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Surface structure and corrosion resistance of short-time heat-treated NiTi shape memory alloy

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ABSTRACT

NiTi alloys are attractive materials that are used for medicine, however, Ni-release may cause allergic reactions in an organism. The Ni-release rate is strongly affected by the surface state of the NiTi alloy that is mainly determined by its processing route. In this study, a NiTi shape memory alloy (50.9 at.% Ni) was heat-treated by several regimes simulating the shape setting procedure, the last step in the manufacture of implants. Heating temperatures were between 500 and 550 °C and durations from 5 to 10 min. Heat treatments were performed in air at normal and low pressure and in a salt bath. The purpose of the treatments was to obtain and compare different surface states of the Ni–Ti alloy. The surface state and chemistry of heat-treated samples were investigated by electron microscopy, X-ray photoelectron spectroscopy and Raman spectrometry. The amount of nickel released into a model physiological solution of pH 2 and into concentrated HCl was taken as a measure of the corrosion rate. It was found that the heat treatments produced surface TiO_2 layers measuring 15–50 nm in thickness that were depleted in nickel. The sample covered by the 15-nm thick oxide that was treated at 500 °C/5 min in a low pressure air showed the best corrosion performance in terms of Ni-release. As the oxide thickness increased, due to either temperature or oxygen activity change, Ni-release into the physiological solution accelerated. This finding is discussed in relation to the internal structure of the oxide layers.

1. Introduction

Nearly equi-atomic NiTi alloys (nitinol) have attracted much attention due to their shape memory effect, superelastic behavior, high tensile strength, good corrosion resistance and biocompatibility. These characteristics make NiTi alloys attractive for biomedical applications, such as stents, which are generally utilized to restore a damaged blood vessel or an oesophagus, among others.

NiTi alloys are generally regarded as highly corrosion resistant, similar to stainless steel or titanium. The reason is the spontaneous formation of a native passive TiO_2 layer on the surface. Even a weak oxidizing environment, such as water, air or humidity, in contact with nitinol at low temperature is sufficient to produce a few nanometers of a passive protective layer. However, in the processing of NiTi alloys they experience various forming, heat- or surface-treating steps, which strongly influence the surface structure, chemistry and, therefore, corrosion performance.

In a human body, various fluids may come into contact with NiTi implants. In particular, serious problems may arise when a strongly acidic fluid, like gastric juice, attacks the surface of the alloy. In general, the corrosion of nitinol has two aspects. First, corrosion is accompanied with nickel release from an implant into the surrounding body fluid and tissue, which may enhance an allergic reaction in a sensitive organism. Second, corrosion may cause pitting and a reduction of mechanical performance of an implant. In an extreme case, an implant broken due to corrosion may produce sharp fragments that are dangerous for surrounding tissue [1].

For these reasons, the corrosion of nitinol has become an important issue in biomedical engineering during the last decade. To slow down this corrosion process, a highly protective adherent layer with a low concentration of nickel and internal defects must cover the surface of nitinol. A number of oxidation treatment procedures have been reported so far to support the preferential Ti oxidation and increase the protective effect against corrosion. These include thermal oxidation either in air or under a low oxygen pressure, etching, passivation in nitric acid, anodization, electrochemical polishing, oxygen ion implantation, laser oxidation, hydrothermal oxidation in water, sol–gel techniques, cathodic deposition and others [2–9].

Most often, the last processing step in the manufacture of nitinol stents is the shape setting. The shape setting treatment means a short-time heating of nitinol at around 500 °C and serves to achieve a desired shape and superelastic behavior of an implant. Heating can be performed in air, argon, vacuum or a salt bath. In oxidizing environments, titanium in nitinol generally oxidizes preferentially over nickel due to the higher thermodynamic stability of TiO_2 as

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Table 1
Summary of heat-treatment (HT) regimes used in this study and their designation.

Sample designation	Heat-treatment regime
CHE	No HT, chemical etching in a $1HF + 4HNO_3 + 5H_2O$ (by volume) solution
NP	HT at 510 °C/10 min in air at a normal pressure
S	HT at 510 °C/5 min in a molten salt bath
500LP	HT at 500 °C/5 min in air at a low pressure of 10 Pa
550LP	HT at 550 °C/5 min in air at a low pressure of 10 Pa

compared to NiO [3]. At sufficiently high temperatures, titanium reacts rapidly even with traces of oxygen present in a surrounding environment. As a result, a TiO_2-enriched and Ni-depleted surface oxide layer forms [10–13]. The corrosion performance of a nitinol implant thus depends on properties of such an oxide layer, particularly, on its thickness, chemistry, adherence and internal structure.

In the literature, there are few studies on the influence of the shape setting treatment on corrosion behavior. For this reason, our study is concerned with short-time heat treatments of nitinol at around 500 °C. Treatments were carried out in various environments in order to simulate different oxidation potentials and the purpose was to prepare and compare various surface states of the Ni–Ti alloy. Corrosion tests were performed in a relatively aggressive solution with pH 2. The solution simulates gastric fluid, so that information obtained by these tests is important for implants, such as oesophageal stents, for example. The fracture of a stent in a patient's body due to corrosion may cause serious problems [14,15].

