Effects of Sn content on the microstructure, phase constitution and shape memory effect of Ti–Nb–Sn alloys

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Abstract

The effect of Sn content on the microstructure, phase constitution and shape memory effect of Ti–16Nb–xSn (x = 4.0, 4.5, 5.0 at%) alloys were investigated by means of optical microscopy, X-ray diffraction, transmission electron microscopy and bending test. With the increase of Sn content, the β phase becomes stable. The solution-treated Ti–16Nb–4Sn alloy is composed of α′′ and β phases at room temperature, whereas the solution-treated Ti–16Nb–5Sn alloy is only composed of β phase at room temperature. TEM observation shows that there is parallel lamellar α′′ martensite with the substructure of (1 ¯1 ¯2) type I twin in the Ti–16Nb–4Sn alloy. There exists the dislocation wall inside the single β phase in the Ti–16Nb–5Sn alloy. The shape recovery ratio decreases with increasing the bending strain and the bending temperature, which is in correspondence with the different deformation mechanisms at different temperature ranges. The shape recovery ratio shows a decreasing trend with the increase of Sn content at the same bending strain and temperature. The maximum completely recovery strain is around 4%.

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Keywords: Ti–Nb–Sn alloys; Microstructure; Phase constitution; Shape memory effect

1. Introduction

Titanium–nickel shape memory alloys are widely used in biomedical fields such as orthopaedics, dentistry and interventional radiology because of their superior shape memory effect and superelasticity [1], yet the possibility of Ni-hypersensitivity and toxicity have been pointed out [2,3]. People devote to the development of Ni-free shape memory alloys. Titanium alloys have been widely used as biomaterials due to their high corrosion resistance, excellent biocompatibility, high strength and low modulus. The β titanium alloys exhibit a martensite transformation from disordered bcc β phase to metastable orthorhombic α′′ martensite phase, which is accommodated primarily by internal twinning. The shape memory effect is associated with the reversion of α′′ to β in titanium alloys. According to studies on both the cytotoxicity of pure metals and polarization resistance-tissue reaction of surgical implant materials, shape memory alloys consisting of Ti, Zr, Nb, Ta and Sn elements would be recommended for biological applications [4]. It was first reported by Baker [5] that shape memory effect resulted from the reversion of α′′ to β in Ti–35 wt% Nb alloy. A maximum 3.25% recovery strain was obtained through aging of short duration at 300–500 °C. However, the microstructure observation has not been conducted. Recently, new kinds of Ni-free biomedical shape memory alloys such as Ti–Nb based alloys (with addition of Ge, Ga, Al, Ta, Sn, etc.) have been developed with the recovery strain of 3–4% [6–14]. It is confirmed the mechanical properties and phase transformation temperature can be adjusted by addition of further alloying elements. Kim et al. [6] have found shape memory effect and superelasticity in the Ti–(22–25) at% Nb and Ti–(25.5–27) at% Nb alloys, respectively. The effect of deformation texture, recrystallization texture and alloying content on the shape memory effect and superelasticity was reported in Ti–Nb–Ge [7], Ti–Nb–Zr [8], Ti–Nb–Al [9] and Ti–Nb–Ta [10,11] alloys. It was revealed by X-ray diffraction pole figure analysis that a {001}β(1 1 0)β deformation texture and a {1 1 2}β(1 1 0)β recrystallization texture were confirmed. There is also reported that Ti–24Nb–4Zr–7.9Sn alloy exhibits ~3.3% maximum recovery strain with unstable elastic and plastic deformation [12]. Nitta et al. [13] have reported that the phase transition temperature in Ti–Nb–Sn alloys is very sensitive to
Nb and Sn contents and a maximum recovery strain of 3.5% is obtained in Ti–18Nb–4Sn alloy. Takahashi et al. found that the superelasticity of Ti–Nb–Sn alloys depends on the alloy composition and heat treatment [14]. However, there is no detailed report on the substructure of martensite, the effects of alloy composition, deformation strain and deformation temperature on the shape recovery ratio in Ti–Nb–Sn alloys. The purpose of this study is to explore them.

2. Experimental methods

The Ti–Nb–Sn alloys with nominal composition of Ti–16Nb–xSn (x = 4.0, 4.5, 5.0 at%) were prepared by arc-melting method under an Ar atmosphere. The ingots were re-melted five times for ensuring homogeneity. Then they were hot rolled to the plates with a thickness of 1.5 mm under 800 °C. The hot-rolled plates were finally solid solution treated at 850 °C for an hour and quenched into iced water. All the samples were prepared by electro-discharge machining from the solution-treated plates.

Surfaces of the samples were mechanically polished via a standard metallographic procedure and then etched in a solution of hydrofluoric, nitric acid and water (10:5:85 in volume). Microstructure of the etched samples was examined using an optical microscope (Aiovett 200 MAT). X-ray diffraction (XRD) was conducted using a Philip X’Pert Pro diffractometer operated at 40 kV and 40 mA. A Ni-filtered Cu Kα radiation (λ = 1.5406 nm) was used. Transmission electron microscopy (TEM) observation was performed using a Philips CM12 operated at 120 kV. TEM thin foil samples were prepared using a twin jet polisher in an electrolyte with 30 mL perchloric acid, 175 mL n-butyl alcohol and 300 mL methanol at −50 °C.

