INFLUENCE OF PROCESSING OF SHAPE MEMORY NITI ALLOY ON ITS CORROSION RESISTANCE

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Abstract

NiTi alloys (nitinol) show the shape memory effect, superelastic behavior, high strength, good corrosion resistance and biocompatibility. These characteristics make them of interest for medical applications, such as dental medicine or manufacture of stents, i.e. tubular implants serving to restore blood vessels. Although nitinol is generally regarded as highly corrosion resistant material, it may corrode in human body under some circumstances with a negative effect on patients. Therefore, it is important to know factors affecting corrosion behavior of nitinol. In the present paper, corrosion behavior of nitinol subjected to various processing regimes is described.

Keywords: NiTi alloy, surface treatment, corrosion

1. INTRODUCTION

Nearly equi-atomic NiTi alloys (nitinol) show shape memory effect, superelastic behavior, high tensile strength and good corrosion resistance and biocompatibility. These characteristics make them of interest for biomedical applications ranging from dental arch wires to stents applied to restore damaged blood vessels. In manufacture of stents, nitinol experiences various thermo-mechanical processing steps which directly influence its mechanical properties, fatigue limit and performance. In addition, processing of nitinol also affects its surface chemistry and, subsequently, corrosion resistance. Although nitinol is generally regarded as being highly corrosion resistant, similarly to stainless steels or titanium, corrosion may be a serious problem in some cases. Corrosion of a nitinol implant in a patient may have two aspects: 1. Due to corrosion, nickel releases into a surrounding body fluids. Unfortunately, nickel is a toxic element that may cause allergic reactions of an organism. 2. In an extreme case, corrosion processes may cause pitting and a reduction of an implant cross-section. This may lead to a serious damage of a stent and its fracture into dangerous sharp fragments. There are several reports in which stent damage and failure due to corrosion are described [1].

Corrosion resistance of nitinol is mainly influenced by its surface chemistry and state. When even a weak oxidizing environment, such as water, air or humidity, is in contact with nitinol, a few nm thick native passive layer dominated by titanium dioxide forms on the nitinol surface. However, there may be defects in this passive layer acting as sites for pitting and accelerated corrosion. Therefore, any treatment leading to an improvement of the passive layer quality would reduce corrosion rate of nitinol. In addition, reduction of nickel concentration in the surface oxide layer is also positive because of a subsequent decrease in nickel release rate and a reduction of the undesirable heterogeneity of the passive layer.

Taking into account thermodynamics of the Ni-Ti-O system, it is beneficial that titanium oxidizes preferentially in wide intervals of oxygen partial pressure and temperature. Therefore, thermodynamics says that, when oxidizing a nitinol, a protective TiO₂-enriched and Ni-depleted oxide layer forms on the surface. Simultaneously, inward diffusion of nickel results in a Ni-enriched and Ti-depleted region beneath the external oxide. At high oxidation temperatures and long times, there may be Ni₃Ti, Ni₄Ti and even pure Ni in this area. Many more or less recent studies confirm this surface substructure after oxidation of nitinol [2-5].
In manufacture of stents, shape setting is generally performed to obtain a desired shape and superelastic behavior. It includes a short-time (several minutes) heating of a nitinol wire at about 500°C. Since nitinol contains high amount of very reactive titanium, it absorbs even traces of oxygen present in a surrounding environment. Therefore, selective oxidation of nitinol always occurs during the shape setting. When the shape setting is the last processing step in manufacture of a stent, it determines its corrosion behavior. In literature, however, there is a lack of information on the effect of oxidation on corrosion. For this reason our study is concerned with a short-time oxidation at 530°C in air. Both surface etched and mirror-polished nitinol are subjected to oxidation to assess development of the surface chemistry and corrosion behavior due to oxidation.

2. EXPERIMENT

NiTi alloy (50.9 at. % Ni) was used as substrate for surface treatments in our experiment. One part of experiments was carried out with a 0.2 mm thick cold drawn and annealed NiTi wire provided by an industrial supplier. Another part of experiments was performed on a NiTi ingot prepared by arc melting of metals (99.99 % purity) under a high-purity helium atmosphere. Two pre-treatments were applied on samples prior to oxidation. 1. chemical etching of the wire in an acid bath (HNO₃:HF:H₂O=4:1:5); 2. mechanical polishing of coupons cut from the ingot to a mirror finish. Chemical etching is a commonly utilized procedure in processing of nitinol that serves to remove surface contaminants, defects and heavy deformation zones after cold drawing. Oxidation was conducted in air at 530°C for 10 minutes. Surface treatments used in our experiment can be summarized as follows: 1. chemical etching, 2. mirror polishing, 3. chemical etching + oxidation at 530°C, 4. mirror polishing + oxidation at 530°C.

