Microstructure and Mechanical Properties of Biomedical Near-β Ti Alloy TLM with Nanostructure by ARB Process

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The composite foils with nanograins of novel near-β type biomedical Ti alloy Ti(1.5–4.5)Zr(0.5–5.5)Sn(1.5–4.4)Mo(23.5–26.5)Nb (TLM in short) were prepared by near Accumulative Roll-Bonding process (ARB). The process, microstructure and mechanical properties of TLM alloy foils were studied and discussed. The results show that the average grains dimension of TLM alloy foils (0.2mm) can reach about 80nm after 97.5% severe plastic deformation (SPD). The TLM alloy materials with nanostructure possess higher tensile strength, lower elastic moduli and higher elongation compared with coarse-grained materials after solid solution and aging strengthening heat treatment.

Keywords: Nanostructure, accumulative roll-bonding process (ARB), microstructure and mechanical properties, near-β type Ti alloys

1. Introduction

Biomedical Ti alloy materials have been widely applied in surgical implants and internal intervening devices resulted from better biocompatibility, but the higher elastic moduli of Ti alloys can cause “stress-shielding” and implants failure⁴. Thereby, it is very important to design and control their mechanical properties such as tensile strength (Rm), yielding strength (Rp0.2), elongation (A5) and modulus (E) etc. and mechanical compatibility matching with hard tissue such as bone and teeth etc...

The severe plastic deformation processing (SPD) has a long history which dated back to the metalworking of ancient China. But the first significant evaluation of the principles of SPD lied in the classic early experiments by Bridgman⁵, the most important contribution is the work of Segal and coworkers⁶ where the technique of equal-channel angular pressing (ECAP) was first introduced and now widely used in many laboratories in the world⁷. In 1998, Saito first developed accumulative roll-bonding process (ARB) and successfully produced ultra-fine grained bulk aluminum plate⁸. The other developed SPD process includes High Pressure and Torsion (HPT) and so on⁹,¹⁰.

The SPD may be used to produce exceptional grain refinement in bulk metals to achieve unusual and beneficial mechanical properties compared with conventional coarse-grained materials which was becoming an important research area having a wide range of industrial applications in commercial pure Ti (CP-Ti), but less concerned β type Ti alloys. On the other hand, the above-mentioned SPD possess cannot produce the materials with smaller dimension such as foils etc.

A novel β type Ti alloy Ti-(1.5–4.5)Zr-(0.5–5.5)Sn-(1.5–4.4)Mo-(23.5–26.5)Nb (wt%, TLM in short) was successfully developed by present authors, which the alloy possess lower modulus, better plasticity and fracture toughness and higher fatigue strength when the tensile strength Rm reach above 900MPa¹¹. In this study, the TLM alloy foils with ultra-finer grains (micro to nano sizes) were first prepared by ARB process in order to further improve the mechanical compatibility, and the process, microstructure and mechanical properties of TLM alloy composite foils were studied and discussed.

2. Experimental

0 grade Ti sponge, pure Zr bar (4 × 2mm, 99.7 wt %), pure Sn bar (5 × 2mm, 99.9 wt %), pure Mo powder and Nb intermetallic intermediate alloy were used as raw materials. The alloy ingots of 25Kg were melted by non-consumable arc melting two times to ensure chemical and microstructure homogeneity and lower impurity contents. The phase transus temperature of α+β to β is 710°C–720°C. After forged above β-transus zone and hot rolled, the plates of 1mm in thickness were gotten. The 1mm plates after solid solution heat treatment at 610°C/1h, 710°C/1h, 810°C/1h were cold rolled into 0.2mm foils which the deforming rate is 80%, then the 0.2mm foils were cut, surface cleaned and then composed in composite plates with the layers of 2, 4, 8 separately. Finally the foils with the same thickness of 0.2mm were prepared by cold-rolling step by step by ARB¹² from the above-mentioned composite plates with different thickness 0.4mm, 0.8mm and 1.6mm. The samples cut from the above-mentioned materials were subjected to a variety of heat treatment. The specimens for tensile mechanical properties, optical metallography, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were prepared and determined using standard techniques and methods.

3. Results and Discussion

3.1 Severe Plastic Deforming and Microstructure Evolution

The typical microstructure of 1mm plates of TLM
alloy after different heat treatment are given in Figure 1. We can see the grains take place recrystallization homogeneously with average dimension 20µm or so at 710°C/1h and 70µm at 810°C/30min, the iso-axial microstructure may endure bigger cold deforming and thus the coarse grains can be crushed completely.

