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Formation of titanium nitride barrier layer in nickel–titanium shape memory alloys by nitrogen plasma immersion ion implantation for better corrosion resistance

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Abstract

Nickel–titanium shape memory alloys (NiTi) are potentially useful in orthopedic implants due to their super-elasticity and shape memory properties. However, the materials are vulnerable to surface corrosion and the most serious issue is out-diffusion of toxic Ni ions from the substrate into body tissues and fluids. In this paper, we describe our fabrication of TiN barrier layers in NiTi by nitrogen plasma immersion ion implantation followed with vacuum annealing at 450 °C or 600 °C. Our results show that the barrier layer is not only mechanically stronger than the NiTi substrate, but also is effective in impeding the out-diffusion of Ni from the substrate. Among the samples, the 450 °C-annealed TiN barrier layer possesses the highest mechanical strength and best Ni out-diffusion impeding ability. The enhancement can be attributed to the consolidation of the Ti–N layer resulting from optimal diffusion at 450 °C.

Keywords: Nickel–titanium shape memory alloy; Plasma immersion ion implantation; Titanium nitride; Corrosion resistance; Hardness

1. Introduction

Nickel–titanium shape memory alloys (NiTi) have potential applications as orthopedic implants because of their super-elastic properties and shape memory effects [1]. However, out-diffusion of harmful Ni from the NiTi substrate during prolonged use inside a human body is a serious issue and the problem must be solved before the materials can be more widely used in orthopedics. Titanium nitride is well known to possess excellent mechanical properties like high hardness, good wear and corrosion resistance, as well as adhesion [2]. Besides, its chemical inertness [3] minimizes the surface chemical reactions and together with its good biocompatibility [4], such a layer may mitigate the leaching of Ni from NiTi.

Titanium nitride thin films have been synthesized using techniques such as laser gas nitriding [5], magnetron sputtering [6], and powder immersion reaction assisted coating [7,8] on NiTi substrates or direct implantation of nitrogen [9]. In this work, we produced a TiN barrier layer by plasma immersion ion implantation (PIII) [10–14]. This technique was chosen due to its ability to treat specimens with complex geometry such as medical implants as well as its high efficiency and low cost. By choosing the proper duty cycle and sample cooling or heating, PIII can be conducted at any designated temperature. This is in contrast to conventional deposition techniques which require a certain temperature for nucleation and film growth. Such advantages have been exploited in the PIII treatment of NiTi alloys by Shevchenko et al., for example [15]. After our PIII experiments, mechanical, electrochemical corrosion, and immersion tests were conducted on the N-treated surface to assess the efficacy of the modified layer with regard to surface property enhancement and Ni impediment. We also

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investigated the effects of post annealing on the surface properties of the materials. The results and possible enhancement mechanism are discussed.

2. Experimental details

Discs 1 mm thick were cut from cylindrical NiTi bars with a Ni atomic percent of 50.8% (SE508 bar), grinded, polished to a shiny surface texture, and then ultrasonically cleaned with acetone and ethanol before implantation was conducted in our plasma immersion ion implanter. The samples were implanted using a sample pulsed bias of −40 kV using a pulse width of 50 μs, and frequency of 200 Hz. The working pressure during PIII was 8.5×10^{-2} Pa while the power applied to the radio frequency plasma source was 1000 W. The nitrogen implant dose was about 9.6×10^{16} cm^{-2}. A portion of the implanted samples were vacuum annealed at 450 °C for 5 h while the rest were annealed at 600 °C for the same period of time. In this paper, sample #1 designates the untreated control sample, and #2, #3 and #4 represent the implanted samples with no annealing, 450 °C, and 600 °C annealing, respectively.

Two samples of each type of treated and control samples were immersed in 25 ml of simulated body fluids (SBF) [16] in polypropylene (pp) bottles. The ion concentrations in the SBF are shown in Table 1. The pp bottles were closed tightly and incubated in a thermostatic chamber at 37±0.1 °C for 5 weeks. All the bottles were shaken gently for a few seconds every 3 days. After 5 weeks, the SBFs in the bottles were analyzed by inductively coupled plasma mass spectrometry (ICPMS) to determine the amount of Ni and Ti leached from the specimens. Nano-indentation tests (MTS Nano Indenter XP) were conducted on five areas to determine the average hardness and Young's modulus of the treated and control samples. A three-sided pyramidal Berkovich diamond indenter was employed. The elemental depth profiles and chemical states were determined by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI 5802. A monochromatic aluminum X-ray source was used and the pass energy was 58.7 eV. The scanning step size was 0.25 eV and the elemental depth distributions were determined using argon ion sputtering XPS. The phases formed after implantation was evaluated by X-ray diffraction (XRD) (Bruker D8 Discover system comprising a general area detector diffraction system and High-Star area detector). Copper was used as the anode material in the XRD machine. The electron accelerating voltage was 40 kV, whereas the anode current was 30 mA. The X-ray incident angle was 2°.

Table 1
Ion concentration of SBF in comparison with human blood plasma

	Concentration (mM)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	2.5	1.5	4.2	148.5	1.0	0.5
Blood plasma	142.0	5.0	2.5	1.5	27.0	103.0	1.0	0.5

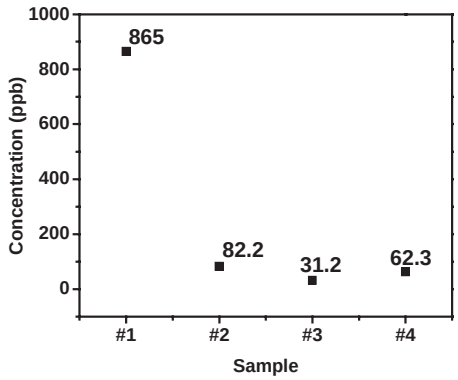

Fig. 1. Ni concentrations detected by ICPMS after SBF immersion test.

3. Results and discussion

Shevchenko et al. [15] performed argon and nitrogen PIII to improve the surface properties of NiTi. The depletion of surface Ni by argon PIII was attributed to the preferential sputtering of Ni during argon ion bombardment which is a well known effect. They also presented depth profiles showing the depletion of surface Ni and biocompatibility of the treated materials. It should be noted that Nitinol (NiTi alloy with equal Ni and Ti concentrations) is a well-established implant material in cardiovascular products. The major concern of the biomedical community is not the high Ni content in the alloy but the release of Ni in wear situations or the accelerated dissolution in case of destruction of the surface. In this respect, the work described in the previous work [15] did not tackle the problem associated with Ni leaching into the environment (biological tissue and fluids) which is the main concern. In this regard, we report more direct results using immersion tests as well as the effects of post-annealing.

Fig. 1 summarizes the ICPMS results of the SBF after the immersion test. The amount of Ni leached out from the control sample is at least 10 times higher that of the treated samples. Thus, the barrier layer is evidently effective in mitigating the out-diffusion of Ni from the substrate. It should be mentioned here that the amount of Ti leached from the control and treated samples are all negligible. Comparing the samples annealed at different temperatures, it can be observed that the 450 °C-annealed sample gives rise to the lowest Ni concentration in the SBF. We have also conducted the same immersion tests on the 20 and 30 kV N-implanted samples and similar results were obtained, that is, 450 °C annealing yielding the best results, followed by 600 °C, and the as-implanted ones being the worse.

The nano-indentation profiles are shown in Fig. 2 and some of the essential readings are summarized in Table 2. The control sample has constant Young's modulus (E) and