We tried to detect the phase transition temperatures of the alloy samples by DSC with heating rate of 10 K/min. Because of small transformation heat, it cannot be determined by DSC. So we use the bending method to measure the phase transition temperature. Fig. 1 gives the schematic illustration for the bending test. The samples were fixed and then bent until the deformation position. When the external force was removed, the samples moved to the “spring-back position”. When heated, it moved to the “heating position” because of the shape memory effect. The shape memory effect tests were carried out at different temperatures and strains. The samples were bent around cylinders with different diameters at different temperatures and then heated up to the temperature above the Af temperature.

3. Results and discussion

3.1. Effects of Sn content on the microstructure and phase constitution of Ti–Nb–Sn alloys

Fig. 2 shows the optical micrographs of the solution-treated Ti–Nb–Sn alloy samples. In all the samples, the grains have regular polygons and the grain boundaries are flat and straight. The change of Sn content has no influence on the grain size.

Fig. 3 shows the X-ray diffraction patterns of the solution-treated Ti–Nb–Sn alloy samples. The XRD profiles in Fig. 3(a) indicates the coexistence of α′′ and β phases in the solution-treated Ti–16Nb–4Sn alloy sample. On the contrary, the solution-treated Ti–16Nb–5Sn alloy sample is only composed of β phase, as shown in Fig. 3(c). From Fig. 3, we can see that the Sn content has influence on the phase constitution of the solution-treated Ti–Nb–Sn alloys. When the Sn content is low, there exists α′′ phase. With the increase of Sn content, the intensity of α′ phase becomes weaker. There exists α′′ (1 1 1) and α′′(0 2 2) peaks in the Ti–16Nb–4Sn alloy sample; only weaker α′′(0 2 2) peak appears in the Ti–16Nb–4.5Sn alloy sample and only single β phase exists in the Ti–16Nb–5Sn alloy sample. Clearly, with the Sn content increasing, the β phase becomes stable.

Fig. 4 shows the TEM micrographs of the solution-treated Ti–16Nb–4Sn alloy sample. Fig. 4(a) is a TEM bright field image revealing the uniform lamellar α′ martensite formed in the parent β matrix. Fig. 4(b) is the corresponding selected-area electron diffraction (SAD) pattern taken from the region marked by A in Fig. 4(a). It is pointed out that the (1 1 2) type I twins were observed as the substructure of α′′ martensite. Fig. 4(c) is an enlargement of α′′ martensite. The α′ martensite is also be tested by XRD in the Ti–16Nb–4Sn alloy sample, which is consistent to the TEM observation. Fig. 4(e) is the SAD pattern taken from the region marked by B in Fig. 4(d), which derived from the β phase. A change in the microstructure has been observed in the Ti–16Nb–5Sn alloy sample. The typical TEM microstructure is the grain of the β phase. However, there are dislocations to be observed. Fig. 5(a) shows the dislocation wall inside the single β phase. Fig. 5(b) shows SAD pattern corresponding to the parent β phase. However, there is no lamellar α′ martensite.

3.2. Effects of Sn content on the shape memory effect of Ti–Nb–Sn alloys

Fig. 6(a) shows the curves of heat flow vs. temperature by DSC for the Ti–Nb–Sn alloy samples. There is not any peak observed because of small phase transformation heat. Fig. 6(b) shows the inclined angle vs. heat temperature curves for the solution-treated Ti–Nb–Sn alloy samples. The inclined angle was defined as the cross angle between “fixed position” and “heated position”. The samples were bent 180° in liquid
nitrogen, and then heated to different temperatures. The As temperature is the temperature at which the inclined angle begins to change. The Af temperature is the final temperature at which the inclined angle cannot change. The As and Af temperatures are determined by tangent rule. Table 1 summarizes the As and Af temperatures measured by bending test for the solution-treated Ti–Nb–Sn alloy samples.

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>As  (°C)</th>
<th>Af  (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–16Nb–4Sn</td>
<td>4</td>
<td>-49</td>
</tr>
<tr>
<td>Ti–16Nb–4.5Sn</td>
<td>-40</td>
<td>-79</td>
</tr>
<tr>
<td>Ti–16Nb–5Sn</td>
<td>20</td>
<td>-40</td>
</tr>
</tbody>
</table>

Fig. 3. X-ray diffraction patterns for the solution-treated Ti–Nb–Sn alloy samples, (a) Ti–16Nb–4Sn, (b) Ti–16Nb–4.5Sn, and (c) Ti–16Nb–5Sn.

