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# Enhanced corrosion resistance of Zr coating on biomedical TiNi alloy prepared by plasma immersion ion implantation and deposition

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ABSTRACT

Zirconium film was prepared on TiNi alloy by plasma immersion ion implantation and deposition (PIIID) technique to enhance its corrosion resistance and prolong its working lifetime. The atomic force microscopy (AFM) results show that the film was relatively smooth with the root mean square roughness being 9.166 nm. The X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) results indicate that the implant element of Zr was oxidation partialness. The potentiodynamic polarization measurements in the Hank's solution at 37 °C show that the corrosion resistance of the alloy was improved by the Zr coating film and the atomic absorption spectrometry (AAS) tests also indicate that Ni ion concentration released from the substrate in the Hank's solution after the polarization test was reduced greatly, in comparison to the unmodified TiNi alloy sample.



## 1. Introduction

Plasma immersion ion implantation and deposition (PIIID), is a widely used technique to implant and simultaneously deposit a wide variety of metallic and ceramic films [1–3]. The advantage of this dual technique is the better adhesion between the film and substrate [4]. For medical implant material, it is important to minimize the corrosion and the release of the metal ions. TiNi alloy, with around 50% Ni content, has been extensively used in orthopedics and interventional therapy, arouse a strong concern of the toxicity of released Ni ion, and had been coated by many different bioceramic films, including DLC [5], TiC [6], TiN [7] and ZrN [8] using PIIID technique by the present author. As an alternative coating, pure metallic coating had been prepared by the present author, such as Ta coating [9]. Because of its adequate mechanical properties, good corrosion resistance and excellent hemocompatibility, Zr is also believed to be an ideal element for the surface modification. In this paper, the Zr-deposited biomedical TiNi alloy was studied by various characterization technologies of thin film.

## 2. Experimental procedure

Ti–50.8 at.% Ni alloy plates (10 mm × 10 mm × 1 mm) were mechanically polished and ultrasonic rinsed in acetone and ethanol, respectively, before loaded into the vacuum chamber. The plasma was produced by two ECR plasma sources under the Ar circumstance, and the $Ar^+$ was used to enhance the sputtering of the Zr target. Ions from the plasma were accelerated by applying a 30-kV pulse and a 200-V DC negative bias voltage to the substrate. In this way implantation and deposition were combined.

The surface morphology of the film was investigated by AFM (DI, model VEECO-4). The valence of the Zr ions and oxygen element on the substrate surface were analyzed by XPS (Kratos, model Axis Ultra). GAXRD (Rigaku D/max-RB) was employed to examine the phase constitutions presented at the surface. The potentiodynamic polarization measurements (CHI650B) were carried out to investigate the corrosion resistance of the film in the Hank's solution at 37 °C. Ni ion concentration released from the substrate after polarization was tested by AAS (Hitachi, model Z_5000).

## 3. Results and discussion

Fig. 1(a) depicts the three-dimensional AFM image of Zr coating, which shows a relatively smooth and compact film feature with the root mean square roughness being 9.166 nm, as measured from Fig. 1(b).

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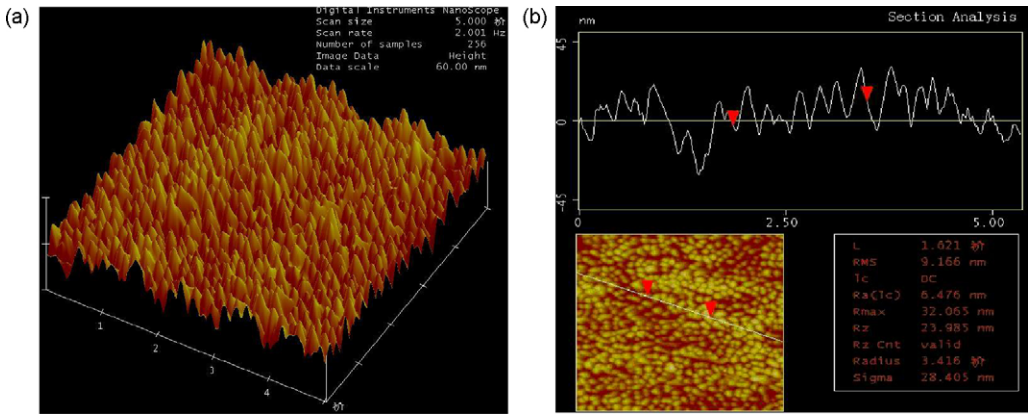


**Fig. 1.** (a) Three-dimensional and (b) two-dimensional AFM images of the Zr-coated TiNi alloy sample.

Fig. 2 displays the overall XPS spectrum for the film on the as-deposited surface and the surface after sputtered for 5 min by argon ion. The spectra indicate the presence of peaks related to both Zr and O species together with a trace of contaminating C on the outmost surface of the film. After 5 min sputtering, the O signal keeps almost unchanged and the C signal disappears, indicating that the C element presents only on the surface and the O element presents in the whole film. Therefore, zirconium and its oxides appear as the composition phases in the prepared film.

