Phase constitution, Mechanical Property and Corrosion Resistance of the Ti-Nb Alloys

B.L. Wang1, 2, a, Y.B. Wang2, b, Y.F. Zheng2, 3, c

1School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
2Center for Biomedical Materials and Engineering, Harbin Engineering University, Harbin 150001, China
3Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing 100871, China

a wbl201@yahoo.com.cn, b wangyanbo@hrbeu.edu.cn, c yfzheng@pku.edu.cn

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Abstract. Recently, people devote to the development of Ni-free shape memory alloys in order to avoid the Ni-hypersensitivity and toxicity and pursue absolute safety. The shape memory effect and superelasticity have been reported in the biomedical Ti-Nb based alloys. The purpose of this paper is to report the phase constitution, tensile property, shape memory effect and corrosion resistance of the Ti-Nb alloys. The phase constitutions of the Ti-Nb alloys are investigated by means of X-ray diffraction (XRD). The results reveal that \( \beta + \alpha'' \) phases are presented in the Ti-35Nb alloy and only \( \beta \) phase in the Ti-52Nb alloy at room temperature. The tensile test and bending tests indicate that the Ti-35Nb alloy exhibits shape memory effect. The shape recovery ratio is near to 80% when the bending strain is 4.4% and decreases with the increase of the total bending strain. The corrosion resistance of the Ti-Nb alloys in the Hank's solution and artificial saliva (pH=7.4) at 37°C are investigated by OCP, Tafel and anodic polarization methods. The results indicate that the Ti-35Nb alloy has a better corrosion resistance in the artificial saliva and can replace the Ti-Ni alloy in the dental application. In the non-oral condition, the Ti-52Nb alloy may be preferable.

Introduction

Titanium-Nickel shape memory alloys are widely used in biomedical fields such as orthopedics, 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. H.Y. Kim et al. [4] have found shape memory effect and superelasticity in the Ti-(22~25) at% Nb and Ti-(25.5~27) at% Nb alloys, respectively. However, there is little study of the corrosion resistance for the Ti-Nb alloy in the simulated body solutions. The purpose of this study is to examine the effects of niobium value on the phase constitute, mechanical property, shape memory effect and corrosion resistance for the Ti-Nb alloys in the Hank's solution and artificial saliva and to propose their future applications.

Experimental methods

Ti-35wt%Nb and Ti-52wt%Nb alloys were prepared using arc-melting method under an argon protection atmosphere. The ingot was re-melted five times for ensuring homogeneity. The ingot was hot rolled into the plate with a thickness of \(~1.3\text{mm}\) at \(800^\circ\text{C}\), and then was solution treated at \(850^\circ\text{C}\) for \(30\text{min}\) and quenched into water. X-ray diffraction (XRD) was conducted using a Rigaku diffractometer (Rigaku DaMax/2400) operated at \(50\text{kV}\) and \(100\text{mA}\). A Ni-filtered Cu K\(\alpha\) radiation (\(\lambda=1.5406\text{nm}\)) was used. Tensile test was performed on Instron 5569 with a rate of \(1\text{mm/min}\). Tensile samples were \(1.15\times3\text{mm}^2\) in section with a gage length of \(50\text{mm}\). The phase transformation...
temperature can not be detected by DSC method for the Ti-Nb alloy sample, so we used the bending method instead. The shape memory effect was evaluated by bend test. The samples were bent at different bending strain and temperature and then heated up to the temperature far above the Af temperature. The electrochemical measurement was performed using a Solartron 1287 potentiostat instrument in the Hank’s solution [5] and artificial saliva [6] (pH=7.4) at 37°C. The samples were wet ground with water-proof silicon carbide papers to 2000 grit, and then polished. Finally they were cleaned using acetone, ethanol and de-ionized water in an ultrasonic bath and dried in air. The sample, a platinum electrode and a saturated calomel electrode (SCE) were used as working electrode, counter-electrode and reference electrode, respectively. The OCP measurement was maintained up to 10h. Tafel plots were conducted at a scan rate of 0.1mV/s. The corrosion potential (E\text{corr}) and corrosion current density (i\text{corr}) were obtained from the Tafel analysis. The anodic polarization were measured from -0.5V to 2V or 2.5V (vs.SCE) with a rate of 1mV/s after dipping the sample into the electrolyte for 30min. The electrolytes were not deaerated.

