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Surface analyses and biocompatibility study of 500 °C oxidized $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ shape memory alloys ☆

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ABSTRACT

$Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ shape memory alloys (SMAs) are oxidized at 500 °C. Considering the surface roughness, the thicknesses of oxide layer and Ni-free layer, the surface Ni concentration, the proper oxidation times for oxidized specimens are found to be 60 min for $Ni_{50}Ti_{50}$ and 30 min for $Ni_{40}Ti_{50}Cu_{10}$. Experimental results reveal that the oxidation is diffusion-controlled with its oxide layer containing titanium oxide and that the surface Ni concentration is much lower than the nominal composition. When $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ SMAs are oxidized at these times, the latter has better corrosion resistance than the former in Hanks' solution at 27 °C. However, the results of cytotoxicity and cell proliferation assays indicate that the biocompatibility of unoxidized $Ni_{40}Ti_{50}Cu_{10}$ is worse than that of unoxidized $Ni_{50}Ti_{50}$, but that of oxidized $Ni_{40}Ti_{50}Cu_{10}$ ranks as good as that of oxidized $Ni_{50}Ti_{50}$.

1. Introduction

NiTi-based shape memory alloys (SMAs) are interesting due to their superelasticity and shape memory effect, which gives them wide biomedical applications, such as self-expanding stents for vascular and urological fields, orthodontic wires and staples for orthopedics [1–3]. In addition, substituting Cu for Ni in the Ni–Ti binary SMAs, such as $Ni_{40}Ti_{50}Cu_{10}$ ternary SMA, has been known to reduce the transformation hysteresis, the superelasticity hysteresis, and the flow stress level in the martensite state for special applications [4–7]. However, due to their high Ni content of about 40–50at.%, Ni in its metallic or oxidized state is detected on the surface of NiTi-based SMAs. Therefore, these SMAs are still controversial as implantation materials because of toxic, allergic, and carcinogenic effects that might be caused by Ni release [1,8,9]. The toxicity of NiTi corrosion products has been shown in vitro, and a transient increase of the Ni blood concentration has been found after NiTi implantation into animals [10,11].

To overcome those possible adverse reactions after long-term NiTi implantation, several studies have been focused on surface modifications such as surface coating, surface oxidation, laser oxidation and ion implantation for improving corrosion resistance to prevent Ni release [2,8,12–14]. It has been reported by Firstov *et al.* that the oxidation treatment of NiTi in air at temperatures close to 500 °C can produce a nickel-free oxide layer which is proposed to improve the biocompatibility of NiTi implants [13]. However, the biocompatibility of oxidized NiTi-based SMAs has not been clearly established to date. The purpose of this study is to determine the proper oxidation time at 500 °C for $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ SMAs to form a smooth Ni-free oxide surface layer. Then, cytotoxicity and cell proliferation assays are used to evaluate the oxidized NiTi-based SMAs for their corrosion resistance in Hanks' solution and their biocompatibility.

2. Experimental procedure

2.1. Material preparation and surface oxidation

$Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ (in at.%) SMAs were prepared from the raw materials of titanium (99.8 wt.%), nickel (99.98 wt.%) and copper (99.99 wt.%) by using a vacuum arc remelter (VAR) with pure titanium as the getter. The casting ingots were hot-rolled into 1-mm-thick sheets at 900 °C and then solution treated at the same temperature for 30 min. The rolled sheets were cut into $10\times10\times1$ mm^3 and $20\times20\times1$ mm^3 specimens. The specimen surface was ground using SiC paper to remove the oxide layer and then polished to a final level of 1.0 μm alumina through a standard metallographic procedure. Subsequently, all of the polished specimens were cleaned ultrasonically in acetone for 10 min to remove grease or organic contamination and then rinsed with deionized water and finally air dried. The specimens of $10\times10\times1$ mm^3 size were used for oxidation tests only and were oxidized in air at 500 °C in a furnace for 30–120 min. After evaluating the proper oxidation times, the specimens of $20\times20\times1$ mm^3 size were oxidized at these times and used for the biocompatibility tests.

