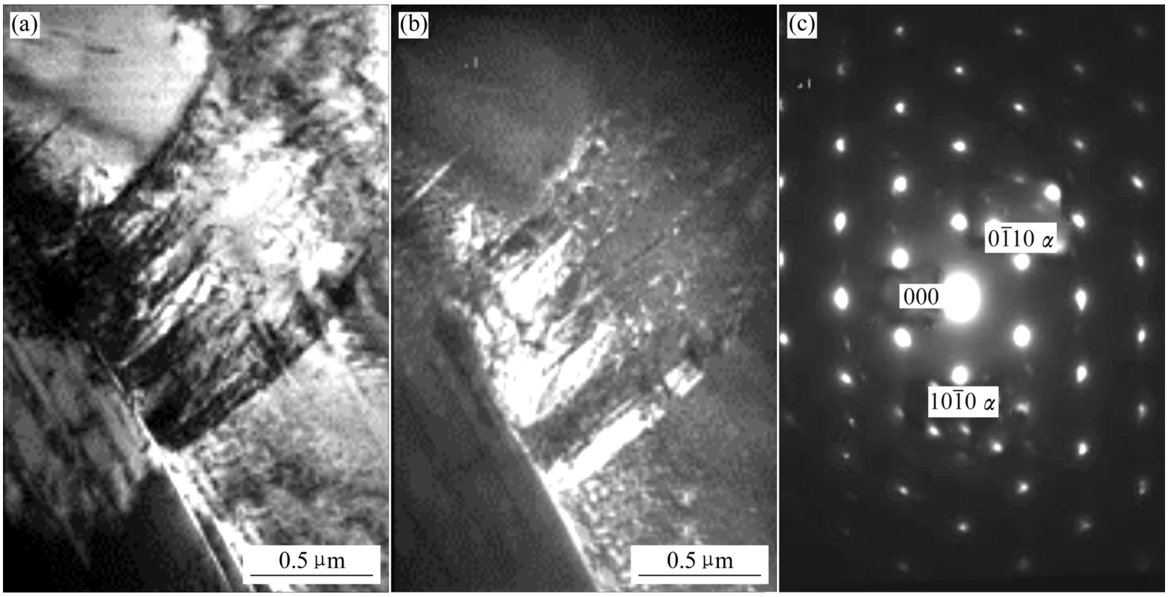

Fig.4 TEM bright field micrograph (a), TEM dark field micrograph (b), and SAED pattern (c) of specimen treated at 820 ℃, AC

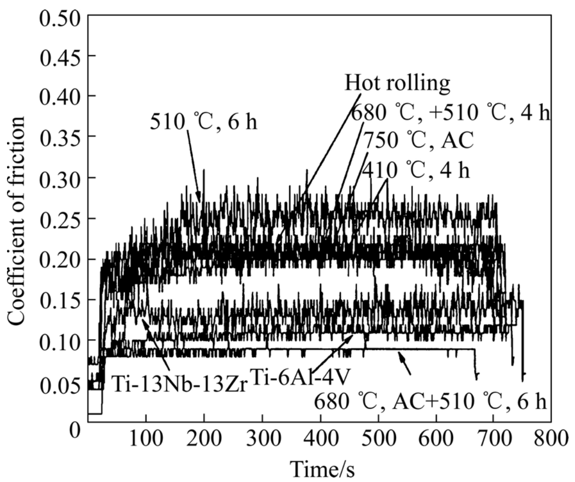

Fig.5 Curves of coefficient of friction vs time of TLM alloy

Table 2 Coefficient of friction for various Ti alloys

Alloy	Heat treatment	Friction coefficient
TLM	Hot-rolled	0.21
	680 ℃, AC+510 ℃, 4 h	0.21
	510 ℃, 4 h	0.21
	750 ℃, AC	0.21
	510 ℃, 6 h	0.25
	680 ℃, AC+510 ℃, 6 h	0.09
Ti6Al4V	As-annealed	0.11
Ti13Nb13Zr	As-aged	0.14

treated at 510 ℃, 6 h, AC. In Fig.6 (b), along the sliding direction, the adhesion is not continuous. The scratch in surface morphologies of other specimens are similar to those of the specimen treated at 510, ℃, 6 h, AC. We

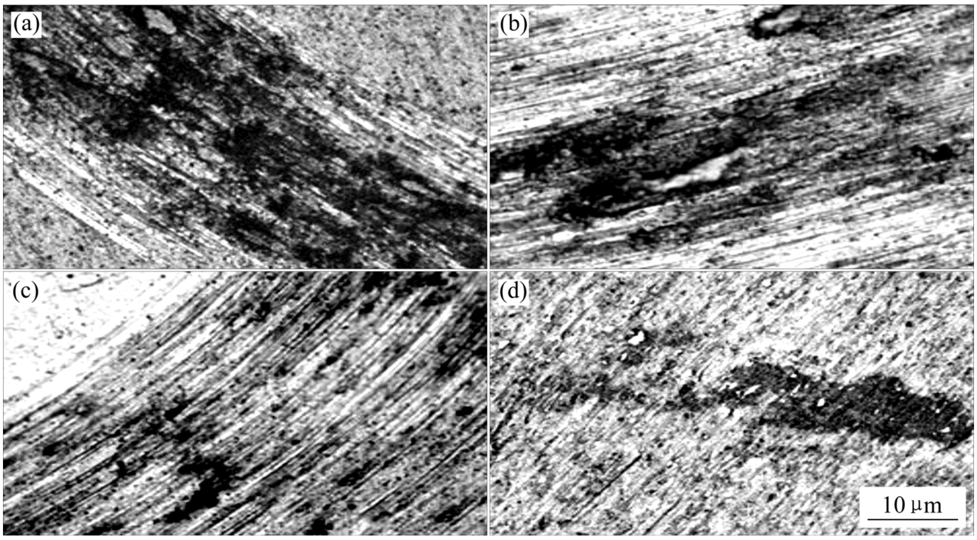

Fig.6 Typical optical metallographs after wear: (a) TLM alloy treated at 510 ℃, 6 h, AC; (b) Aged Ti-13Nb-13Zr; (c) As-annealed Ti-6Al-4V; (d) TLM alloy treated at 680 ℃, AC+510 ℃, 6 h

can see that the TLM alloy treated under 680 ℃, AC+510 ℃, 6 h, AC possesses better wear resistance than that of others, even better than that of the annealed Ti-6Al-4V alloy and aged Ti-13Nb-13Zr alloy[11].

4 Conclusions

1) Whether cooled from $\alpha+\beta$ dual phase region or β single phase region, metastable β phase is a predominant phase (bcc structure) for TLM alloy.

2) TLM alloy cooled from $\alpha+\beta$ dual phase region is mainly composed of β phase, primary α phase and a little needle-like α'' martensite phase. The selected-area electron diffraction patterns of TEM reveal the following orientation relationship: $[321]_{\alpha''}//[100]_{\beta}$, $(01\bar{1})_{\beta}//(1\bar{1}\bar{1})_{\alpha''}$, $[000\bar{1}]_{\alpha}//[\bar{1}00]_{\beta}$, $(01\bar{1})_{\beta}//(10\bar{1}0)_{\alpha}$. While the TLM alloy cooled from β single phase region is mainly composed of some primary α and much more metastable β phases.

3) TLM alloy treated at 680 ℃, AC+510 ℃, 6 h, AC possesses better wear resistance than that of others, even better than that of the as-annealed Ti-6Al-4V alloy and as-aged Ti-13Nb-13Zr alloy, which is consistent with the results of microscopic observation after wear test.

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