Effects of anodic oxidation in H$_2$SO$_4$ electrolyte on the biocompatibility of NiTi shape memory alloy


$^a$ School of Materials Science and Engineering, Southeast University, Nanjing, 211189, China
$^b$ School of Public Health, Southeast University, Nanjing 210096, China
$^c$ Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China

ABSTRACT

Effects of anodic oxidation in H$_2$SO$_4$ electrolyte on the biocompatibility of NiTi shape memory alloy (SMA) were investigated by characterizing surface structure, blood compatibility, wettability, release of harmful Ni ions of anodized NiTi SMA. Although titania film resulting from anodic oxidation in H$_2$SO$_4$ electrolyte has a porous structure, it can effectively block out-diffusion of Ni from NiTi SMA to simulated body fluid (SBF).

Comparing with chemical polishing, anodic oxidation in H$_2$SO$_4$ electrolyte can also improve the wettability, blood compatibility, thromboresistance of NiTi SMA.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The high content of Ni (about 50 at.%) in biomedical NiTi SMA$^{[1,2]}$ is of great health concern because excess release of Ni ions may cause allergic reactions and promote carcinogenesis and toxic reactions$^{[3,4]}$. Although there is a thin native titanium oxide surface layer$^{[5]}$, nickel in the metallic or oxidized state is detected on NiTi and its amount depends on surface treatments$^{[6]}$. Hence, an artificial titanium oxide layer can enhance surface properties and reduces Ni out-diffusion from NiTi.

Since NiTi SMA contains a large amount of Ti, it can be readily oxidized. Many oxidation methods including thermal oxidation$^{[7]}$, laser oxidation$^{[8]}$, Fenton's oxidation$^{[9]}$ as well as anodic oxidation$^{[10,11]}$ were hitherto used for surface modification of NiTi. For example, Cheng et al. recently studied microstructural characterization of surface oxide films after anodic oxidation in a methanolic electrolyte or in acetic acid, and corrosion behavior of anodized NiTi in Hank's solution$^{[10,11]}$.

However, up to now, there have not been systematical studies on the biocompatibility including wettability, blood compatibility, leaching of Ni ions of anodized NiTi SMA. In this work, the effects of anodic oxidation in H$_2$SO$_4$ electrolyte on the biocompatibility of NiTi SMA...
were evaluated employing SEM, XPS, ICPMS, hemolysis analysis and platelet adhesion test.

2. Experimental

NiTi (50.8 at% Ni) SMA rectangular blocks with dimensions of 10 mm × 10 mm × 1 mm were chemically polished with a solution containing H2O, HF, and HNO3 with a 5:1:4 ratio for 5 min. They were divided into two groups. The first group was denoted as the CP one. The second was treated by anodic oxidation at 5 A for 60 min in an electrolytic cell (the AO one). The electrolyte was a 1 mol/L H2SO4 aqueous solution.

Surface morphology was observed by a Philips XL30 FEG SEM. XPS on a VG Scientific ESCALAB 5 spectrometer was used to analyze survey spectra and high-resolution Ti 2p, O 1s and Ni 2p spectra. Contact angles, the release of Ni ions, hemolysis ratios and thromboresistance were investigated by liquid drop method, ICPMS, hemolysis test and platelet adhesion test as described in our previous work [9].

3. Results and discussion

Fig. 1 depicts the SEM photographs of the surfaces of the CP one and the AO one. The white particle-shape phase appearing in the CP one is Ti2Ni, which were confirmed using an energy-dispersive analysis by X-rays. After anodic oxidation, an oxide film with porous structure was present on the AO one.

Fig. 2 shows typical XPS survey spectra of the surfaces of NiTi SMAs. The dominant surface elements are Ni, Ti, O, C for the CP one and Ti, O, C for the AO one. There is no Ni element present on the surface of the AO one, however, the upper surface amount of Ni on the CP one can reach about 11.4 at%. The result suggests that the AO one was covered with a titanium oxide film depleted in Ni. The presence of C can be attributed to surface contamination by carbon-containing molecules absorbed from the environment.