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2.2. Analyses of the properties of oxidized surface

The surface properties of oxidized $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ SMAs were studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), α-stepper, and glow-discharge optical spectrometry (GDOS). The surface oxides formed were examined by XRD (PANalytical X'PRO X-ray) with Cu-Kα radiation (λ=0.154 nm) under 30 kV voltage, 20 mA current and 20°–80° scattering angle. The morphology and roughness of the oxidized surface were observed under an SEM (Philips XL30) and measured by an α-stepper (Veeco Dektak^{3}ST), respectively. The depth profiles of O, Ni and Ti concentrations in the oxidized layer were carried out by GDOS (LECO GDS-750 QDP) with a DC voltage in the range of typically 500–1000 V.

2.3. Potentiodynamic test

Potentiodynamic polarization of the oxidized specimen was performed using a potentiostat (Sintong Chem. Ind. Co. Ltd., Taiwan) in Hanks' balanced salt solution (HBSS, Sigma, H9269, USA) at 27 °C. HBSS was selected as the electrolyte because it is a commercial solution with ionic concentration similar to human plasma [1]. Ag/AgCl was used as the reference electrode and the working electrode was the oxidized specimen with a voltage scanning rate of 2 mV/sec. The applied voltage and the current between the oxidized specimen and the platinum counter electrode were recorded automatically by the data acquisition system.

2.4. Biocompatibility assay

Cytotoxicity assay and cell proliferation assay were carried out to evaluate the biocompatibility of oxidized $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ SMAs. The sterilized samples were placed into 24-well plate with 3 ml normal medium (DMEM culture medium containing 10% FBS and 1% penicillin, Sigma-Aldrich, USA). After incubating at 37 °C for 3 days, the medium was collected for testing. The 3T3 cells (mouse fibroblast) were seeded out at a density of 1×10^4/well in a 96-well plate. After incubating for 12 h, the normal medium was replaced by the collected medium and the cell culture was continued for 1 and 3 days. The harvested cells were subjected to the following assays.

2.4.1. Cytotoxicity assay

The following process conformed to the standard procedure (CytoTox 96® Non-radioactive Cytotoxicity Assay, Promega): (1) transfer 50 μl supernatant to 96-well plate; (2) add 50 μl substrate mix buffer to each well; (3) incubate for 30 min at room temperature (protected from light); (4) add stop solution to each well; (5) transfer 100 μl supernatant to enzymatic assay plate; and (6) record the absorbance at 490 nm by an ELISA (Enzyme-linked immunosobent assay) reader. The activity of lactate dehydrogenase (LDH) in the supernatant was measured as an indicator for cytolysis.

2.4.2. Cell proliferation assay

Cell proliferation assay was also conducted in accordance with the standard protocol (Cell Proliferation Reagent WST-1, Roche): (1) remove supernatant and add 200 μl WST-1 buffer to each well; (2) incubate for 2.5 h at 37 °C (protected from light); (3) transfer 100 μl supernatant to enzymatic assay plate; and (4) record absorbance at 550 nm by the ELISA reader. The absorbance of supernatant at 550 nm obtained by ELISA reader was measured as an indicator for cell viability or cell proliferation.