Figure 1. Microstructure of TLM alloy plates (1mm) after heat-treatment (a)610°C/30min; (b)710°C/30min; (c)810°C/30min

The TLM alloy composite foils of 0.2 mm in thickness were prepared by ARB process with 4 deforming rates of 80%, 90%, 95% and 97.5%, their microstructure are shown in Figure 2. It is found that the grains have been crushed to finer dimension along rolling process streamline. When the deforming rates reach 95%, the grains turned to finer fiber-like morphology and no obvious boundary between layer and layer (Figure 2(c), 2(d)). Figure 3 shows the XRD analysis of TLM alloy foil after 97.5% deforming. It is found the content of α phase reach 19% from 10% under 90% deforming. The reason can be explained as; with increasing of the deforming rates, the temperature increment makes some β phase decomposing, and then α phase starts nucleating into β phase matrix, thus the microstructure of TLM alloy will transform to α + β dual phase from single β phase which result in better mechanical properties matching.

3.2 Grains Fined and Mechanical Properties

With the grains fined of Ti alloys, there are a variety of interesting changes in mechanical properties. The tensile mechanical properties of TLM alloy foils (0.2 mm in thickness) after 80% cold deforming is shown in Table 1. We can see, with the temperature of solid solution treatment increasing, the Rm, Rp0.2 and Aej lower gradually, whereas E rise slowly. Especially, the TLM foil No. A possess lowest E value, 38GPa which is very close to that of natural bone. On the other hand, it is also found that the sample A have higher Rp0.2/E and Rp0.2/Rm which means better mechanical biocompatibility and suitable to used in the surgical implants.

The mechanical properties of cold-rolled composite foils (0.2mm) of TLM alloy are shown Tab. 2. It is found that, with increasing of cold deforming rates (or number of composite layers), the grains dimension decreases from 200nm to 80nm, and the strength Rm, Rp0.2 and modulus E rise gradually. The regularity of mechanical properties can be analyzed by SEM morphology (Figure 4). We can see that the grains dimension decrease slowly when the deforming rates rise. When the accumulated cold deforming rate reach...
97.5%, the TLM alloy composite foils can be crushed to 80nm or so in width, the boundary thickness between layers is only about 200nm which show the foils have achieved melting fusion welding (Figure 4(c)). In general speaking, the accumulated ARB process can lead to the temperature increment of 200 ~ 300°C which result in mechanical atom diffusion bonding to reduce the effect of cold-deforming hardening, thereby, the nano-size effects can improve the workability of TLM alloy, and also delay the fracture of TLM alloy foils which can be proved by Figure 5.

3.3 Plastic Deforming and Strengthening Mechanism

The near β type Ti alloys such as Ti-13Nb-13Zr have been the most attractive implanting material candidate recently[35], which possess lower moduli of elasticity, improved corrosion and wear resistance, higher strength and toughness matching by means of adequate process and heat treatment etc. The novel near β type TLM alloy mainly contains acicular martensitic $\alpha'$ or $\alpha''$ phase after β solution treated (ST) and water quenching (WQ), and iso-axial meta-stable $\beta$ phase ($\beta_{ms}$) after β solution treated and air cooling (AC) (Figure 6(a)), which shows lower strength, better plasticity and much lower moduli of elasticity. The $\beta_{ms}$ start to dissolve during aging (STA) above 500°C and then large quantities of finer secondary $\alpha$ phase ($\alpha_s$) with dot shape or needle shape (Figure 6(b)) are formed in $\beta$ matrix, thus, the $R_m, R_p$ and $E$ values increase and $A_5$ lower. The different microstructure evolutions of TLM alloy can be required by means of different process and heat treatment systems[36].

In this paper, we can see, with the grains dimension reach nano-size by ARB process, the TLM alloy also possesses excellent bio-mechanical properties matching with higher tensile strength $R_m$ and lower moduli of elasticity $E$. The difference of the materials strengthening mechanism between STA and ARB process can be described as follows: TLM alloy treated at STA (Figure 6(b)) results in dispersion strengthening (or precipitation strengthening) and finer grain strengthening. Whereas

Table 2. Mechanical properties of cold-rolled foils of TLM alloy composite foils (0.2mm)

