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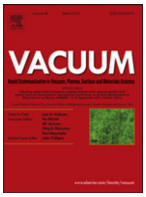

Structure and properties of TiC/Ti coatings fabricated on NiTi by plasma immersion ion implantation and deposition

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ABSTRACT

A titanium carbide (TiC) nanostructured coating and Ti intermediate layer are fabricated on NiTi by plasma immersion ion implantation and deposition (PIII&D) to improve the surface properties. The chemical composition and structure are determined by X-ray diffraction, Auger electron spectroscopy, scanning electron microscopy, and atomic force microscopy. Nano-indentation is used to evaluate the mechanical properties of the thin film and the biological characteristics are assessed by electrochemical measurement and soaking tests in simulated body fluids. Based on the potentiodynamic polarization and Ni release data after the polarization test, the Ti/TiC nanostructure coating has better corrosion resistance compared to the NiTi substrate and there is significantly less Ni ion release from the NiTi substrate into the simulated body fluids than the uncoated NiTi alloy.

1. Introduction

Plasma immersion ion implantation and deposition (PIII&D) which combines the advantages of energetic ion bombardment and low-energy film deposition is a widely used technique to fabricate metallic and ceramic coatings. Usually, a cathodic arc is adopted as the source of metallic ions and the metal plasma is usually filtered by a bent magnetic duct to remove deleterious macro-particles [1–3]. PIII&D is also not restricted by the line-of-sight limitation compared to conventional beam-line ion implantation and is thus particularly useful for the surface treatment of samples with a complex geometry [3–5].

NiTi alloys are widely used in biomedical applications [6,7] because of their unique super-elasticity and shape memory effects. The materials are usually protected by a thin surface oxide film but this passive film is not stable due to the existence of Ni and can be easily destroyed under harsh conditions leading to intense surface corrosion [6–8]. To overcome this problem, surface modification is frequently conducted. Preparation of a multi-layered structure with Ti as the intermediate layer can improve the adhesion strength and corrosion resistance [9,10]. PIII&D has been successfully employed to improve the corrosion behaviour, biocompatibility, and tribological surface properties of NiTi alloys, Ti alloys, and steels by forming a robust surface ceramic layer, which the thickness is approximately 100–900 nm. However, some studies indicate that the efficacy of the barrier layer depends more on the density than absolute thickness [11–16]. Titanium carbide has a broad range of industrial applications because of its high hardness and melting point, thermal stability, low friction, high electrical and thermal conductivity as well as excellent chemical inertness. In this study, Ti/TiC thin films are produced on NiTi by PIII&D and magnetron sputtering to improve the surface properties.

2. Experimental details

$Ni_{50.8}Ti_{49.2}$ (at%) disks 1.5 mm thick and 30 mm in diameter were polished to a near mirror finish, ultrasonically cleaned in acetone, absolute ethanol, and deionized water for 15 min each at 40 °C, and air dried. After cleaning with argon sputtering, a Ti intermediate layer was first deposited at room temperature by DC magnetron sputtering of a high purity (99.98%) Ti target 50 mm in diameter. Ti deposition was conducted at an Ar pressure of 0.5 Pa for 100 min at 150 W sputtering power (deposition rate ~4.8 nm/min). Afterwards, the TiC thin film was deposited by PIII&D. A pure titanium cathode (99.99%) and carbon cathode (99.98%) were used

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to produce titanium and carbon ions. The vacuum chamber was evaluated to 8×10^{-4} Pa and titanium and carbon plasmas were generated by pulsed cathodic arc plasma sources at the repetition frequency of 10 Hz. The pulse duration of the arc discharge was 1200 μs and the high negative bias and implantation duration were kept at -24 kV and 300 μs, respectively. A deposition rate of up to 2 nm/min was obtained, resulting in a film thickness between 90 and 160 nm after the standard processing time of 90 min. No external heating or cooling was employed and the sample temperature was below 70 °C at the end of deposition.

The crystalline structure was determined by X-ray diffraction (GIXRD) (Philips X'Pert) in the continuous scanning mode using Cu K_α radiation ($\lambda = 0.154056$ nm). Auger electron spectroscopy (AES) was used to determine the surface composition and depth profiles of the Ti/TiC thin films. The surface morphology, film uniformity, and homogeneity were studied by atomic force microscopy (AFM, NanoScopeV MultiMode System, Veeco) and scanning electron microscopy (SEM, Philips XL-30). The mechanical properties such as Young's modulus (E) and hardness (H) were evaluated by nano-indentation (MTS Nano Indenter XP, USA). The film composition was determined by X-ray photoelectron spectroscopy (XPS, PHI 5802) using monochromatic Al K_α radiation. An argon ion beam was used to sputter off about 20 nm to remove contaminants from the surface before acquiring the Ti2 p and C1s spectra.

The potentiodynamic polarization test was performed on a Zennium electrochemical workstation in simulated body fluids (SBF) at 37 ± 0.5 °C. Inductively-coupled plasma mass spectrometry (ICPMS, PerkinElmer Optima 2100 DV) was used to measure the amounts of Ni released to the SBF from the coated and uncoated samples after the potentiodynamic polarization test.