Surface morphology and chemistry of samples was observed by scanning electron microscopy (SEM, Hitachi S4700), Raman spectrometry (Labram HR) and x-ray photoelectron spectroscopy (XPS, ESCA Probe P).

Corrosion behavior of treated samples was measured by exposure test. Samples were immersed in a model physiological solution (9 g/l NaCl, pH=2 adjusted by an addition of HCl) for three days at 37°C. Afterwards, nickel, as the main allergic constituent of nitinol, released into the solution was determined by ICP mass spectrometer ELAN 6000.

3. RESULTS AND DISCUSSION

3.1 Surface structure and chemistry

Fig.1a presents a SEM image of the chemically etched sample. Due to chemical etching in the acid bath, a typical dimple-like morphology is obtained.

XPS profiling, see Fig.2, and Raman spectrometry (not shown) detect an about 10 nanometer thin amorphous oxide layer on the etched surface.

The oxide layer results from competition between two chemical reactions. First one includes dissolution of TiO₂ passive layer in hydrofluoric acid to form soluble fluoride complexes:

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \left[\text{TiF}_6\right]^{2-} + 2\text{H}_2\text{O}
\]  

(1)

Second process is preferential oxidation of titanium by nitric acid back to titanium dioxide that is accompanied by inward diffusion of nickel:

\[
\text{Ti} + 4\text{NO}_3^- + 4\text{H}^+ \rightarrow \text{TiO}_2 + 4\text{NO}_2 + 2\text{H}_2\text{O}
\]  

(2)
Simultaneously, nickel present in the alloy also dissolves into the etching solution to form nickel cations:

\[
\text{Ni} + 2\text{H}^+ \rightarrow \text{Ni}^{2+} + \text{H}_2 \quad (3)
\]

The last reaction is responsible for a very low surface nickel concentration on the chemically etched sample, see Table 1.

![Surface morphology of the chemically etched (a) and chemically etched + oxidized (b) sample (SEM).](image)

**Fig.1.** Surface morphology of the chemically etched (a) and chemically etched + oxidized (b) sample (SEM).

![Elemental profiles through the surface region on the investigated samples (XPS).](image)

**Fig.2.** Elemental profiles through the surface region on the investigated samples (XPS).

After oxidation of the chemically etched wire in air, the surface is covered by a homogeneous oxide layer, see Fig.1b. This layer consists of clearly visible grains of about 30-50 nm in size. Raman spectrometry indicates that rutile is a predominating phase in the oxide. Apparently, oxidation temperature of 530°C is enough to accelerate diffusion and to induce crystallization of growing oxide. It is also seen in Fig.1b that the oxide layer is very thin, because the original dimple-like surface morphology is retained after oxidation. XPS
elemental profile in Fig. 2 indicates a thickness of the oxide of about 80 nm. When oxidizing the mirror polished sample, the surface is covered by a similar fine-grained surface oxide with the rutile crystalline structure (not shown).

In Table 1, nickel surface concentrations determined by XPS are summarized. These concentrations may be closely related to the rate of nickel release from nitinol into a human body. As stated before, the lowest Ni concentration is observed for the chemically etched sample. This results from nickel dissolution in the acidic bath, according to the Eq. (3).

Table 1. Nickel surface concentrations on the investigated samples.

<table>
<thead>
<tr>
<th>surface treatment</th>
<th>Ni concentration (in at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mirror polished</td>
<td>6.0</td>
</tr>
<tr>
<td>mirror polished + oxidized at 530°C/10 min</td>
<td>1.1</td>
</tr>
<tr>
<td>chemically etched</td>
<td>0.6</td>
</tr>
<tr>
<td>chemically etched + oxidized at 530°C/10 min</td>
<td>2.1</td>
</tr>
</tbody>
</table>

On the other hand, the highest concentration is measured on the mirror polished sample. On this sample, only a very thin (about 3 nm) native passive oxide layer is detected by XPS, see elemental profiles in Fig. 2. Due to the preferential oxidation of Ti caused by the more negative Gibbs energy of TiO2 formation, as compared to NiO, surface concentration of nickel reduces in comparison to the bulk alloy, but this reduction is not as significant as on other samples.