Fig. 7(a) shows the curves of the total bending strain on the shape recovery ratio at −196 and −70 °C for the solution-treated Ti–Nb–Sn alloy samples. The Ti–Nb–Sn alloy samples were deformed to 4, 6, 8 and 10%. Then they were heated above the Af temperature after unloading. From these curves we can see that the shape recovery ratio decreases when the bending strain increases. At 4% bending strain, the shape recovery ratio can reach 100% for the solution-treated samples except for the Ti–16Nb–5Sn alloy sample. At 10% bending strain, the shape recovery ratio is about 70%. The maximum completely recovery strain is 4%. The reason is that the plasticity deformation increases when the bending strain increases. The same phenomenon has been reported in Ti–10V–2Fe–3Al alloy [15] and Ti–30–Nb–3Pd alloy [16], with the maximum recovery strain being 3 and 2%, respectively. All the result show the trends in terms of the evolution of the shape memory effect with the amount of initial strain: (i) almost perfect recovery is possible for low initial strain; (ii) the shape memory effect decreases with the increase of the initial strain. However, the shape recovery ratio for the Ti–16Nb–5Sn alloy sample bent to different strains at −70 °C decreases quickly. The reason may be attributed to that the As temperature is close to the bending temperature and the alloy sample may be in the parent phase condition. The plasticity deformation for parent phase is unrecoverable. From these curves we can also see that the shape recovery ratio shows a decreasing trend with the increase of Sn content at the same bending strain and bending temperature.

Fig. 7(b) shows the curves of the shape recovery ratio vs. bending temperature for the solution-treated Ti–Nb–Sn alloy samples. The samples were deformed to 4% at −180, −80, −60, −40, −20, 0, 20, 40, 60 °C, and then heated up to the
Fig. 4. (a) TEM micrograph of lamellar $\alpha''$ martensite in the solution-treated Ti–16Nb–4Sn alloy sample, (b) the corresponding SAD pattern taken from the region marked by A, (c) an enlargement of $\alpha''$ martensite, (d) parent phase, and (e) the corresponding SAD pattern taken from the region marked by B.
Fig. 5. (a) Dislocation wall and (b) SAD pattern of β phase, parallel to [1 1 1]_β in the Ti–16Nb–5Sn alloy sample.

Fig. 6. (a) The curves of heat flow vs. heat temperature and (b) the curves of inclined angles vs. heat temperature for the solution-treated Ti–Nb–Sn alloy samples.

Fig. 7. The curves of shape recovery ratio vs. bending strain (a) and bending temperature (b) for the solution-treated Ti–Nb–Sn alloy samples.
temperature above the Af temperature. There are three regions for all Ti–Nb–Sn alloy samples. For the Ti–16Nb–4Sn alloy sample, the region when the bending temperature is lower than −40 °C is the first region where the sample can recover completely. The second region lies in the interval between −40 and 20 °C where the shape recovery ratio decreases quickly with the increase of the bending temperature. When the bending temperature is higher than 20 °C, the shape recovery ratio is almost zero, which is the last region. For the other two alloys, there are still three regions, but only the interval is different. Such regularity is determined by different deformation mechanisms at different temperatures. In the temperature range of −180 to −40 °C, the Ti–16Nb–4Sn alloy sample can recover completely. This may due to the rearrangement of martensite variants or stress-induced-martensite phase transformation. Since the stress-induced transformation may occur between As and Ms temperatures and the stress-induced martensite is stable below the As temperature, a complete shape memory recovery is possible on subsequent heating through the As and Af temperatures. We can deduce that the As temperature for the Ti–16Nb–4Sn alloy sample should be −40 °C. For the last two regions, there may be two possible deformation mechanisms. One possibility is slip deformation. The critical stress for inducing martensite increases with increasing temperature. On the other hand, the stress for slip decreases with increasing temperature. Slip occurs if the stress level for slip becomes lower than the stress to induce the martensite. The strain which arises from the slip of martensite or β parent phase is unrecoverable Thus, the strain by slip deformation increases with increasing temperature, causing the recoverable strain to decrease. The other possibility is the pseudoelasticity at temperatures above −40 °C, which can also result in the decrease of shape memory ratio at subsequent heating segment. Since no martensite can be retained upon the release of deformation, hence no shape memory recovery strain can be obtained; the Af temperature should be about 20 °C.

4. Conclusions

(1) The solution-treated Ti–Nb–Sn alloy samples have almost the same average grain size. The solution-treated Ti–16Nb–4Sn alloy sample is composed of α′′ and β phases at room temperature. There is only β phase observed for the Ti–16Nb–5Sn alloy sample at room temperature.

(2) The parallel lamellar α′′ martensite in the solution-treated Ti–16Nb–4Sn alloy is observed. The substructure of martensite is (1 1 2) type I twin. In other solution-treated alloys, stripped dislocations and dislocation wall are observed inside the β phase grain. Sn content has influence on the microstructure and the phase constitution of the Ti–Nb–Sn alloys.

(3) The shape memory effect of Ti–Nb–Sn alloys is influenced by the bending strain and the bending temperature. The shape recovery ratio decreases with the increase of the bending strain and the bending temperature according to different deformation mechanisms at different temperatures. The maximum completely recovery strain is about 4%.

References