The electrochemical behavior of a Ti$_{50}$Ni$_{47}$Fe$_3$ shape memory alloy

C. Li, Y.F. Zheng *

State Key Laboratory for Turbulence and Complex System and Department of Mechanics and Engineering Science, Peking University, Beijing 100871, PR China

Received 31 July 2005; accepted 28 November 2005
Available online 20 December 2005

Abstract

The corrosion performance of Ti$_{50}$Ni$_{47}$Fe$_3$ alloy in 0.9% NaCl physiological, artificial saliva and Hank’s solutions with different pH values at 37 °C was investigated by means of open circuit potential (OCP) measurement and linear polarization (LP) measurement techniques, respectively. The OCP stabilized at $-0.2925$, $-0.3111$ and $-0.3454$ mV/SCE in sequence for 0.9% NaCl, artificial saliva and Hank’s solutions, respectively. LP results demonstrated that the Ti$_{50}$Ni$_{47}$Fe$_3$ alloy has a low passive current and a wide passive range. The surface roughness and in-depth distribution of the passive films after immersion in corrosion media was characterized by using Atomic Force Measurement (AFM) and X-ray electron spectroscopy (XPS). AFM results shows that the electrochemical measurements have little influence on the surface roughness of the Ti$_{50}$Ni$_{47}$Fe$_3$ alloy, and the XPS analysis results revealed that the outer passive film consisting mainly of a layer of TiO$_2$ which is deemed to be important for all biomaterials.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Corrosion; Ti$_{50}$Ni$_{47}$Fe$_3$ alloy; Shape memory alloy

1. Introduction

Nickel–Titanium alloy has been extensively used in the field of biomedical engineering, such as endovascular stent, orthodontic archwire and orthopedic implant due to its unique properties [1–4]. Despite the intensive clinical applications of TiNi alloy in many cases, Ni which poses several potential risks to organisms of body is of great concern with its biocompatibility [5]. Recently, surface modification methods have been used in order to improve the biological properties of TiNi alloy. Another method also used by some researches was adding a third element to TiNi alloy. G. Rondelli and B. Vicentini investigated the effect of copper on the localized corrosion resistance of Ni–Ti shape memory alloy [6]. Wen et al. have also suggested that the corrosion resistance of NiTiCu alloys is better than that of TiNi alloys [7]. Pelton and Lee design a kind of stent made of superelastic Ni–Ti–W alloy. The added tungsten in specified amounts improve the radiopacity of the TiNi stent [8].

The aim of the present paper is to study the electrochemical behavior of a Ti$_{50}$Ni$_{47}$Fe$_3$ alloy after adding Fe element to TiNi alloy in hope of enhancing anti-corrosion properties of the alloy.

2. Experimental procedures

2.1. Preparation of Ti$_{50}$Ni$_{47}$Fe$_3$ alloy

The Ti$_{50}$Ni$_{47}$Fe$_3$ (at.%) alloy was produced by an arc-melting furnace under the protection of argon atmosphere. Prior to melting, the working chamber was purged with argon for about 30 min. The ingot was melted five times to ensure the homogeneity of the ingots. It was then hot rolled at 800 °C into sheet with 3 mm in thickness and further cold rolled to about 1.2 mm in thickness.

2.2. Fabrication of specimens for electrochemical test

Corrosion specimens with the size of $13 \times 13 \times 1.2$ mm were cut from the cold rolled sheet and treated at 800 °C for 30 min followed by water quenching. The working surface of the samples was ground on SiC paper and then polished to a mirror finish. Finally the samples were cleaned ultrasonically in acetone, ethyl alcohol and distilled water for about 10 min in sequence, respectively. The Open Circuit Potential (OCP) measurements were conducted by a working station (CHI650B, CHN), and Linear Polarization (LP) measurement was performed using a potentiostat/galvanostat (Model 283, E G and G USA). A platinum and a saturated calomel electrode
(SCE) are used as the counter and the reference electrode, respectively. All measurements were tested in simulated body fluids, namely 0.9% NaCl solution, Hank’s solution and artificial saliva solution at 37±1 °C with pH=2.4, 5.4 and 7.4, respectively. OCP measurement was maintained up to 24 h, and the linear polarization measurements were performed at potentials ranging from −500 to 1300 mV vs. SCE in the anodic direction with a scan rate of 60 mV/min. All samples were immersed into the electrolyte for 30 min before polarization measurements.

2.3. Surface characterization

A Nano-scope III Atomic Force Microscopy (AFM), Digital Instruments, Inc. was used to observe the morphologies of Ti50Ni47Fe3 alloy specimens before and after electrochemical measurements. The in-depth distributions of the passive films were characterized using an ESCA PHI 500 spectrometer with a Al Kα X-ray source. The ion sputter profiling was performed with a 1 keV Ar⁺ ion beam over a 5 × 5 mm area at an angle of 50° with respect to the surface of the passive film, and the ion sputtering time lasts 23,880 s.

3. Results and discussion

The surface roughness plays an important role for biomedical implants, it has been reported that biomaterials with appropriate surface roughness would improve the bioactivity of the implants [9]. In our study, not only the surface roughness is detected, but also the section analysis is investigated. Fig. 1 depicts the AFM images of Ti50Ni47Fe3 alloy before and after electrochemical treatment. It can be observed that after Tafel and LP measurements, the surface roughness of Ti50Ni47Fe3 alloy changed from 11.04 to 6.51 and 5.81, respectively. Fig. 2 shows the results of section analysis of Ti50Ni47Fe3 alloy. The surface roughness values of Ti50Ni47Fe3 alloy obtained is listed in Table 1. As the results show, electrochemical measurements have little influence on the surface roughness of the Ti50Ni47Fe3 alloy.