High-resolution XPS collections of Ti and Ni binding energy regions for the AO one were recorded as shown in Fig. 3. The Ti 2p XPS spectrum exhibits two dominant peaks, which have been identified as being Ti4+ (TiO2) 2p3/2 at 458.8 eV and Ti4+ (TiO2) 2p1/2 at 464.6 eV. No remnants of TiNi in intermetallic NiTi state could be found. In contrast, Ni element in any chemical states could not be detected from Ni 2p XPS spectrum, which proves that there is a titania film depleted in Ni formed on the AO one.

Table 1 summarizes the ICPMS results of concentrations of release Ni ions in SBF for different immersion times, hemolysis ratios and water contact angles of NiTi SMAs. Obviously anodic oxidation significantly reduces Ni release from NiTi substrate. Although titania film resulting from anodic oxidation in H2SO4 electrolyte has a porous structure, it can effectively block out-diffusion of Ni from NiTi SMA to SBF.

Table 1

<table>
<thead>
<tr>
<th>NiTi SMA</th>
<th>Ni ions concentrations in SBF</th>
<th>Hemolysis ratio</th>
<th>Water contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 weeks</td>
<td>5 weeks</td>
<td></td>
</tr>
<tr>
<td>CP-NiTi</td>
<td>314.6 ppb</td>
<td>715.6 ppb</td>
<td>4.26%</td>
</tr>
<tr>
<td>AO-NiTi</td>
<td>4.9 ppb</td>
<td>105.7 ppb</td>
<td>1.34%</td>
</tr>
</tbody>
</table>
Hemolysis ratios determined from both ones are less than 5%, which suggest both samples can meet the requirements for biomedical implants. However, a higher hemolysis ratio (4.26%) means that more hemolysis occurs on the CP surface. Contact angle of the CP one is 65.5°. After anodic oxidation, contact angle of NiTi SMA decreases to 58.3° due to the formation of titania film. It shows the wettability and blood compatibility of NiTi SMAs are improved by anodic oxidation.

The morphology of adhered blood platelets on NiTi SMAs after 3 h of incubation is shown in Fig. 4. The number of adherent platelets on the AO one is much less than on the CP one. Accumulation and pseudopodium of platelets are also serious on the CP one as indicated by the three-dimensional structures connected by pseudopodium in Fig. 4a. In contrast, the platelets on the AO sample form a single layer and are isolated (Fig. 4b). There is no sign of accumulation and only slight pseudopodium can be observed. Hence, platelet adhesion is reduced remarkably on the AO one and the thromboresistance of NiTi SMAs can be improved by anodic oxidation. This may be related to intrinsic electrical characteristics of titania film [12]. The formation of thrombus on an artificial material is correlated with charge transfer from the inactive state of fibrinogen to the material surface [4]. Titania as a semiconducting material has a wide energy band gap about 3.2 eV [13]. Fibrinogen also has an electronic structure similar to a semiconductor with a narrower band gap (1.8 eV) and the conduction and valence bands fall inside the energy gap of titania [14]. Hence, from this perspective, it is difficult for charges to transfer from the valence band of fibrinogen into the titania and consequently, this may be one of the reasons why thrombus formation is inhibited.

4. Conclusions

Anodic oxidation in H₂SO₄ electrolyte results in formation of titania film depleted in Ni on NiTi SMA. Although the titania film has a porous structure, it can still effectively block out-diffusion of Ni from NiTi SMA to SBF. Moreover, the wettability, blood compatibility, thromboresistance of NiTi SMA can also be improved by anodic oxidation in H₂SO₄ electrolyte.

Acknowledgements

This work was supported by NCET-06-0464, NSFC-50501007, 863 Project of China (2006AA032445), NSF of Jiangsu (BK2007515), NSG Foundation, SRG of HK (7001999).

References


Fig. 4. SEM morphology of adherent platelets on the surface of NiTi SMAs after 180 min incubation in PRP: (a) the CP one; (b) the AO one.