3. Result and discussion

Fig. 1 depicts the XRD patterns of the Ti/TiC thin films deposited on silicon at 3° grazing angle and normal direction. As shown in Fig. 1(a), the (220) plane is the preferred structure of the TiC coating which is similar to that reported in Ref. [17], although the (111) and (200) planes are the common ones in TiC and the (200) plane has the lowest energy in TiC [18–20]. Fig. 1(b) shows that a Si (400) peak with a very small half width stemming from the substrate is visible at about 70°. With further increase in the incidence angle up to the normal angle, the TiC peak intensity diminishes for increasing (400) reflections from the Si substrate. The results indicate that the coating is quite thin, and near the coated surface through which the X-ray penetrates despite grazing incidence, there is a reorientation between (220) and (200).

Fig. 2 shows the (220) and (200) pole figures and (220) phi-scan diagrams of the TiC coating deposited on the Ti intermediate layer. For comparison, the (200) plane results and analysis are also presented. As shown in Fig. 2(a) and (b), the height of the pole figures spectrum describes the intensity of the (220) crystallographic plane compared to the (200) plane, disclosing that the crystallographic planes of the TiC nanostructure are mostly the (220) one. The XRD phi-scan analysis can identify the in-plane orientation [21] and as shown in Fig. 2(c), the (220) phi diffraction peak is quite intense implying that the TiC coating is crystalline. On the other hand, the phi-scan diffraction and distinct intensity maxima are observed from the (220) crystallographic plane thereby confirming the in-plane texture of the (220) TiC coating.

Fig. 3 shows the chemical composition of the Ti/TiC thin film and the C1s and Ti2 p spectra of the thin film. The Ti2 p XPS signal at binding energy of 460.8 eV and C1s peak at about 281.6 eV indicates that the coating is TiC [22,23] with a C/Ti ratio of 1.087 as determined by XPS.

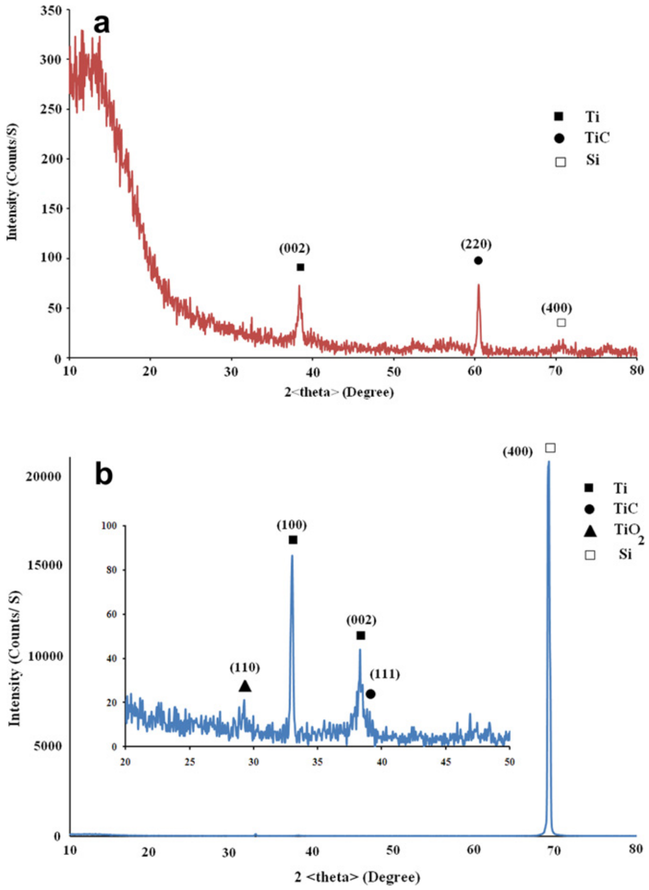

Fig. 1. XRD pattern of the Ti/TiC thin film: (a) 3° grazing incidence and (b) normal.

Fig. 4 displays the AES spectra and carbon AES depth profile of the Ti/TiC thin films. Fig. 4(a) shows clear Ti and C peaks on the coating surface. The C KLL peak (at 265 eV), Ti $L_{2,3}M_{2,3}M_{2,3}$, and Ti $L_3M_{2,3}V$ peaks (at 382 and 419 eV, respectively) correspond to titanium carbide (TiC) [24–26]. Fig. 4(b) delineates four distinct regions, namely the surface layer, interfacial layer, Ti intermediate layer, and substrate. The surface is a C-rich region and the carbon content diminishes gradually with depth in the Ti/TiC thin films. This may be related to two states. Firstly, TiC has a metastable composition and so the Ti/C ratio may depend on thermodynamic and kinetic conditions. Secondly, the voltage plays an important role in the diffusion depth in PIII&D, especially for carbon because of the stability of carbon is less than that of titanium in this case. The graded structure arises from an energetic ion implantation during PIII&D and there is also an interfacial layer between the TiC and Ti intermediate layer. The interfacial layer is made of titanium and carbon as base elements. It has a graded TiC composition and contains oxygen as an impurity (10% O, 15% C, and 75% Ti). The surface of the Ti intermediate layer removed by 5 kV Ar+ sputtering prior to deposition is approximately 80 nm thick. Oxygen in the residual vacuum contributes to oxygen contamination and presence of some titanium oxide. The TiO_2 phase may also be a result of environmental contamination and diffusion from the materials beneath (Ti intermediate layer).

Fig. 5 shows the AFM images of the Ti intermediate layer and TiC thin film deposited on the Ti intermediate layer. A homogeneous granular surface is observed from the Ti intermediate layer and TiC film confirming the columnar structure and fine grains. The surface of the TiC nanostructured coating possesses microstructures (rough