Oxidation at 530°C of both polished and etched sample leads to Ni surface concentrations of 1-2 %. There is a considerable depletion in Ni in the surface oxide caused by the preferential oxidation of Ti and simultaneous inward diffusion of Ni, see also Fig. 2. Contrary to the polished and etched samples, oxidation at 530°C causes the formation of a sub-surface region slightly depleted in Ti and enriched in Ni. It is evident that the nickel accumulation in this area results from preferential oxidation of titanium associated with nickel inward diffusion.

It may be expected that the Ni accumulation beneath the external oxide on the samples oxidized at 530°C does not accelerate nickel release, provided that the external TiO2 oxide is compact. On the other hand, any defects worsening the compactness of the oxide would get the nickel reservoir into contact with a liquid. On the surface, there would be a large cathode (TiO2) and a small anode (Ni-enriched metal in contact with a solution). This situation might cause a rapid Ni release and a pitting corrosion.

3.2 Corrosion

The rates of Ni-release from the samples into the model physiological solution with pH=2 are illustrated in Fig. 3. It is evident, that the oxidation at 530°C can influence the rate of element release either negatively or positively, depending on the original state of the material.
For the polished sample, the oxidation reduces the rate of Ni dissolution in the corrosion medium. It can be explained on the base of the surface chemistry of both polished and oxidized samples. On the polished one, there is a very thin passive layer relatively rich in nickel (6 %), see Fig.2 and Table 1. In contrast, the polished + oxidized sample is covered by a thicker (about 80 nm) TiO₂ layer with a lower surface concentration of Ni (1 %). Therefore, nickel releases at a lower rate, because outward diffusion of Ni from the reservoir beneath the oxide (Fig.2) towards the surface controls this process.

Quite different situation is observed for the chemically etched and etched + oxidized samples, see Fig.3. One can see that the oxidation strongly accelerates nickel release, despite the large Ni-depleted region and the low Ni surface concentration on this sample, see Fig.2 and Table 1. After three day exposure, total amount of nickel released from the oxidized sample into the solution is about 4 μg/cm², i.e. about fifty times larger amount as compared to the etched one (~0.08 μg/cm²). It is evident that chemical etching is very effective to suppress corrosion. Although this treatment produces a very thin oxide layer (Fig.2), the surface concentration of nickel and the rate of Ni release are the lowest from all the investigated treatments. As stated before, the low Ni concentration is attributable to both nickel inward diffusion and simultaneous nickel dissolution in the etching solution. Another reason for the excellent corrosion protection may be in a good compactness of the amorphous oxide formed due to chemical oxidation at low temperature. Moreover, water, the major constituent of the etchant, may play a role in the chemical oxidation of nitinol. It is well known that boiling water can be utilized for the surface treatment of various oxidized metals, for example, anodized aluminum. This treatment is known as sealing and causes formation of compact hydrated compounds on the surface showing excellent protection against corrosive environments. Perhaps, a similar process, i.e. partial hydration of titania improving its compactness and density, also occurs at low temperatures during etching of nitinol. Contrary to the chemically etched state, oxidation at 530°C/10 min produces a thick, crystalline and grainy titania with grain size and thickness of about 50 and 80 nm, respectively, see Fig.1b and 2. Oxidation temperature is sufficient to accelerate diffusion and crystallization of originally amorphous and homogeneous oxide formed due to chemical etching. Simultaneously, oxygen diffuses through the oxide and reacts with Ti to form new TiO₂ grains depleted in nickel. As a result, the characteristic surface morphology and relief are formed. It is believed that relatively thick grainy oxide layers formed at high temperatures probably contain a larger amount of structural defects, as compared to thin oxide layers prepared at low temperatures. One source of these defects may be cooling from the oxidation temperature during which stress is induced in the oxide layer, due to differences between thermal expansion of oxide and substrate. It is known that the thicker the oxide, the higher the stress. Therefore, small cracks may form in the oxide during cooling, representing sites at which water solution gets into contact with the Ni reservoir beneath the oxide. Consequently, Ni rapidly releases from the material (Fig.3).
4. CONCLUSIONS

In this work, four surface treatments of nitinol were compared in terms of surface chemistry and corrosion rate: mirror polishing, chemical etching, combination of polishing and oxidation at 530°C, combination of chemical etching and oxidation at 530°C. Results obtained indicate that chemical etching provides the best corrosion resistance in view of nickel release. Technologically important result of our research is that a short-time oxidation at about 500°C, which commonly occurs during the shape setting procedure in the manufacture of stents, may negatively affects corrosion performance, particularly in the case of the chemically etched nitinol.

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