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PIIID-formed (Ti, O)/Ti, (Ti, N)/Ti and (Ti, O, N)/Ti coatings on NiTi shape memory alloy for medical applications

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ABSTRACT

(Ti, O)/Ti, (Ti, N)/Ti and (Ti, O, N)/Ti composite coatings were fabricated on NiTi shape memory alloy via plasma immersion ion implantation and deposition (PIIID). Surface morphology of samples was investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM). Cross-sectional morphology indicated that the PIIID-formed coatings were dense and uniform. X-ray diffraction (XRD) was used to characterize the phase composition of samples. X-ray photoelectron spectroscopy (XPS) results showed that the surface of coated NiTi SMA samples was Ni-free. Nanoindentation measurements and pin-on-disc tests were carried out to evaluate mechanical properties and wear resistance of coated NiTi SMA, respectively. For the *in vitro* biological assessment of the composite coatings in terms of cell morphology and cell viability, osteoblast-like SaOS-2 cells and breast cancer MCF-7 cells were cultured on NiTi SMA samples, respectively. SaOS-2 cells attached and spread better on coated NiTi SMA. Viability of MCF-7 cells showed that the PIIID-formed composite coatings were noncytotoxic and coated samples were more biocompatible than uncoated samples.

1. Introduction

Since 1970s, a considerable amount of scientific and technological efforts have been dedicated to investigating clinical applications of a NiTi shape memory alloy (SMA, 50.8 at.% Ni) in orthopedics and dentistry, owing to its shape memory and superelastic properties [1,2]. In spite of its excellent mechanical properties, problems associated with the lifespan and long-term biocompatibility of the NiTi SMA are attracting growing attention because of the increased and increasing human longevity as a consequence of better healthcare. Human body fluid containing water, dissolved oxygen, proteins and various ions is extremely corrosive to metallic prostheses. After the long-term exposure to the chemically aggressive environment, metallic prostheses are susceptible to failure due to corrosion, corrosive fatigue, corrosive wear, etc. In addition, during the long-term implantation, wear and wear debris generated from orthopedic joint implants could initiate a cascade of complex cellular events that would lead to aseptic loosening of joint prostheses [3]. Therefore, the normal lifetime of metallic prostheses for total joint replacements ranges from 10 to 15 years under load bearing conditions [4], which means that patients who receive metallic prostheses below the age of 65 will require at least one revision surgery.

Another major challenge in long-term implantation of NiTi SMA is its long-term biocompatibility. Ni ions influenced both the gene expression level and cholesterol metabolism, leading to the suppression of cell proliferation and cell differentiation [5]. Shih et al. reported that the supernatant and precipitates of the corrosion product of NiTi SMA wires were toxic to the rat aortic smooth muscle cells [6]. Apart from allergy or particle-induced inflammation, high Ni ion concentrations may result in tissue inflammation in the vicinity of a NiTi SMA implant in vivo [7]. Furthermore, there are concerns that toxic Ni ion release gives rise to potentially carcinogenic effects after long-term implantation due to the carcinogenicity of NiTi compounds and Ni ions [8]. Therefore, NiTi SMA implants should be covered by a suitable coating not only for shielding themselves from chemically aggressive body fluids but also for protecting surrounding body tissues against toxic corrosion products and potentially carcinogenetic Ni ions diffused out of the metal. In some orthopedic applications, NiTi SMA implants should also possess osteoconductivity for achieving a stable bonding with bone. The fabrication of a multifunctional coating on NiTi SMA implants thus becomes very attractive.

Various surface modification techniques, such as sol–gel process, H_2O_2-oxidation, thermal oxidation treatment, electrochemical deposition

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and magnetron sputtering, were investigated with the aim of improving the long-term biocompatibility, wear and corrosion resistance of the NiTi SMA [9–15]. Plasma immersion ion implantation and deposition (PIIID) is one of the promising techniques for the surface modification of NiTi SMA implants due to its suitability to treat objects with complex geometries and internal structures, convenient control of the coating composition, and efficient batch treatment for mass production [16]. Moreover, a hybrid process that involves ion implantation and ion deposition during the PIIID process usually forms not only a thicker coating than that fabricated by conventional plasma immersion ion implantation (PIII) technique but also an atomically intermixed layer between the coating and metal substrate, resulting in high bonding strength for the coating [17]. But the microstructure and properties (especially biocompatibility) of PIIID-formed coatings have not been extensively investigated for medical applications. The biocompatibility of commercially pure Ti is mainly attributed to the titanium oxide (TiO_2) layer that spontaneously forms on its surface and titanium nitride (TiN) is often served as a coating on Ti alloys to enhance their wear resistance. Therefore, in the current study (Ti, O)/Ti, (Ti, N)/Ti and (Ti, O, N)/Ti composite coatings were fabricated on the NiTi SMA using PIIID. An investigation into the surface characteristics, mechanical and in vitro biological properties of the above-mentioned composite coatings can certainly open avenues for creating coatings with better long-term biocompatibility and higher wear resistance.