Results and discussion

The phase constitution of the Ti-Nb alloys

Fig.1 shows the X-ray diffraction (XRD) patterns of the solution-treated Ti-Nb alloy samples measured at room temperature. The XRD profiles in Fig.1 show that there exists \( \beta + \alpha' \) phases for the solution-treated Ti-35Nb alloy and there is only \( \beta \) phase observed for the Ti-52Nb alloy. Niobium, as a \( \beta \) stabilizing element, can stabilize \( \beta \) phase. When the niobium overruns a constant value, the \( \beta \) phase can be retained for the \( \beta \) titanium alloy quenched from the \( \beta \) phase. This is the reason that the Ti-52Nb alloy consists of only \( \beta \) phase while \( \alpha' \) phase is observed in the Ti-35Nb alloy.

The mechanical properties of the Ti-Nb alloys

Fig.2 shows the tensile stress-strain curves for the Ti-Nb alloy samples at room temperature. There is a two yield plateaus observed in the Ti-35Nb alloy sample because of the rearrangement of martensite or the stress inducing martensite transformation, which suggests that there maybe exists shape memory effect in the Ti-35Nb alloy. This result is consistent with the result of XRD. However, in the Ti-52Nb alloy, the deformation is only attributed to the \( \beta \) phase.

![Fig.1 X-ray diffraction patterns of the Ti-Nb alloy.](image1)

![Fig.2 The tensile stress-strain curves for the Ti-Nb alloy.](image2)

Fig.3 shows the shape recovery ratio vs. heating temperature curves for the Ti-35Nb alloy sample. The sample was bent 180° in liquid nitrogen, and then heated at different temperatures. The As and Af temperatures are 190°C and 270°C respectively. Fig.4 shows the curves of the total bending strain on the shape recovery ratio at different temperature (-40--30°C, 20°C and 100°C). The Ti-35Nb alloy samples were deformed to 4.43%, 5.58%, 8.04%, 10.63 and 16.59%. Then they were heated above the Af temperature after unloading. For all the test temperature, the shape recovery ratio decreases with the increase of the total bending strain. At 4.43% bending strain, the shape recovery ratio can reach 73.9, 74.3 and 77.4% for the Ti-35Nb alloy samples. So, in order to obtain the complete recovery, the total bending strain should be less than 4%. The reason is that the
plasticity deformation increases when the bending strain increases. From these curves, we can also see that the bending deformation temperature has no influence on the shape recovery ratio at the test temperature range because all the test samples are at the same conditions. The experimental result indicates that there is no shape memory effect in the Ti-52Nb alloy.

The corrosion resistance properties of the Ti-Nb alloys

Fig. 5 shows the curves of the OCP vs. time for the Ti-Nb alloy samples in the Hank's solution and artificial saliva (pH=7.4). In the Hank's solution, for the Ti-52Nb alloy sample, the OCP is found to stabilize at -0.17V (vs.SCE); for the Ti-52Nb alloy samples, the OCP stabilizes at -0.08V~0.07V (vs.SCE). The OCP value of the Ti-52Nb alloy sample is significantly higher than that of the Ti-35Nb alloy in the Hank's solution, which indicates that the Ti-52Nb alloy is more stable and has better corrosion resistance than that of the Ti-35Nb alloy in the Hank's solution. In the artificial saliva, the Ti-35Nb and the Ti-52Nb alloy samples are -0.27V and -0.46V (vs.SCE), respectively. So, in the artificial saliva, the Ti-35Nb alloy is more stable and has better corrosion resistance. From these results, we can also see that the OCP values of the Ti-Nb alloy are influenced by the test solutions. The Ti-35Nb alloy has higher OCP value and better corrosion resistance in the artificial saliva than that in the Hank's solution (pH=7.4); while vice versa for the Ti-52Nb alloy.

The corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) for the Ti-Nb alloy samples in the Hank's solution and artificial saliva (pH=7.4) are listed in Table 1. It is found that the $i_{corr}$ for the Ti-Nb alloy samples is influenced by the value of niobium and the simulated solutions. The Ti-35Nb alloy sample has lower $i_{corr}$ value than that of the Ti-52Nb alloy sample in the artificial saliva; The Ti-52Nb alloy sample has lower $i_{corr}$ value than that of the Ti-35Nb alloy sample in the Hank's solution. In addition, the $i_{corr}$ values of the Ti-35Nb alloy sample in the artificial saliva are lower than that in the Hank's solution, which suggests that the Ti-35Nb alloy has better corrosion resistance in the artificial saliva. The Ti-52Nb alloy has better corrosion resistance in the Hank's solution. These results are consistent with the results of OCP measurement.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolytes</th>
<th>$E_{corr}$ [V vs.SCE]</th>
<th>$i_{corr}$ [µA/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti35Nb</td>
<td>Hank's</td>
<td>-0.299</td>
<td>3.12</td>
</tr>
<tr>
<td>Ti35Nb</td>
<td>Saliva</td>
<td>-0.297</td>
<td>2.16</td>
</tr>
<tr>
<td>Ti52Nb</td>
<td>Hank's</td>
<td>-0.319</td>
<td>0.33</td>
</tr>
<tr>
<td>Ti52Nb</td>
<td>Saliva</td>
<td>-0.465</td>
<td>4.36</td>
</tr>
</tbody>
</table>

Fig. 5 OCP vs. time curves for the Ti-Nb alloy.

Fig.6 (a) ~ (c) show the anodic polarization curves for the Ti-35Nb alloy samples and Ti-52Nb alloy samples in the Hank's solution and artificial saliva (pH=7.4). The Ti-Ni alloy sample is used.
as a control. From these curves, we can see that the anodic polarization curves of the Ti-35Nb alloy sample and the Ti-52Nb alloy sample in the Hank's solution are nearly coincident, which means that these two alloys have almost the same corrosion resistance in the test condition. Comparing with the Ti-Ni alloy sample in the Hank's solution, the Ti-Nb alloy samples exhibit the same corrosion resistance in the high anodic potential range. However, the Ti-Ni alloy sample has better corrosion resistance than that of the Ti-Nb alloy samples in the low anodic potential range because of its lower current density value. In the artificial saliva, the Ti-35Nb alloy sample has better corrosion resistance than that of the Ti-52Nb alloy sample and the Ti-Ni alloy sample, because the Ti-35Nb alloy sample has the lowest current density although it exhibits repassivation. The corrosion resistance of the Ti-52Nb alloy sample is better than that of the Ti-Ni alloy sample. So, the Ti-35Nb alloy is a potential candidate to replace the Ti-Ni alloy in the dental and orthodontic treatment fields. From these curves, we can also see that the simulated solution has influence on the anodic polarization behavior for the Ti-Nb alloy samples. The Ti-Nb alloy has lower current density value in the artificial saliva than in the Hank's solution.

![Fig.6 The comparison of anodic polarization curves](image)

**Conclusions**

1. The XRD results show that the increase of the niobium value stabilizes β phase. So, the Ti-35Nb alloy consists of α" and β phases; while the Ti-52Nb alloy consists of only β phase.

2. The tensile test results show that the Ti-35Nb alloy maybe has shape recovery effect which is confirmed by the results of XRD and bending test.

3. The As and Af temperature are obtained by bending test. The shape recovery ratio of the Ti-35Nb alloys decreases with the increase of the bending strain. The bending deformation temperature has no influence on the shape recovery ratio at the test temperature range.

4. Based on the experimental results of OCP, Tafel and anodic polarization, the Ti-35Nb alloy exhibits better corrosion resistance in the artificial saliva (pH=7.4) than the Ti-52Nb alloy and the Ti-Ni alloy. It maybe replaces the Ti-Ni alloy in the dental and orthodontic treatment fields. While in some non-oral conditions, the Ti-52Nb alloy may be preferable. The Ti-Nb alloy has a large potential for biomedical applications.

**References**


