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Corrosion behavior of NiTi alloy in fetal bovine serum

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ABSTRACT

The corrosion behavior of NiTi alloy in fetal bovine serum (FBS) at 37 °C is investigated using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma mass spectrometry (ICP-MS). The presence of FBS moves the OCP to the negative direction and makes the oxide film thinner and more porous than that in phosphate buffer saline (PBS, pH = 7.4). The impedance of the oxide film formed in FBS is smaller than that in PBS, but the total interface impedance is bigger in FBS because of the formation of a surface bio-film. Pits form on the NiTi alloy after immersion in FBS for 200 h but they are not observed on the sample immersed in PBS. XPS shows that the composition of the oxide film formed in FBS is similar to that formed in PBS and it is composed of mainly Ti oxides with a small amount of Ti hydroxide. Hydrated Ti is observed on the outermost surface of the NiTi alloy. The thickness of the oxide film on the NiTi alloy immersed in PBS is 17 ± 3.0 nm and that on the sample immersed in FBS is 10 ± 3.2 nm. The results are consistent with those obtained by EIS. The presence of FBS can accelerate leaching of Ni ions and the mechanism is investigated and discussed.

1. Introduction

Nitinol, a nearly equiatomic nickel–titanium alloy discovered in 1962 has been studied extensively for biomedical applications because of its unique shape memory effect, super-elasticity, as well as good biocompatibility [1–3]. However, human body fluids constitute a complicated electrochemical system and after implantation into the human body, corrosion of NiTi alloy occurs spontaneously to lower the free energy of the system. The corrosion behavior of NiTi alloy in simulated body fluids (SBF) has been studied and the good corrosion resistance of NiTi alloy is ascribed to the passivating film composed of primarily TiO_2 [4–7]. However, SBFs such as Ringer's or Hanks' solution contain only inorganic species with concentrations equal to those in human body fluids, but human body fluids are a complicated electrochemical system which contains not only inorganic species but also organic giant molecules such as serum proteins. Williams and co-workers [8] studied the corrosion behavior of Ti–6Al–4V, Ti–6Al–7Nb, and Ti–13Nb–13Zr in protein solutions and found the presence of albumin could improve their corrosion resistance. They suggested that a metal/protein/hydroxide complex could form on the surface thereby inhibiting the dissolution of metals. Fujimoto and co-workers [9] used different electrolytes to study the corrosion behavior of type 304 and 316L stainless steels and found that the fetal bovine serum (FBS) could decrease their corrosion resistance. They ascribed it to the presence of proteins which could increase the activity of the anodic process and decrease it in the cathodic process. Contu et al. [10] used electrochemical impedance spectroscopy (EIS) to investigate the electrochemical characteristics of commercial pure titanium (CP-Ti), Ti–6Al–4V, Ti–6Al–7Nb and Co–Cr–Mo alloys in FBS. They proposed that the compact adsorbed protein layer on the implant surface could act as a barrier to hinder charge transfer thus increasing the corrosion resistance. Nonetheless, up to now, not much work has been carried out to evaluate the influence of organic species such as proteins on the corrosion behavior of NiTi alloy, although this topic is very important to clinical applications.

In most studies involving industrial parts, the main concern is the corrosion resistance of the materials itself and the impact of corrosion products to the environment is usually negligible [11]. However, for biomedical implants, both of them are important equally. In the corrosion process of NiTi alloy in human body, the corrosion products such as Ni ions leach out from the bulk materials into surrounding tissues. Experiments based on the gene expression profiles demonstrate that Ni ions can suppress cell metabolism, differentiation, proliferation and induce cell apoptosis through changing the expression level of related genes [12]. It has also been reported that nickel ions can combine with biomolecules

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thereby acting as a possible source of allergy and toxicity [13]. Many researchers have measured the amounts of Ni ions leached from NiTi substrate after different immersion time in SBF [14–16], but data in real physiological environment such as FBS are still lacking.

In this work, we aim at studying the influence of FBS on the corrosion behavior of NiTi alloy at 37 °C using electrochemical methods. X-ray photoelectron spectroscopy (XPS) is used to determine the structure and thickness of the surface oxides. Scanning electron microscopy (SEM) is utilized to observe the surface morphology of NiTi alloy after immersion. The amounts of released Ni ions are measured by inductively coupled plasma mass spectrometry (ICP-MS). The phosphate buffer saline (PBS) solution is also used as an electrolyte to better understand the effects of organic molecules on the corrosion behavior of NiTi alloy.

2. Experimental details

Commercial NiTi alloy (50.7 at.% Ni) with dimensions of 10 mm × 10 mm × 2 mm was used in our experiments as the working electrode. A copper wire was attached to one side of the working electrode by tin solder and mounted in epoxy resin with an exposure area of 1 cm^2. It was then wet grinded with silicon carbide paper, polished with 2 μm diamond paste, and ultrasonically rinsed in acetone, alcohol, and distilled water for 5 min successively before immersing into electrolytes. The electrolytes were FBS (Gibco, Life Technologies AG, Basle, Switzerland) and PBS (pH = 7.40). Before introduction into the electrode cell, FBS was mixed with the PSN antibiotic solution and Nystatin suspension in the ratio of 100–1 ml.

