EFFECT OF Nb ON THE PHASE TRANSFORMATION IN BIOCOMPATIBLE TiNb-BASED ALLOYS

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Abstract

The effect of niobium content on phase transformations in two binary alloys on the base of TiNb was studied. The temperatures of phase transformations for Ti22Nb and Ti25Nb alloys after rotary forging were identified using Differential Thermal Analysis. The niobium concentration in both alloys was determined by means of EDAX analysis. For both alloy compositions, the microstructure formed of alpha and beta phases was observed before and after Differential Thermal Analysis by means of optical and scanning electron microscopes. The metallographic study was completed with microhardness measurement. The microhardness values proved decreasing tendency with increasing niobium content. After DTA measurement, microhardness increased due to the alpha precipitation.

Keywords: Beta titanium alloy, TiNb, DTA, microhardness

1. INTRODUCTION

Biocompatible materials for applications in traumatology and orthopedics typically require a combination of excellent biocompatibility and convenient mechanical properties. The mechanical characteristics, especially the Young’s modulus must be as close as possible to those of bone to avoid or minimize the bone atrophy due to the stress shielding effect [1]. The new generation of low modulus beta titanium alloys based on TiNb system which are free of cytotoxic elements presents superelastic behavior and possesses the very good mechanical properties for use as medical metallic implants. According to recent studies [2,3,4], the shape memory behavior of TiNb alloys is concentration dependent and is related with martensitic transformation. The temperature of martensitic transformation \( M_s \) (martensite start temperature) shows Nb content dependence and decrease by 40 °C with 1 at.% increase of Nb content for Ti(20-28)Nb alloys. Superelastic behavior due to stress induced martensite transformation was observed in the Ti(26-27)Nb alloys at room temperature. Superelasticity of TiNb based alloys can only take place if \( \beta \) phase is maintained. The maximum transformation strain ranges from about 3 to 4 % for TiNb based alloys exhibiting superelasticity at room temperature that could be sufficient for most medical applications [5].

In the present paper, the influence of Nb content on the temperature of phase transition \( \beta\leftrightarrow\alpha \), microstructure feature and on the microhardness has been investigated in two promising biocompatible alloys based on TiNb system.

2. EXPERIMENTAL

TiNb master alloy (55/45 wt.%) and Ti pieces were used to prepare experimental alloys with the nominal compositions of Ti22Nb and Ti25Nb (at.%) by plasma melting. The ingots were transformed into the wires of 3 mm in diameter by rotary forging at 850°C.

The phase transformation behavior was controlled by means of Differential Thermal Analysis (DTA) with use of Setaram SETSYS 18TM apparatus. The samples of weight of about 115 mg and of cylindrical shape with 3 mm in diameter and 3 mm of height were analyzed in corundum crucibles at constant heating and cooling
rate of 5 °C/min in high purity Ar (6N) atmosphere. Prior to the DTA analysis, the samples were slightly ground and cleaned in acetone by simultaneous impact of ultrasound.

The microstructure feature was studied before (as-forged state) and after DTA analysis by means of optical microscope (OM, OLYMPUS DP GX51) and scanning electron microscope (SEM) FEI QUANTA 450 FEG equipped with EDAX APOLLO X probe. The samples for metallographic observation were electrolytically polished and etched for 2-5 s in solution of HF, HNO₃ and C₂H₆O₃ (2:1:2). The niobium content was measured by EDAX microanalysis. The Vickers microhardness of specimens was measured by means of the Future - Tech FM - 100 device with load of 0.2 kg for 7s and indentation step of 1 mm.

3. RESULTS AND DISCUSSION

The results of EDAX microanalysis in Table 1 confirmed the demanded composition of both alloys, thus the plots of DTA measurement (Fig.1) correspond to phase transformation in Ti22Nb and Ti25Nb alloys. The temperature intervals or peaks related to microstructure changes are summarized in Table 2.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Element</th>
<th>Ti22Nb</th>
<th>Ti25Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>At.%</td>
<td>78.46</td>
</tr>
<tr>
<td></td>
<td>Nb</td>
<td>At.%</td>
<td>21.54</td>
</tr>
</tbody>
</table>

Table 1 Average values of EDAX microanalysis of the content of elements in TiNb alloys