3. Results and discussion

3.1. XRD tests

In order to reveal the formed phases of surface oxides, the specimens of $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ SMAs oxidized at 500 °C for 30–120 min were subjected to XRD analysis. Experimental results show that with increasing oxidation time no significant change in the oxidized products can be seen. Fig. 1 reveals the XRD results of $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ specimens oxidized at 500 °C for 30 min, 60 min and 120 min. From Fig. 1(a), it can be seen that two main phases, B19' and TiO, are formed in the oxidized layer of $Ni_{50}Ti_{50}$ SMA. From Fig. 1(b), it can be seen that five main phases, B19, B2, TiO, $TiNi_3$ and Cu_2O, are formed in the oxidized layer of $Ni_{40}Ti_{50}Cu_{10}$ SMA. The identified phases shown in Fig. 1(a) are in agreement with the equilibrium phase diagram of Ni–Ti–O proposed by Firstov *et al.* [13]. However, the peak intensity of $TiNi_3$ phase appearing at 70° is more obvious for $Ni_{40}Ti_{50}Cu_{10}$ SMA than that for $Ni_{50}Ti_{50}$ SMA. This feature indicates that the Ni replaced by Cu in NiTi SMAs can enhance the $TiNi_3$ formation.

3.2. SEM observation and surface roughness

SEM surface images of specimens oxidized at 500 °C for 30–120 min are shown in Fig. 2(a) and (b) for $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ SMAs, respectively. From Fig. 2, it can be seen that with increasing oxidation time the oxidized surfaces of $Ni_{50}Ti_{50}$ and $Ni_{40}Ti_{50}Cu_{10}$ SMAs become rougher. At the same time, at the same oxidation time, the oxidized surface of $Ni_{40}Ti_{50}Cu_{10}$ SMA is rougher than that of $Ni_{50}Ti_{50}$. Fig. 3 plots the surface roughness of oxidized specimens vs. the oxidation time. The surface roughness is measured by the α-stepper

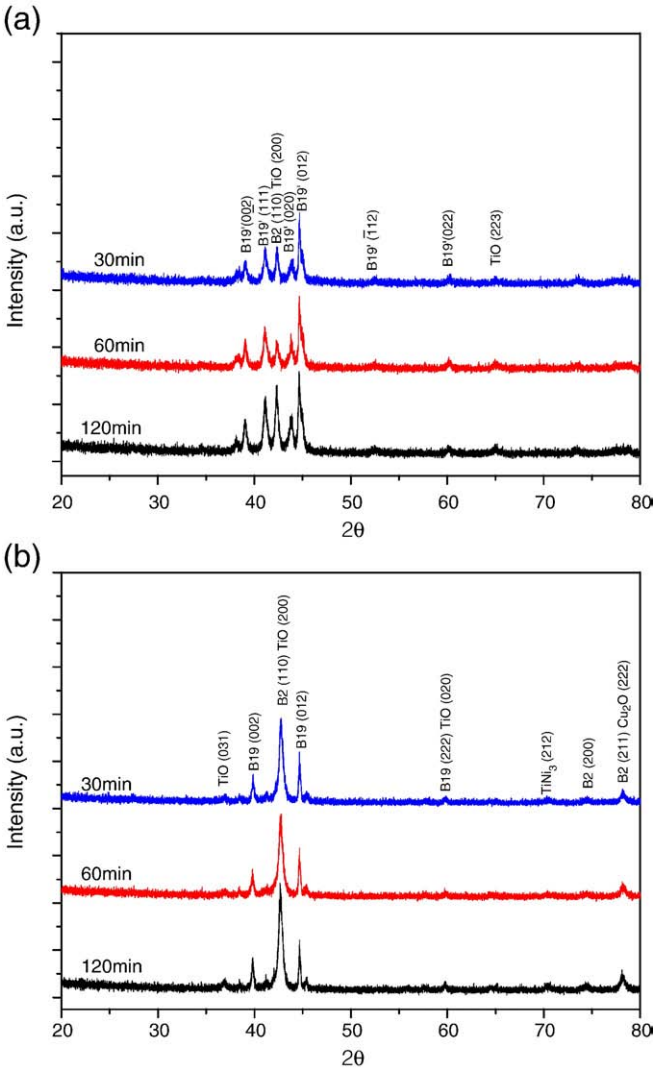

Fig. 1. XRD results of (a) $Ni_{50}Ti_{50}$ and (b) $Ni_{40}Ti_{50}Cu_{10}$ SMAs oxidized at 500 °C for 30 min, 60 min and 120 min.