The electrochemical measurements were conducted in a three electrode cell of 50 ml at a constant temperature of 37 ± 0.5 °C. A saturated calomel electrode (SCE) was used as the reference electrode and platinum wire as the auxiliary electrode. All the potentials reported here are referenced to the SCE. The electrochemical measurements were carried out using CHI660C electrochemical workstation (Chenhua Co. Shanghai, China). The open circuit potential (OCP) of the electrode was continuously monitored for 200 h with interruptions at 20 h and 200 h to measure the EIS at OCP over a frequency range of 1 mHz–100 kHz by means of a sinusoidal perturbation potential amplitude of 10 mV. The Zview 3.1 software was used to analyze the EIS results.

X-ray photoelectron spectroscopy (XPS) was used for chemical analysis of the NiTi surface. XPS spectra were obtained on the Axis Ultra, Kratos (UK) using monochromatic Al K$_\alpha$ radiation (150 W, 15 kV, 1486.6 eV). The pressure in the analytical chamber was 10^{-9} Pa. The binding energies were calibrated relative to the C 1s peak (284.8 eV) from hydrocarbons adsorbed on the surface of the samples. Depth profiles were acquired using 4 kV Ar$^+$ ion bombardment with the pressure of 10^{-5} Pa. The sputtered area was 5 mm × 5 mm and the collection area was 250 μm × 250 μm. Three areas were depth profiled to obtain the average film thickness. The place where the concentration of oxygen drops to one half of the maximum concentration near the surface is taken to be the film thickness. To estimate the sputtering rate, a standard SiO$_2$ sample was analyzed under the same conditions and the sputtering rate was 0.4 nm/min. The survey spectra were obtained at constant pass energy of 160 eV and high-resolution Ti 2p, Ni 2p, C 1s, N 1s and O 1s spectra were recorded at constant pass energy of 80 eV and the XPSpeak 4.1 software was to analyze the XPS data. The background signals were removed by the Shirley mode and processed by Gaussian/Lorentzian (G/L = 4.0) peaks. Field-emission scanning electron microscopy (FE-SEM, JSM-7000F) was utilized to observe the surface morphology of NiTi alloy after immersion at an accelerating voltage 20 kV.

To measure the amount of Ni ions in the electrolyte, the polished and cleaned specimens mounted in epoxy resin with an exposure area of 1 cm^2 were immersed in a 80-ml polyethylene bottle with 50 ml of FBS and PBS. The bottles were closed tightly and incubated in a thermostatic chamber at 37 ± 0.5 °C for 200 h. Afterwards, the Ni concentration in the electrolyte was determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo Scientific Corp, USA). Three parallel samples were used for each group to obtain averages in the experiment.

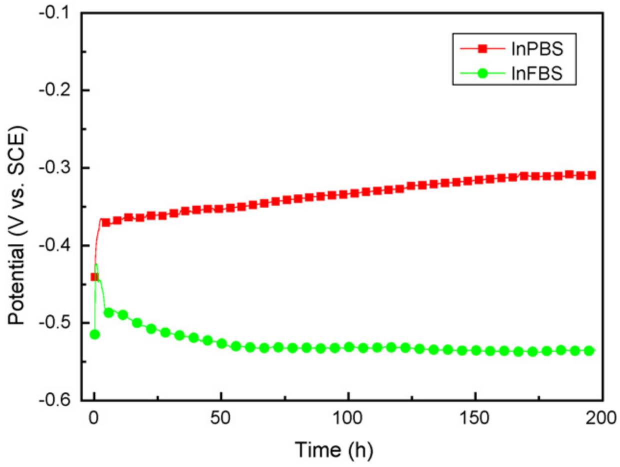

Fig. 1. Evolution of OCP with time recorded for NiTi alloy in PBS and FBS solutions at 37 °C.

3. Results and discussion

3.1. Open circuit potential measurements

Fig. 1 shows the evolution of the OCP with time acquired from the NiTi alloy in PBS and FBS solutions. It is clear that the steady state OCP value of the NiTi alloy in FBS is negative to that in PBS. In PBS, the OCP value rises rapidly at the beginning and then gradually slows finally reaching a steady state. In FBS, the OCP value rises rapidly like in PBS but after reaching about 0.425 V, it suddenly decreases rapidly before gradually reaching a steady state.

According to electroneutral theory, during electrochemical reactions, decrease in the anodic dissolution current moves the OCP to the positive direction to balance the cathodic reduction current [17]. During immersion in an electrolyte, the dissolved oxygen adsorbs on NiTi electrode surface and reacts preferentially with titanium forming a protective film mainly consisting of Ti oxide [5,18] which inhibits the conductivity of ions at the electrode/electrolyte interface. As a result, the anodic dissolution current decreases as indicated by the rise in the OCP. After a balance between formation and dissolution of the oxide film is established, a stable anodic dissolution current and therefore a steady OCP value is obtained. The fact that the steady state OCP value in the presence of organics such as proteins is negative compared to inorganic solutions such as PBS and Hanks' solution is consistent with previously reported results [9,10,17]. In fact, it has been reported that the adsorption of organics on the electrode can inhibit the transportation of oxygen from the electrolyte to electrode/electrolyte interface, making the Ti oxide film thinner. On the other hand, the proteins in FBS adsorbed on the interface can bind with metal ions and transport them into the electrolyte [8]. Both of them can increase the anodic dissolution current and move the OCP to the negative direction to balance the cathodic reduction current.