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Bioactive (Si, O, N)/(Ti, O, N)/Ti composite coating on NiTi shape memory alloy for enhanced wear and corrosion performance

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ABSTRACT

In this investigation, (Si, O, N)/(Ti, O, N)/Ti composite coating was synthesized on a NiTi shape memory alloy (SMA) substrate (50.8 at.% Ni) via plasma immersion ion implantation and deposition (PIIID) followed by magnetron sputtering, with the aim of promoting bioactivity and biocompatibility of NiTi SMAs. Nano featured (Si, O, N)/(Ti, O, N)/Ti coating was approximate 0.84 ± 0.05 μm in thickness, and energy dispersive X-ray (EDX) spectroscopy showed that Ni element was depleted from the surface of coated samples. X-ray diffraction (XRD) did not identify the phase composition of the (Si, O, N)/(Ti, O, N)/Ti coating, probably due to its thin thickness and poor crystalline resulting from low-temperature coating processes (<200 °C). X-ray photoelectron spectroscopy (XPS) analyses confirmed that a Ni-free surface was formed and Si element was incorporated into the composite coating via the magnetron sputtering process. Additionally, phase transformation behaviors of uncoated and coated NiTi SMA samples were characterized using differential scanning calorimetry (DSC). Wear and corrosion resistance of uncoated and coated NiTi SMA samples were evaluated using ball-on-disc tests and potentio-dynamic polarization curves, respectively. The (Si, O, N)/(Ti, O, N)/Ti coated NiTi SMA samples showed enhanced wear and corrosion resistance. Furthermore, the (Si, O, N)/(Ti, O, N)/Ti composite coating facilitated apatite formation in simulated body fluid (SBF) and rendered NiTi SMA bioactivity.

1. Introduction

NiTi shape memory alloy (SMA) with an approximately equiatomic composition was first introduced to the area of medical applications in 1971 as orthodontic wires [1]. Since then, numerous commercial medical products of NiTi SMAs have been developed, covering different fields including orthopedics, cardiovasology, urology, dentistry, etc., due to their shape memory effect, super elastic property, relatively low Young's modulus (~30 GPa) closer to that of cortical bone (20–30 GPa), and biocompatibility in non-chronic clinical applications [2]. Compared to conventional metallic materials, such as stainless steels, NiTi SMAs exhibiting shape memory effect generate more continuous and gentler force to correct misaligned teeth or avoid separation of fractured bones. Moreover, elastic recoverable stain of NiTi SMAs can reach up to 10%, providing more damage tolerance, while for elastic metallic materials it is approximately 0.1%. The greater mismatch in Young's modulus between metallic materials and the surrounding bones is, the more bone becomes stress shielded. The lack of mechanical stimuli on the bone usually gives rise to bone resorption which eventually results in failure and loosening of implants. In comparison with that of Co–Cr alloys (200–220 GPa) and stainless steel (approximately 200 GPa), NiTi SMAs have lower Young's modulus of ~30 GPa in the martensitic state, and therefore may reduce the stress shielding effect as orthopedic implants.

However, there are still healthy concerns about long-term clinical applications of NiTi SMAs. As human body fluids contain various inorganic ions (such as sodium, chloride, phosphate, sulfate, etc.), physiological environment is very aggressive for fully implantable metallic devices. After implantation, corrosion occurs on the surface of NiTi SMAs and results in mechanical properties degradation. More worse, overdose of Ni ion release and corrosion products are thought to trigger carcinogenesis. Therefore, not only are NiTi SMA implants required to be protected from corrosion caused by human body fluids, but also the Ni ions from NiTi SMA substrate should be blocked not to release into surrounding tissues.

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In orthopedics, unsatisfactory bioactivity is another major challenge for long-term fixation and stability of NiTi SMA implants, even if their Young's modulus is closer to cortical bone. As other bioinert metallic biomaterials, NiTi SMAs cannot directly form intimate interface with bone, and fibrous tissues usually encapsulate metallic implants. Takeshita et al. quantitatively compared the bone contact area to Ti, NiTi SMA and Ti-6Al-4V implants, and reported that NiTi SMA showed a significantly low bone contact than Ti or Ti-6Al-4V [3].

Although it was believed that wear resistance of NiTi SMAs was superior to that of stainless steel, NiTi SMAs are hardly used to fabricate medical devices subjected to wear, such as the heads of artificial hip joints. The wear debris arising from metallic implants often invokes an inflammatory and immunological response. This in turn causes blood clotting process, leukocytes, macrophages and, for severe cases, giant cells to move in on the foreign wear particles, resulting in interfacial problems between the implant and the host tissue [4].

The effective method to solve the above-mentioned problems with NiTi SMAs is to coat various bioactive and biocompatible coatings on their surface [5]. Initial research in the field focused on the development and optimization of coatings from single material system. Cheng et al. prepared a 200 nm-thick TiO_2 coating on a NiTi SMA via a two-step hydrothermal method to improve the corrosion resistance [6]. Jin et al. investigated into the influence of TiN coating on in vitro biocompatibility of a medical NiTi SMA, after a plasma arc treatment [7]. However, more recent research efforts have explored composite coating containing essential trace elements from multiple materials. By incorporating different materials, composite coatings have significantly improved performance over their single-material counterparts. Sr-, Mg-, and Si-containing bioactive $Sr_2MgSi_2O_7$ ceramic coatings were synthesized via plasma spray technique, and exhibited multiple functions such as reducing inflammatory reaction, downregulating osteoclastic activities, maintaining bioactivity, etc. [8]. Zheng et al. reported a $SrO–SiO_2–TiO_2$ sol–gel coating on a NiTi alloy to enhance corrosion resistance and cellular behaviors [9]. But multifunctional coatings with the capability of strong bonding strength, improved bioactivity, and enhanced wear and corrosion resistance still have not been extensively investigated for long-term clinical applications of NiTi SMAs.