<table>
<thead>
<tr>
<th>Samples</th>
<th>deforming rate/%</th>
<th>$R_m$/MPa</th>
<th>$R_{p,0.2}$/MPa</th>
<th>$E$/GPa</th>
<th>Average grains dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(2-layers)</td>
<td>90</td>
<td>995</td>
<td>875</td>
<td>62</td>
<td>200nm (width)</td>
</tr>
<tr>
<td>E(4-layers)</td>
<td>95</td>
<td>1000</td>
<td>890</td>
<td>66</td>
<td>120nm (width)</td>
</tr>
<tr>
<td>F(8-layers)</td>
<td>97.5</td>
<td>1050</td>
<td>910</td>
<td>70</td>
<td>80nm (width)</td>
</tr>
</tbody>
</table>

Figure 6. The microstructure of TLM alloy (a)750°C/1h, AC (b)750°C/1h, AC and aged at 510°C/1h, AC (c) Cold rolled with deforming rate 97.5%
TLM alloy after ARB may result in nano-grain strengthening accompanying with nano-grains re-orientation, recovery and partial recrystallization, and also result from martensite from large quantity of residual meta-stable β phase (Figure 3) when the tensile deforming is performed (see Figure 7).

Figure 7. TEM microstructure of TLM alloy foils (0.2 mm) after 2 cold deforming rates (a) 90% with 2 layers (b) 97.5% with 8 layers.

On the other hand, it is also found from Figure 7 that the larger quantity of nano-grains of α + β dual-phase restricts the movement of dislocation, and thus enhance the tensile strength of TLM alloy. There is no twin crystal appearance from TEM which means the phase transformation is helpful to microstructure refined, the nano-grains boundary slip and martensite phase transformation not only can make the microstructure finer, but also the stress induced or assisted martensite occur which result in higher elongation in Figure 5b.

Biomedical Ti alloys should possess better mechanical compatibility other than biocompatibility. Apart from lower $E$ and $R_{p0.2}/E$ values, the alloy simultaneously should possess enough strength, plasticity, toughness etc., But strength, moduli of elasticity, plasticity and toughness are a complex contradiction. Generally speaking, with increasing of the strength, the fracture toughness and plasticity decreases accordingly, whereas the moduli of elasticity increase. So when we try to obtain lower $E$ to meet surgical implanting materials, we have to think about the better matching of other mechanical properties. Some previous papers reported that the $E$ values of some metals with nano-grains was lowered compared with its coarse-grains materials, but the recent reports proved that the lower $E$ values was caused from the inner defects of sample prepared which is in accordance with our results (see Table 2). Of course, the different cold deforming textures of nano-grains probably influence the mechanical properties. It is proved that the circular textures are helpful to improve the process properties, and the textures along diameter direction are helpful to improve strength and plasticity(7). Other than textures factors, the dimensional effect of rods, tubes and foils etc. is also an influential factor to mechanical properties. The mechanical properties of metal materials also have closer dependence on their chemical composition, especially Nb is helpful to lower moduli of elasticity of Ti alloys(8).

In fact, there are different requirements for micro-structure and mechanical properties upon biomedical Ti alloys used in different surgical implants such as joints, stents etc. It is mistaken idea to simply pursue only one of the mechanical properties whether it is higher or lower. So a better biomedical Ti material should firstly be easily wrought to the rods, plates, foils, tubes, wires etc., then their microstructure mechanical properties could be adjusted in a large slope by controlling the adequate process and heat treatment, finally the appropriate matching of mechanical compatibility including the strength, elastic modulus, plasticity, fracture toughness, fatigue limitation and also wear resistance etc. can be achieved by means of controlling the grains size, phase compositions and microstructure morphology etc. The novel TLM Ti alloy possesses the above-mentioned features and would be promising biomaterials to substitute the present 316L stainless steel, CoCr alloy, and Ti6Al4V alloys etc.

4. Conclusions

(1) The TLM alloy foils of 0, 2nm in thickness could be easily prepared by ARB. With increasing of the deformation rates, the grains could be fined to 80nm in width for the composite foils with 8 layers, and the $R_{m}, R_{p0.2}$ and $E$ rise gradually. With the temperature of ST increasing, the $R_{m}, R_{p0.2}$ and $A_{s}$ lower gradually, whereas $E$ rises slowly. Especially, the lowest $E$ value could reach 38GPa which is very close to that of natural bone.

(2) With increasing of the deforming rates, the boundaries among layers for TLM alloy composite foils have achieved melting fusion welding by mechanical atom diffusion bonding which leads to the increasing of the $R_{m}, R_{p0.2}$ and $E$. Thereby the materials strengthening mechanism is different between ARB and STA, one is dispersion strengthening or precipitation strengthening for STA treatment, and the other is nano-grain strengthening for ARB process.

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REFERENCES