Mechanical Properties and Corrosion Behavior of a Beta Titanium Alloy

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Abstract. Recently, people devote to the development of beta titanium alloys which have better biocompatibility because of the addition of Mo, Nb, Ta, Zr, Sn, et al. In this paper, the effects of heat treatment and cold roll deformation on the mechanical properties of the Ti-11.3Mo-6.6Zr-4.3Sn alloy (TMZS) are investigated by tensile test. The results show that the excellent combination of strength and ductility can be obtained by heat treatment or cold deformation. The TMZS alloy can obtain intermediate modulus, stronger than nickel titanium, weaker than stainless steel. The corrosion resistance of this alloy in the Hank's solution, 0.9% NaCl physiological solution and artificial saliva with different pH values at 37°C are investigated by means of open-circuit potential (OCP), Tafel and potentiodynamic anodic polarization techniques. All the test results suggest that the TMZS alloy has excellent corrosion resistance in the three simulated solutions especially in the artificial saliva and has a large potential for biomedical application. In addition, the pH value and simulated solutions have some influence on the corrosion resistance of the TMZS alloy.

Introduction

Stainless steel, Ti-6Al-4V, and Nickel-Titanium alloys have been used in many medical applications due to its excellent mechanical properties and corrosion resistance [1]. Unfortunately, it has been reported that the elements of aluminium and vanadium have the potential toxicity, potential inhibition of apatite formation and possible neurological disorders [2-3]. The possibility of Ni-hypersensitivity and toxicity has also been pointed out [4-5]. So, the search for more biocompatible biomedical materials has been a major field. In order to pursue absolute safety, people devote to the development of β titanium alloys which have better biocompatibility because of the addition of Mo, Nb, Ta, Zr, Sn, et al. Ti-Mo-Zr-Sn β titanium alloy has been used in orthodontic treatment because of its intermediate stiffness between stainless steel and the Nickel-Titanium memory alloys, good flexibility and springback characteristics along with predictable forces for consistent control [6]. The purpose of this study is to examine the effects of heat treatment and cold deformation on the mechanical properties for the Ti-11.3Mo-6.6Zr-4.3Sn alloy. Furthermore, in order to extend the application of this alloy, the electrochemical corrosion behavior of the TMZS alloy has also been studied in the Hank's and NaCl solutions in this paper, except for in oral environment.

Experimental methods

Ti-11.3Mo-6.6Zr-4.3Sn alloy, which was abbreviated as TMZS alloy, was prepared using arc-melting method under an argon pressure of 0.05Pa. The ingot was re-melted five times for ensuring homogeneity. The ingot was hot rolled into the plate with a thickness of ~1.3mm at 800°C. The hot-rolled plate was solution treated at 760°C for 1h and quenched into water. Some of the solution-treated plates were then aged at 482°C for 4, 5 and 6h. Some were directly cold rolled to total reduction of 50%, with approximately 5% reduction per pass. Some of the cold-rolled plates were aged at 482°C for 5h. All of them were cooled in air. Tensile test was performed on Instron 5569.
with a rate of 1mm/min. Tensile samples were 1.15×3mm² in section with a gage length of 50mm.

The corrosion test samples prepared from the solution-treated plate were wet ground with waterproof 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. Three simulated body solutions, i.e. the Hank's solution [7], the 0.9%NaCl solution and the artificial saliva [8], were used, the pH values of which were precisely maintained at 2.4, 5.4 and 7.4. The electrochemical measurement was performed using a Solartron 1287 potentiostat instrument at 37℃ . 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 from -0.6V to +0.6V (vs.SCE) at a scan rate of 0.1mV/s. The corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) were obtained from the Tafel analysis. The potentiodynamic anodic polarization were measured from -0.5V to +2V (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 mechanical properties of the TMZS alloy

Fig.1(a) shows the tensile stress-strain curves for the TMZS alloy samples with different processing techniques. The solution-treated sample exhibits the highest elongation and the lowest tensile strength. With the increase of aging time, the strength of the TMZS alloy samples increases and the elongation decreases because of the precipitation harden from the second phase. At the same time, the elastic modulus increases compared with the solution-treated sample. The former is ~95-100GPa; the latter is ~70GPa. The sample which aged for 5h has the excellent combination of the strength and ductility although the tensile elastic modulus is higher. This can also be obtained by cold deformation without the increase of tensile elastic modulus. It can be induced that the combination of strength and ductility can be further increased by reducing the total reduction. The sample with cold deformation and aging has the highest tensile fracture strength but lowest elongation. Fig.1(b) shows the tensile properties comparison of the TMZS alloy, NiTi and Stainless steel. The TMZS alloy can obtain moderate, continuous forces, stronger than nickel titanium, weaker than stainless steel and the tensile elastic modulus of the TMZS alloy is between NiTi and Stainless steel, which provides another selection for clinical application.

The corrosion resistance properties of the TMZS alloy

Fig.2 shows the representative diagrams of OCP versus time for the TMZS alloy samples in the three simulated body solutions (pH=7.4). Following the initial increase, the OCP stabilizes at -0.12V (vs.SCE) in the artificial saliva (pH=7.4). The OCP increases towards the noble direction during the early hours followed by stabilization suggests that a protective passive film forms rapidly on the metal surface in the artificial saliva and remains stable during the whole immersion time. In the Hank's and 0.9% NaCl solutions, the OCP decreases, reaching -0.32V and -0.37V (vs.SCE) at ~0.5h. This suggests that the characteristics of the passive film change in this two
medium, leading to a reduced corrosion resistance. Furthermore, in this two medium, the OCP is still not stable after 10h, which means that the time for the TMZS alloy sample changes from the active to passive in the artificial saliva is longer than that in the other two solutions. From these curves, we can also see that the OCP value of the TMZS alloy sample in the artificial saliva is significantly higher than that in the other two. All of these results indicate that the TMZS alloy in the artificial saliva is the most stable and has better corrosion resistance.