Fig. 3 displays the high-resolution XPS spectra relative to Zr peaks on the as-deposited surface and the surface after sputtered for 5 min, respectively. In Fig. 3(a), the peak at 182.1 eV is very close to that reported for $Zr^{4+}$ $3d_{5/2}$ in $ZrO_2$ and passive layers on zirconium and its alloy [10], whilst the binding energies of the other two peaks are 180.4 eV and 184.6 eV, which can attribute to zirconium carbide and non-stoichiometric $Zr_3O_{1-X}$ phases, respectively. These suggest that the outmost surface of zirconium film is not oxidized entirely by the air. After 5 min sputtering, the outmost surface layer was etched and the XPS spectra of the new fresh layer shows that the positions of Zr 3d peaks are 179.1 eV, 181.9 eV, 183.5 eV and 185.7 eV, respectively. These positions are slightly different from those of pure zirconium and the shape of the spectra are also different from that of the zirconium oxide, which are speculated to be composed of zirconium and zirconium non-stoichiometric $Zr_3O_{1-X}$.

The GAXRD pattern for the film is shown in Fig. 4, which also reflects the formation of Zr and non-stoichiometric $Zr_3O_{1-X}$ phases, in coincidence with the results of XPS studies. Obviously, because the pressure in the vacuum chamber is very low ($(6–8) \times 10^{-2}$ Pa), there is not enough oxygen for formatting the stable oxide phase of $ZrO_2$, so only the undesired $Zr_3O_{1-X}$ phase might be formed during

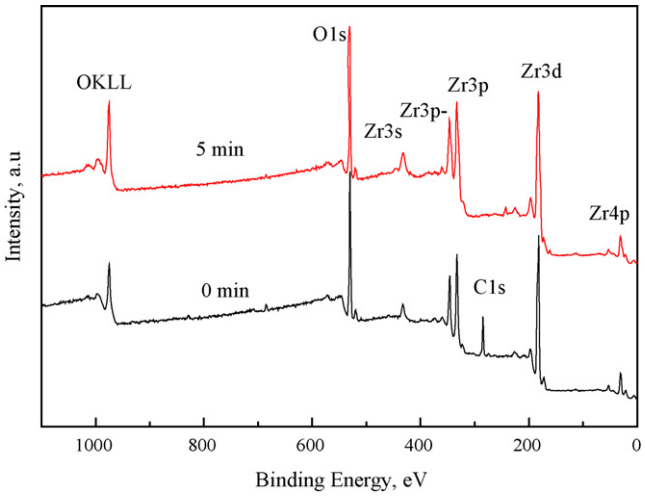


**Fig. 2.** Survey XPS spectra of the Zr-coated TiNi alloy samples after argon sputtering for 0 min and 5 min.

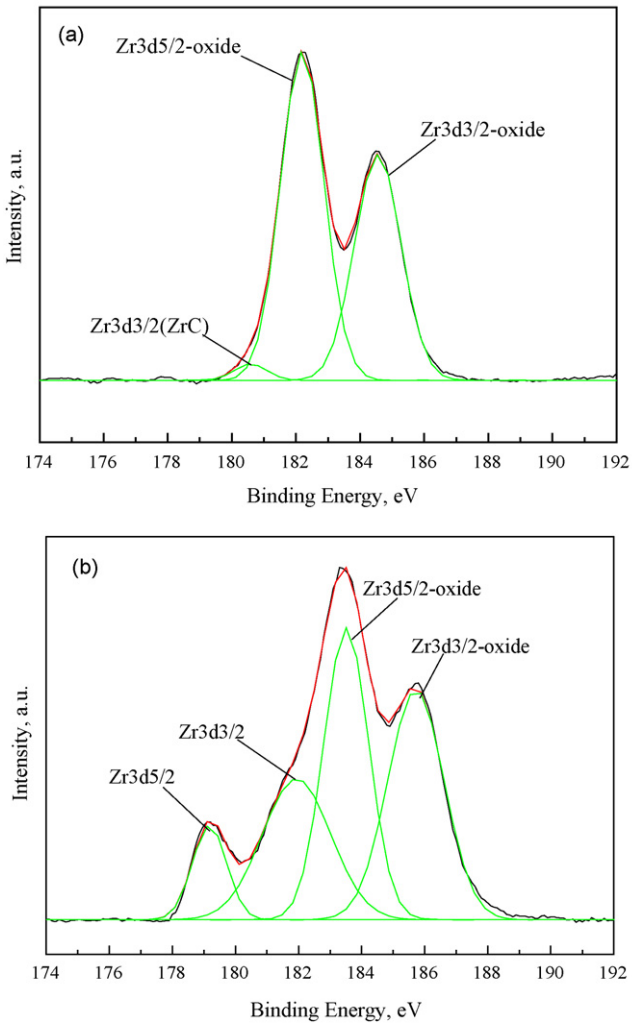


**Fig. 3.** High-resolution XPS spectra of Zr3d on the surface of Zr-coated TiNi alloy samples after argon sputtering for 0 min (a) and 5 min (b).

