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

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A B S T R A C T
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.

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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
Ni50.8Ti49.2 (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
to produce titanium and carbon ions. The vacuum chamber was evaluated to $8 \times 10^{-4}$ 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 $\mu$s and the high negative bias and implantation duration were kept at $-24$ kV and 300 $\mu$s, 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 $K_{\alpha}$ 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 $K_{\alpha}$ radiation. An argon ion beam was used to sputter off about 20 nm to remove contaminants from the surface before acquiring the Ti2p and Cls spectra.

The potentiodynamic polarization test was performed on a Zennium electrochemical workstation in simulated body fluids (SBF) at $37 \pm 0.5$°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 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$_{3}$M$_{2,3}$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 so the Ti/C ratio may depend on thermodynamic composition and environmental contamination and diffusion from the materials beneath the TiC nanostructured coating possesses microstructures (rough
surfaces) containing aggregates of TiC grains and the Ti intermediate layer helps to produce a relatively smooth and dense surface. Asperities with a similar range of heights are distributed on the Ti nanostructured coating as an intermediate layer. Actually the TiC nanostructure is made of a lot of nano grains, which have many TiC crystallites. The mismatch in the coefficients of thermal expansion influences the NiTi alloy—ceramics bonding [27]. During deposition of the TiC nanostructures coating by PIII&D, generation of stress between the metal substrate and TiC coating as a result of differences in thermal contraction and expansion decreases the bonding strength of the coating. Furthermore, mechanical stress is accumulated during subsequent deposition of the TiC coating [27]. The Ti intermediate coating can be regarded as a mechanically interlocking area which can increase the bonding strength between the NiTi alloy and TiC coating. It can be supposed that during the formation of the TiC nanostructured coating, diffusion of the components occurs and there is possibly a chemical reaction at the interface between the Ti intermediate layer and TiC nanostructured coating. The graded structure arises from energetic ion implantation during PIII&D which also leads to the formation of TiC$_x$O$_y$ phase. However, the exact nature of the chemical bonding requires further research and more work is being conducted in our laboratories. The TiC film with an RMS (root-mean-square) roughness of 13.2 nm is more uniform and smoother than the Ti intermediate layer which has a surface RMS roughness of 17.4 nm. The average hardness and modulus values of the Ti/TiC thin films and uncoated NiTi are summarized in Table 1, and the hardness and the elastic modulus of the Ti/TiC thin film are higher than those of the NiTi substrate.

The open circuit potentials ($E_{ocp}$) versus immersion time measured from the Ti/TiC thin film and bare NiTi in SBF at 37 °C are shown in Fig. 6. The open circuit potential of Ti/TiC is higher than that of NiTi. The potential of NiTi increases slowly in the early stage of immersion and reaches a steady-state value of about −190 mV (SCE) with further increasing immersion time, whereas the

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**Fig. 2.** XRD diagram of the Ti/TiC thin film: (a and b) XRD pole figure of the (200) and (220) crystallographic plane, respectively, (c) XRD phi-scan diagram of the (220) crystallographic plane.

**Fig. 3.** XPS spectra of the surface after Ar ion sputtering to clean the top 20 nm.
Fig. 4. Auger results obtained from the Ti/TiC thin film: (a) Auger survey spectra and (b) Carbon depth profile.

Fig. 5. Surface micrograph and morphology of the TiC coating deposited by PIII&D on the Ti intermediate layer: (a) AFM image of Ti intermediate layer and (b) AFM image of TiC nanostructured coating.
potential of Ti/TiC coating decreases gradually and stabilizes at a value of \(-120\) mV (SCE). The different potentials are related to the formation of a surface oxide film.

![Image](35x75 to 282x253)

**Fig. 6.** Open circuit potentials of the Ti/TiC thin film and bare NiTi versus immersion time in SBF at 37 °C.

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(R_{\text{rms}}) (nm)</th>
<th>(H) (GPa)</th>
<th>(E) (GPa)</th>
<th>Max load (mV)</th>
<th>Indentation depth (nm)</th>
</tr>
</thead>
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<tr>
<td>NiTi alloy</td>
<td>17.4</td>
<td>2.744</td>
<td>64.312</td>
<td>192.5</td>
<td>2040</td>
</tr>
<tr>
<td>Ti/TiC thin film</td>
<td>13.2</td>
<td>5.541</td>
<td>105.298</td>
<td>192.5</td>
<td>1120</td>
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**Table 2**