Fig. 3 is the OCP vs. time diagrams of Ti50Ni47Fe3 alloy in the three corrosion media at pH=7.4. As the figure shows OCP values decrease significantly at the beginning of the immersion, which indicates the corrosion of the air-formed passive film. After about 6000 s, OCP values vary little with the increasing of immersion for Ti50Ni47Fe3 alloy in 0.9% NaCl and saliva solutions. The final OCP values obtained are −0.2925, −0.3111 and −0.3454 mV/SCE in sequence for 0.9% NaCl, saliva and Hank’s solutions, respectively.

LP diagrams shown in Fig. 4 demonstrate that Ti50Ni47Fe3 alloy has low corrosion current and high breakdown potential, and the $E_b$ is above 1000 mV/SCE. For the three corrosion media at pH=2.4, 5.4, and 7.4, the diagrams show similar tendency which indicates pH values have little influence on the electrochemical behavior of Ti50Ni47Fe3 alloy.

Fig. 5 shows the XPS depth profiles of the Ti50Ni47Fe3 alloy after electrochemical measurement at Hank’s solution at pH=7.4. It can be easy observed the Ti, Ni, Fe, and O atomic concentrations change with the increasing of depth. As the figure shows that there exists little Ni on the surface of Ti50Ni47Fe3 alloy after electrochemical measurement, its atomic concentration increases with the increasing of depth. This characteristic is useful for biomedical application of this alloy. The
atomic concentration of Ti increases significantly at the outer layer of the passive film and then decreases after about $4 \times 10^3$ s sputtering. The atomic concentration of O decreases with the increasing of depth.

Fig. 6 depicts the typical XPS survey spectra of Ti$_{50}$Ni$_{47}$Fe$_3$ alloy with different Ar sputtering time after electrochemical measurement in Hank’s solution at pH=7.4. As the figure shows, the peak intensity with different sputtering time demonstrates the change of element content. The surface was mainly composed of C1s and O1s peaks at the beginning, and then the intensity of C1s and O1s peaks decreases sharply. The intensity of Ni2p peak keeps increasing along the increasing of sputtering time, while the intensity of Ti2p peak increases.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>RMS (nm)</th>
<th>Original sample</th>
<th>After Tafel test</th>
<th>After LP test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface analysis</td>
<td></td>
<td>11.04</td>
<td>6.51</td>
<td>5.81</td>
</tr>
<tr>
<td>Section analysis</td>
<td></td>
<td>5.49</td>
<td>5.34</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Fig. 3. The OCP vs. time diagrams of Ti$_{50}$Ni$_{47}$Fe$_3$ alloy in corrosion media at pH=7.4.
at first and then keeps decreasing. As can be seen that the results drawn from the figure is in accordance with Fig. 5.

**Fig. 7** is the Ti2p XPS spectra of Ti50Ni47Fe3 alloy in Hank’s solution at pH=7.4. XPS profile analysis shows that there are little Fe and Ni ions on the outer layer of Ti50Ni47Fe3 alloy after electrochemical measurement at Hank’s solution at pH=7.4, while much Ti and O ions in the state of TiO2 which is demonstrated by the position of main peak of Ti2p spectra obtained after 120 s sputtering exist on the outer surface layer. With the increasing of sputtering time, The Ti2p high-resolution peaks first change to broad peaks and it consists of a very broad peak after 8880 s sputtering, at this time the O and Ti elements are in the state of non-stoichiometric Ti oxide states. With further sputtering main peak Ti2p spectra corresponded are

**Fig. 4.** Linear polarization diagrams of Ti50Ni47Fe3 alloy in different corrosion media at pH=2.4, 5.4 and 7.4. (a) 0.9% NaCl solutions, (b) Hank’s solutions, and (c) artificial saliva solutions.

**Fig. 5.** XPS depth profiles of the Ti 50Ni47Fe3 alloy after electrochemical measurement in Hank’s solution at pH=7.4.

**Fig. 6.** Typical XPS survey spectra of Ti50Ni47Fe3 alloy with different Ar sputtering time after electrochemical measurement in Hank’s solution at pH=7.4.

**Fig. 7.** Ti2p XPS spectra of Ti50Ni47Fe3 alloy in Hank’s solution at pH=7.4.
detected to shift to the direction of low binding energy, it is the character of metal Ti.

4. Conclusion

The surface of the Ti₅₀Ni₄₇Fe₃ alloy before and after electrochemical measurements has a low surface roughness, and electrochemical measurements have little influence on the surface roughness of the Ti₅₀Ni₄₇Fe₃ alloy.

Electrochemical measurements results demonstrated that the Ti₅₀Ni₄₇Fe₃ alloy has a low passive current, lower than $1 \times 10^{-5}$ A/cm², and a wide passive range.

It is found that the passive on the outer surface of the Ti₅₀Ni₄₇Fe₃ alloy mainly consists of TiO₂, and it is important for improving the biocompatibility and anti-corrosion properties of the Ti₅₀Ni₄₇Fe₃ alloy.

References