2. Experimental

NiTi alloy (50.9% Ni; hereafter, all concentrations are in at.% unless otherwise stated) was used for heat treatments in our experiments. The 0.45-mm-thick wire with a tensile strength of 1580 MPa and A_f of 25 °C was provided by an industrial supplier. According to the supplier specifications, the wire was cold drawn (45% deformation) and annealed. Detailed specifications of the annealing conditions were not given.

The NiTi wire was first subjected to chemical etching in a $1HF + 4HNO_3 + 5H_2O$ (by volume) solution in order to remove traces of previous processing steps and to obtain a defined and unified surface state. Prior to heat treatments, the surfaces of all samples were carefully washed and dried. In this study, heat treatment regimes were selected to reflect real conditions of the shape setting procedures used by manufacturers of medical stents. Therefore, they were performed at different temperatures between 500 and 550 °C in air both at ambient pressure and at a low pressure of 10 Pa and also in a molten salt bath containing a mixture of 60% KNO_3 and 40% $NaNO_3$. Low pressures are sometimes used to prevent excessive oxidation of nitinol. The advantage of the shape setting in salt baths is the fast heat transfer from the bath to the treated wire and therefore the short time needed for the shape setting. After each heat treatment, the wire was immediately quenched into cold water. Detailed descriptions of heat treatment procedures applied in our experiment and their designation are given in Table 1. All heat-treated samples appeared in characteristic interference colors ranging from light golden to a dark blue color.

The surface morphology of samples was observed by scanning electron microscopy (SEM, Hitachi S4700, an acceleration voltage of 10 kV, in the regime of secondary electrons). Due to the very low thickness of surface layers on samples, the phases present were not detected by X-ray diffraction, but a Raman spectrometer Labram HR (excitation source – laser with a wavelength of 532 nm operating at 40 mW) was used for this purpose. Additionally, the chemical composition of the surface and elemental profiling in the sub-surface regions of samples were characterized by an X-ray photoelectron spectroscope (XPS) ESCA Probe P (a pressure in the analytical chamber of 2×10^{-8} Pa, monochromatic Al Kα X-ray source, binding energy calibration with respect to the energy of Au 4f7/2 peak, Ar pressure during sputter depth profiling 3×10^{-3} Pa, energy of Ar^+ ions during sputtering 5 keV, calibration of the sputtering rate with respect to titanium dioxide). Chemical compositions were calculated from areas of deconvoluted elemental peaks by analytical software CasaXPS version 2.3.14. The thickness of TiO_2 layer was estimated as a thickness at which a Ti:O ratio is 1:2 or lower. A Ti:O ratio lower than 1:2 indicates oxygen adsorption on the surface TiO_2. Detailed spectra of Ti 2p and Ni 2p were recorded using a constant pass energy of 20 eV at a 0.1-eV step size.

The corrosion behavior of both chemically etched and heat-treated samples was determined by the immersion test. Three samples for each surface state were tested. Samples were exposed to a simulated physiological solution containing 9 g/l NaCl with pH 2 (adjusted by the addition of HCl) at a temperature of 37 °C. The low pH value was used in this experiment because it simulates a gastric juice environment. The immersion period was 168 h. Simultaneously, the corrosion behavior was also determined in a concentrated HCl. Samples were exposed to this strongly aggressive environment for 6 h at 20 °C. In both corrosion tests, the corrosion rate was taken as the concentration of nickel released into corrosive medium. Nickel concentrations in the simulated physiological solution and in the concentrated HCl were measured by ICP mass spectrometry (ELAN 6000) and by atomic absorption spectrometry (GBC 932 plus), respectively.

3. Results and discussion

3.1. Structure, chemical and phase composition

Fig. 1a presents a SEM view of the CHE surface. One can see than the surface is not flat. Instead, chemical etching causes the formation of small dimples of a few micrometers in size on the surface. There are also scratch marks resulting from the cold drawing process in which spherical or elongated non-metallic inclusions are observed. These inclusions consisting mainly of titanium carbides originate from the melting process of nitinol and from its contamination by the melting crucible. Oxidation in air at 510 °C/10 min modifies the surface structure, as shown in Fig. 1b. In contrast to the CHE sample, the oxide layer formed at high temperature has a typical grainy morphology with a grain size of about 20 nm. It has been demonstrated in a number of studies [16] that surface treatments of nitinol performed at room or slightly higher temperatures generally produce amorphous surface oxides. The reason is that slow diffusivities of species prevent the formation of ordered crystalline arrangements of atoms. At about 500 °C diffusion becomes sufficiently faster to produce crystalline oxide layers that are more thermodynamically stable. The surface morphologies of the S and 500LP samples presented in Fig. 1c and d are almost identical to the previous one because they consist of fine grains of about 20 nm in size. It appears that oxygen activity, which is different in the treatments illustrated by Fig. 1b–d, does not influence the oxide grain size significantly. The main factor affecting the grain size is heat-treatment temperature, which is demonstrated in Fig. 1e where a view of the 550LP sample is shown. Although the oxygen partial pressure was identical to that of the 500LP, the grain size grew considerably from approximately 20 to50 nm as the temperature increased by 50 °C. It was already suggested in our previous work [11] that nanometer-sized titania grains grow relatively fast above 500 °C due to the high driving force of this growth.

Survey XPS spectra of the investigated samples are almost identical, and they mainly contain characteristic peaks of Ti, O, and contamination C; see Fig. 2 for illustration. As far as nickel