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<tr>
<th>Sample</th>
<th>(E_{\text{ocp}}) (mV)</th>
<th>(E_{\text{corr}}) (mV)</th>
<th>(i_{\text{passive}}) ((\mu)A cm(^{-2}))</th>
<th>(E_b) (mV)</th>
<th>Ni (mg L(^{-1}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiTi alloy</td>
<td>-190</td>
<td>-333</td>
<td>20.18</td>
<td>71</td>
<td>5.0685</td>
</tr>
<tr>
<td>Ti/TiC thin film</td>
<td>-120</td>
<td>-722</td>
<td>6.2</td>
<td>273</td>
<td>0.0228</td>
</tr>
</tbody>
</table>

![Image](303x523 to 551x727)

**Fig. 7.** Potentiodynamic polarization curves and SEM image of the Ti/TiC thin film and NiTi alloy in SBF at 37 °C.

**4. Conclusion**

A robust corrosion-resistant TiC/Ti thin film is produced by depositing TiC on NiTi by PIII&D after a Ti intermediate layer is deposited by magnetron sputtering. The phi-scan diffraction and pole figures reveal the in-plane texture of (220) orientation in the TiC coating. The smooth and homogenous surface of the TiC thin film is confirmed by atomic force microscopy. Based on the

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**Notes:**
- Open circuit potentials of the Ti/TiC thin film and bare NiTi after immersion in SBF solution for 1 h and Ti/TiC thin film after immersion for 120 h on a semi-logarithmic scale. The results are summarized in Table 2. The corrosion potential \(E_{\text{corr}}\) of the NiTi alloy is smaller than that corresponding to the open circuit potential \(E_{\text{ocp}}\) (Fig. 6). The variation is probably due to the depassivation phenomenon on the surface during cathodic scanning [28]. As shown in Fig. 6, the anodic polarization curves of the samples are similar in the passive region. In the passive region of the NiTi alloy, abruptly changing current densities can be observed at 29 mV (SCE) – 71 mV (SCE). It implies passive film breakdown and repassivation. The current densities stabilize above 71 mV (SCE). However, the potential is higher than 110 mV and the current density increases rapidly indicating the occurrence of pitting corrosion, as shown in the SEM image. This phenomenon is typical of NiTi alloys [28]. However, it should be noted that the passive region in the Ti/TiC thin film after immersion for 120 h in SBF is larger than that of NiTi. The compact morphology of TiC changes the breakdown potential \(E_b\) to about 273 mV. The more extended the passivation region, the higher the corrosion resistance the NiTi alloy possesses. The anodic branch of the Ti/TiC thin film can be divided into two passivation regions, a wide region initially related to TiC and another one associated with the Ti intermediate layer. Oxidation requires the penetration of a sufficient amount of anions through the coating and corrosion may occur at the interface. In addition, defects can promote corrosion at the interface. Similarly, abruptly increasing current densities are observed at around 20 mV (SCE) and then the current densities decrease slowly with increasing potentials. It is attributed to the sequential formation and repassivation of the micro-pits in the Ti intermediate layer. Finally, anions in the SBF such as chloride penetrate into the Ti/TiC system thus increasing the current density rapidly followed by pitting corrosion as shown by the dark zone in the SEM image.

Release of nickel ions from the Ti/TiC thin film and NiTi alloy after the potentiodynamic polarization test is summarized in Table 2. The amount of Ni released from the uncoated NiTi is about 222 times higher than that from the Ti/TiC/NiTi system. A TiC coating has been reported to mitigate Ni leaching by a factor of 11 compared to the bare NiTi alloy [29]. In this respect, the amount of Ni released from TiC nanostructured coating deposited on a Ti intermediate layer is about 222 and 20 times smaller than those from the bare NiTi alloy and TiC coating without an intermediate layer, respectively. The surface layer is obviously effective in mitigating out-diffusion of Ni. It should also be mentioned here that the amount of Ni leached from the coated NiTi is negligible after 120 h immersion in SBF. However, Ni released from biomedical implants *in vivo* can be deleterious and so further reduction may be required. Consequently, further work is being conducted on the effects of coating thickness, structure, as well as the stability of the carbon arc which tends to become unstable after 2 h of operation together with the associated influence on the film homogeneity and stoichiometry.
electrochemical and dissolution test results, the corrosion resistance of the coated NiTi is enhanced significantly by this graded coating and leaching of Ni is also drastically depressed.

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