The corrosion potential ($E_{corr}$) and corrosion current density ($i_{corr}$) for the TMZS alloy samples in the three different simulated body solutions are listed in Table 1. It is found that the $i_{corr}$ for the TMZS alloy samples is influenced by the simulated saliva. The $i_{corr}$ values of the TMZS alloy samples in the Hank's solution and artificial saliva are lower than that in the 0.9% NaCl solution, which suggests that the TMZS alloy have better corrosion resistance in the Hank's solution and artificial saliva than that in the NaCl solution. In addition, the pH value of the simulated solutions has also influence on the corrosion resistance for the TMZS alloy samples. The $i_{corr}$ values of the TMZS alloy samples are changed with the change of the pH values. However, the $i_{corr}$ values for the TMZS alloy samples in the three simulated solutions are all low, in the range of 1~6µA/cm$^2$, which means that the TMZS alloy has excellent corrosion resistance in the three simulated body solutions.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
<th>$E_{corr}$ [V vs.SCE]</th>
<th>$i_{corr}$ [µA/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hank's</td>
<td>2.4</td>
<td>-0.234</td>
<td>1.32</td>
</tr>
<tr>
<td>Hank's</td>
<td>5.4</td>
<td>-0.429</td>
<td>0.86</td>
</tr>
<tr>
<td>Hank's</td>
<td>7.4</td>
<td>-0.317</td>
<td>3.61</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.4</td>
<td>-0.247</td>
<td>2.98</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.4</td>
<td>-0.327</td>
<td>3.12</td>
</tr>
<tr>
<td>NaCl</td>
<td>7.4</td>
<td>-0.289</td>
<td>6.19</td>
</tr>
<tr>
<td>Saliva</td>
<td>2.4</td>
<td>-0.255</td>
<td>3.23</td>
</tr>
<tr>
<td>Saliva</td>
<td>5.4</td>
<td>-0.287</td>
<td>2.51</td>
</tr>
<tr>
<td>Saliva</td>
<td>7.4</td>
<td>-0.213</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Fig.2 OCP vs. time curves for the TMZS alloy.

Fig.3 (a)-(c) show the potentiodynamic anodic polarization curves for the TMZS alloy samples in the Hank's, NaCl and artificial saliva solutions with different pH values. For all test conditions, the TMZS alloy samples exhibit distinctively wide passive regions at the whole anodic potential range. There is no breakdown of the passive film until 2V vs.SCE for all the samples. The polarization behavior can be termed as stable passivity. From these curves, we can see that the alternation of pH value has influence on the corrosion behavior for the TMZS alloy samples in the three simulated body solutions. In the Hank's solution, when the anodic polarization potential is low, the current density value decreases with the increase of the pH value. When the anodic potential is high, the polarization curves for the TMZS alloy samples in the Hank's solution are nearly coincident. In the 0.9% NaCl solution, the alternation of pH value has also influence on the corrosion behavior. In the artificial saliva, the current density decreases with the increase of the pH value, especially for the TMZS alloy sample in the artificial solution (pH=7.4), which shows the lowest current density value for all the test conditions. The TMZS alloy sample in the artificial saliva (pH=7.4) has the best corrosion resistance. However, within the oxidation potential range (-58 to +212mV vs.SCE) in the normal human oral cavity [9], all the samples examined in this study show excellent corrosion resistance. Fig.3 (d) shows the anodic polarization behavior comparison of the TMZS alloy samples in the Hank's, NaCl and artificial saliva solutions (pH=7.4). It is obviously that the current density value decrease as such sequence: from in the NaCl solution to the Hank's solution to the artificial saliva. This result is confirmed with that of the OCP and Tafel analysis. As a comparison, we also studied the corrosion behavior for the NiTi alloy in the Hank's, NaCl solutions and artificial saliva (pH=7.4). According to the experimental results, we can draw a conclusion that the corrosion resistance of the TMZS alloy is compatible to or a little better than that of the NiTi alloy at the same test condition. So, the TMZS alloy may be replace the NiTi in some biomedical applications.
Conclusions

(1) The excellent combination of the strength and ductility for the TMZS alloy can be obtained by aging or cold deformation. The TMZS alloy can obtain moderate, continuous forces, stronger than NiTi, weaker than stainless steel, which provides another selection for clinical application.

(2) The corrosion behavior of the TMZS alloy is influenced by the alternation of pH value and the simulated body solutions.

(3) Based on the experimental results of OCP, Tafel and anodic polarization, the TMZS alloy exhibits better corrosion resistance in the artificial saliva than that in the Hank's and NaCl solutions, although the TMZS alloy has excellent corrosion resistance in the three simulated body solutions.

(4) The corrosion resistance of the TMZS alloy is compatible to or a little better than that of the NiTi alloy being used in many biomedical fields at the same test condition. So, the TMZS alloy has a large potential for biomedical applications and maybe replaces the NiTi in some conditions.

References