2. Materials and methods

2.1. Fabrication of PIIID-formed coatings

NiTi SMA (containing 50.8 at.% Ni) discs (Φ10 mm × 1 mm) provided by Dr. Zhen-Tao Yu from Northwest Institute for Non-ferrous Metal Research, China, were abraded using SiC grinding paper from 120 to 4000 grit successively and then ultrasonically cleaned in acetone and ethanol separately for 15 min (designated "uncoated" hereafter). The fabrication of (Ti, O)/Ti, (Ti, N)/Ti and (Ti, O, N)/Ti composite coatings on polished and cleaned NiTi SMA discs was performed using a multi-purpose PIIID facility [18]. The PIIID processing parameters used are listed in Table 1. For coating formation, the vacuum chamber of the PIIID facility was firstly evacuated to a base pressure of 5.0×10^{-3} Pa. To remove any pollutant or surface oxide, sputtering of the metal sample surface using argon plasma was conducted prior to PIIID. After sputtering cleaning, a Ti transition layer, which was to increase the bonding strength between a composite coating (to be formed) and the NiTi SMA substrate, was firstly fabricated on uncoated NiTi SMA samples using a pulsed cathodic arc plasma source. For the fabrication of (Ti, O)/Ti and (Ti, N)/Ti composite coatings, O_2 and N_2 plasmas were generated respectively in the vacuum chamber through radio-frequency (RF) glow discharge. Consequently, either a (Ti, O) or a (Ti, N) layer was synthesized on the Ti layer to form a two-layer (Ti, O)/Ti or (Ti, N)/Ti composite coating (designated "(Ti, O)/Ti coated" or "(Ti, N)/Ti coated" hereafter). For synthesizing the (Ti, O, N)/Ti composite coating, the ratio of O_2 to N_2 in the vacuum chamber was maintained at 1:2 during PIIID and a mixture of O_2 and N_2 plasmas was generated in the PIIID equipment through RF glow discharge. Therefore, Ti, N_2 and O_2 plasmas were simultaneously induced and a (Ti, O, N) composite layer was thus formed on the Ti layer for NiTi SMA (designated "(Ti, O, N)/Ti coated" hereafter).

Table 1
PIIID parameters for the fabrication of (Ti, O)/Ti, (Ti, N)/Ti and (Ti, O, N)/Ti composite coatings.

Type of Coating	(Ti, O)/Ti	(Ti, N)/Ti	(Ti, O, N)/Ti
Gas	O_2	N_2	O_2 and N_2
Target bias (kV)	20	20	20
Voltage pulse width (μs)	60	60	60
Pulse repetition rate (Hz)	50	50	50
Working pressure (Pa)	3.0×10^{-1}	3.0×10^{-1}	3.0×10^{-1}
Processing time (h)	3.0	3.0	3.0

2.2. Surface characterization

The surface morphology of uncoated and coated NiTi SMA samples was examined using an atomic force microscope (AFM, Veeco diMultimode V, USA). Five random areas of 5 μm × 5 μm per sample were detected under the tapping mode for AFM analyses. After cutting, grinding and polishing, the cross-sectional morphology of coated samples was observed using a scanning electron microscope (FE-SEM, LEO 1530, Germany). To analyze the phase composition of surfaces of uncoated and coated samples, X-ray diffraction (XRD, D8 ADVANCE, Germany) operated with Cu Kα radiation was performed at room temperature over the 2θ range of 20°–60° and at a scanning rate of 0.05°/s. The surface chemical composition of samples was studied using X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Theta Probe, USA).

2.3. Phase transformation temperatures

The phase transformation temperatures of uncoated and coated NiTi SMA samples were measured using differential scanning calorimetry (DSC, Perkin Elmer Pyris 6 DSC, USA). Due to the capability limitation of the facility in terms of the sample dimension, uncoated and coated NiTi SMA samples were cut into smaller dimension (about one quarter of the disc sample in dimension). Firstly, NiTi SMA samples were cooled down from room temperature to −50 °C and kept isothermal for 3 min. Subsequently, the DSC measurement was conducted by heating the samples up to 50 °C where samples were also kept isothermal for 3 min, and then the samples were cooled down to −50 °C again. The heating as well as cooling rates were 5 K/min and all measurements were performed under a constant nitrogen flow.

2.4. Evaluation of mechanical properties and wear resistance

2.4.1. Nanoindentation measurement

The surface hardness and elastic modulus of coated NiTi SMA samples were determined using a nano-indentation system (Nano Indenter® G200, MTS Corp. USA) under the depth control mode. An indenter with a Berkovich tip was used. To minimize the influence of mechanical properties of the substrate, the indentation depth was kept below 15% of the coating thickness (100 nm) [19]. The nanoindentation was performed perpendicular to the surfaces of coated and uncoated samples and reached the depth of 100 nm from the surface of samples after 20 s. The maximum load was hold for 5 s at the indentation depth of 100 nm from the surface. The computer calculated the hardness and elastic modulus from the load–displacement curves, according to the Oliver–Pharr method [20]. 25 indentations at different areas were made for each sample and three samples were investigated for each type of coating.

2.4.2. Pin-on-disc tests

To assess the wear resistance of uncoated and coated NiTi SMA samples, pin-on-disc wear tests were conducted. During wear tests, a 0.1 N contact load was applied on samples through a Si_3N_4 ball with a diameter of 4 mm and the disc samples rotated at a constant speed of 300 rpm. The diameter of the sliding tracks was 6 mm. After wear tests, the width of wear tracks was measured using optical microscopy. To verify the repeatability of results, three samples were evaluated for each type of coating.