Ti25Nb exhibited an endothermic peak near 160 °C that corresponds to precipitation of some amount of α phase [6]. As the both alloys were hot forged at 850°C, thus above the β transus, the final forged microstructure (Fig.2) consisted of retained β phase with small or none α precipitates formed during cooling after thermo-mechanical treatment. Unlike Ti25Nb no clear peaks at first stages of heating could be detected for Ti22Nb, only very slight corrugated plot could be observed, thus no more precipitation of an important amount of α phase could be expected. Another endothermic peaks at higher temperatures correspond to transition from α+β microstructure to β phase in both alloys, it means at 484 and 458 °C for Ti22Nb and Ti25Nb, respectively. The exothermic peaks during cooling were detected at rather different temperatures that would correspond on heating. Although Ti22Nb exhibits two peaks, at 290 and 101 °C, another phase
that $\alpha$ could not be determined by neither optical nor scanning electron microscope. The peak at 131 °C in Ti25Nb could be related with $\alpha$ phase precipitation.

**Table 2** Temperature intervals and peaks determined from DTA plots for TiNb alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ti22Nb</th>
<th>Ti25Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>peak (°C)</td>
<td>interval (°C)</td>
</tr>
<tr>
<td>heating</td>
<td>-</td>
<td>150-200</td>
</tr>
<tr>
<td></td>
<td>484</td>
<td>337-530</td>
</tr>
<tr>
<td>cooling</td>
<td>290</td>
<td>337-249</td>
</tr>
<tr>
<td></td>
<td>101</td>
<td>133-73</td>
</tr>
</tbody>
</table>

**Fig. 2** OM micrographs of TiNb alloys after rotary forging: a) Ti22Nb with prolonged $\beta$ grains and $\alpha$ precipitates and b) Ti25Nb with deformed $\beta$ grains

**Fig. 3** OM micrographs of TiNb alloys after DTA measurement: a) Ti22Nb and b) Ti25Nb with equiaxed $\beta$ grains and very fine $\alpha$ precipitates

The optical micrographs of rotary forged samples before and after DTA measurement are shown in **Figs.2** and **3**, respectively. Elongated grains typical for rotary forging (hot working) were found in longitudinal sections of samples (as seen in **Fig.2a**) and very fine recrystallized grains are typical for cross section (as
seen in Fig.2b). Unlike Ti25Nb alloy low Nb content in Ti22Nb promoted more evident precipitation of $\alpha$ phase in hot deformed microstructure. Change of microstructure after DTA in Ti22Nb and Ti25Nb samples is shown in Fig.3. For both alloys, very fine precipitates of $\alpha$ phase are observed in the equiaxed grains of $\beta$ phase as well as at grain boundaries.

Microhardness measurement revealed lower values for higher Nb content for as-forged state as well as after DTA analysis (Table 3). As it was reported in [6,7] lower microhardness of Ti25Nb samples is due to $\beta$ phase stabilized by higher Nb contents. In Fig.4, it can be seen that microhardness increased after DTA for both alloy compositions. In the case of Ti22Nb the values increased by 41 HV unlike Ti25Nb where the rising was only by 10 HV. Based on metallographic observation the higher microhardness values are due to the precipitation of $\alpha$ phase that confirmed the peaks on DTA curves.

Table 3 Vickers microhardness (HV) values of two TiNb alloys in rotary forged state and after DTA measurement

<table>
<thead>
<tr>
<th>Alloy Treatment</th>
<th>Ti22Nb</th>
<th>Ti25Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value (HV)</td>
<td>230</td>
<td>219</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Mean value (HV)</td>
<td>261</td>
<td>229</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>8</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 4 Average values of Vickers microhardness measurement of rotary forged Ti22Nb and Ti25Nb alloys before and after DTA analysis

4. CONCLUSIONS

Based on the results of the DTA measurement, metallographic observation, EDAX microanalysis and Vickers microhardness measurement of two TiNb based alloys with nominal compositions of 22 and 25 at.% Nb following conclusions could be drawn:

1. content of Nb in as-forged Ti22Nb and Ti25Nb alloys reached of 21.54 at.% and 25.24 at.%, respectively, that shows good agreement with demanded compositions;
2. Endothermic peaks on the DTA curves at heating revealed that first precipitation of \( \alpha \) phase passed in retained \( \beta \) grains after hot deformation and then it was followed by transition from \( \alpha+\beta \) to \( \beta \) structure;

3. Microhardness of Ti25Nb alloy exhibited lower values than in the case of Ti22Nb alloy due to higher Nb content and stabilized \( \beta \) structure;

4. Finally, higher microhardness values after DTA for both alloy compositions corresponded to precipitation of \( \alpha \) phase.

**ACKNOWLEDGEMENTS**

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