Plasma immersion ion implantation and deposition is a hybrid process that involves ion implantation and deposition, and usually forms an atomically intermixed layer between metallic substrate and coating, resulting in high bonding strength [10]. In contrast, coatings formed by electrochemical deposition or sol–gel process are prone to dileminate from substrates under load-bearing condition due to weak bonding strength. Unlike plasma spray or heat treatment, PIIID is a low temperature process (below 200 °C). It can not only effectively avoid altering phase transformation temperatures of NiTi SMAs before and after the treatment, but also minimize the dimension variation resulting from high temperature [11]. Magnetron sputtering is a powerful and flexible technique which can be used to coat components with a wide range of materials – any solid metal or alloy and a variety of compounds [12,13]. By combining the merits of these two techniques without interrupting vacuum during the coating process, coatings with both outstanding mechanical properties and diverse essential trace elements can be fabricated for long-term medical applications. Si is an essential trace element for normal growth and development of bone. However, Si-containing coating on NiTi SMAs is rarely reported for medical applications. In this study, (Si, O, N)/(Ti, O, N)/Ti coating was fabricated on the surface of NiTi SMA (containing 50.8 at.% Ni) via PIIID and subsequent magnetron sputtering process without disturbing vacuum, and surface characteristics of the Si containing coating were investigated. In addition, bioactivity, wear and corrosion resistance of uncoated and coated NiTi SMA were compared. The potential mechanisms behind the improved bioactivity, wear and corrosion resistance were discussed as well.

2. Materials and methods

2.1. Fabrication of (Si, O, N)/(Ti, O, N)/Ti coatings

NiTi SMA (50.8 at. % Ni) raw material provided by Northwest Institute for Non-ferrous Metal Research, China, was cut into discs (Φ10 mm × 1 mm in size). After being polished to mirror surface by grinding papers, the discs were ultrasonically cleaned with acetone, alcohol and distilled water separately for 15 min (these samples are denoted as "uncoated" hereafter). A multi-purpose PIIID facility which can continuously carry out PIIID and magnetron sputtering processes without disturbing vacuum system, was used to fabricate the (Ti, O, N)/Ti and (Si, O, N)/(Ti, O, N)/Ti composite coatings [14]. Prior to the coating process, a base vacuum pressure of 5.0×10^{-3} Pa was obtained, followed by argon plasma sputtering to further clean the surface of NiTi SMA samples. During the PIIID coating process, the working pressure was 3.0×10^{-1} Pa. The working pressure To increase the bonding strength between composite coatings and the NiTi SMA substrate, a Ti transition layer was then prepared via a pulsed cathodic arc plasma source equipped with the PIIID facility, and the processing time is 1 h. Subsequently, radio-frequency (RF) glow discharge technique was used to simultaneously generate O_2 and N_2 plasmas (the ratio of O_2 to N_2 = 1:2). Due to the presence of Ti, N_2 and O_2 plasmas in the chamber at the same time and 2 h of processing, a (Ti, O, N) composite layer was formed on the Ti transition layer (these samples are denoted as "(Ti, O, N)/Ti coated" hereafter). After the PIIID treatment, Si, O and N elements were incorporated onto the (Ti, O, N) composite layer through RF magnetron sputtering in an atmosphere of O_2 and N_2 plasmas, using the same multifunctional PIIID facility without disturbing the vacuum (these samples are designated as "(Si, O, N)/(Ti, O, N)/Ti coated" hereafter). To avoid significant coating thickness variation, the RF magnetron sputtering process was carried out for only 10 min.

2.2. Surface characterization

The surface topography and cross-sectional morphology of NiTi SMA samples were observed using a scanning electron microscope (FE-SEM, LEO 1530, Germany). Surface topography at nano scale was further characterized for coated samples using an atomic force microscope (AFM, Veeco diMultimode V, USA). Elemental mapping on the cross-sections of coated samples was carried out using an energy dispersive X-ray (EDX) spectrometer equipped with the SEM. Grazing angle X-ray diffraction (XRD, D8 ADVANCE, Germany) analyses were conducted to determine the phase composition of uncoated and coated samples, using Cu Kα radiation operated at an incidence angle of 1°, a voltage of 40 kV and a current of 40 mA. 2θ range of XRD analyses was set to 20–70° at a scanning rate of 0.05°/s and the diffraction peaks were identified according to the powder diffraction files. X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Theta Probe, USA) was performed to identify surface chemical composition.

2.3. Phase transformation behaviors

The phase transformation behaviors of uncoated and coated NiTi SMA samples were characterized using differential scanning calorimetry (DSC, Perkin Elmer Pyris 6 DSC, USA). Due to mass limitation of the DSC measurement, NiTi SMA samples were cut into around one quarter of the disc sample in dimension. Firstly, the sample was cooled down to −50 °C and kept for 3 min to establish thermal equilibrium. Subsequently, the DSC measurement started