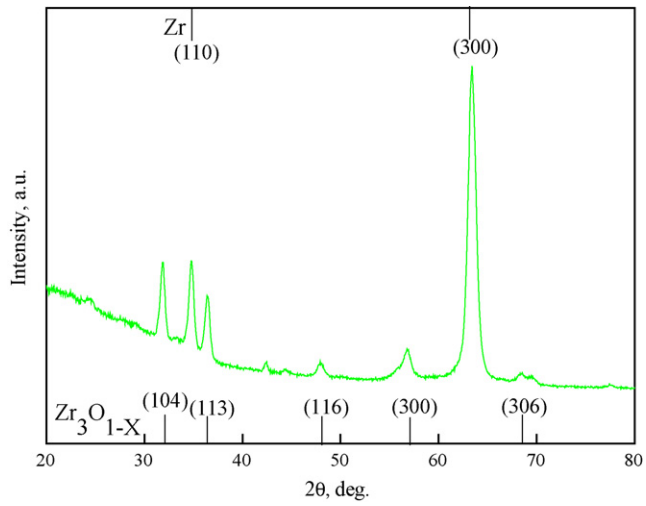


**Fig. 4.** The glancing-angle X-ray diffraction pattern of the Zr-coated TiNi alloy sample.

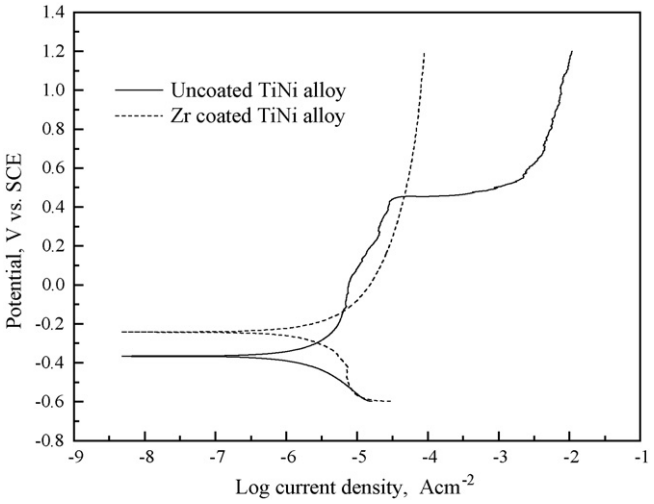


**Fig. 6.** Potentiodynamic polarization curves of TiNi alloy plate with/without zirconium film in the Hank's solution.

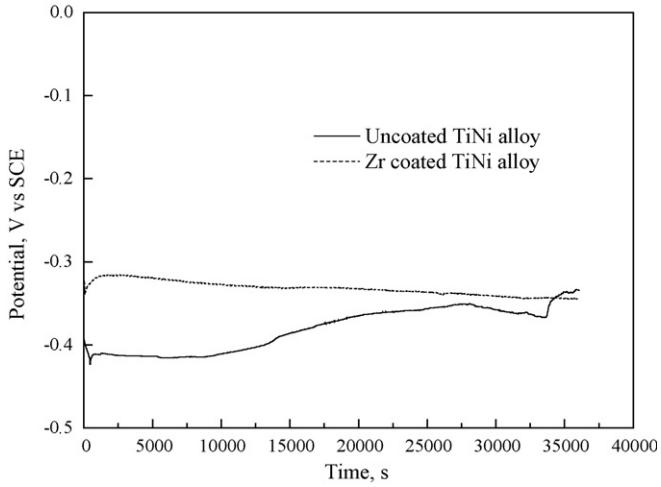


**Fig. 5.** OCP curves of TiNi alloy plate with/without zirconium film in the Hank's solution.

the implantation and deposition process, or during the exposure of sample into the air after taking out from the vacuum chamber.

The corrosion potential values as a function of immersion time for uncoated and coated TiNi alloy samples in the Hank's solution with a pH value of 7.4 at 37 °C have been investigated by the immersion experiment in the open circuit condition, as shown in Fig. 5. It can be seen that the open circuit potentials for zirconium film coated sample keeps a steadier and higher value than the uncoated substrate. This fact indicates that the zirconium film has the higher thermal dynamic stability than that of the substrate. Anodic polarization curve measurements are determined by increasing the potential from the open-circuit potential measured after the immersion of 30 min to 1.2 V, as shown in Fig. 6. The uncoated TiNi substrate shows a rapid increase of the current density resulting from the impact of $Cl^-$ together with the evolution of oxygen in the transpassive region. However, for the zirconium film coated sample, the current density in the anodic region is very low at the scanned potential range, and the current density keeps almost unchanged with the increase of the anodic potential, exhibiting the excellent corrosion resistance.

The Ni ion concentration released from TiNi substrate was measured by AAS method after polarization test. It is shown that the uncoated TiNi substrate releases much higher amount of Ni ion (about 6.377 mg/L) than that of the Zr-coated TiNi sample (about 0.423 mg/L).

## 4. Conclusions

Zirconium film has been successfully deposited on TiNi alloy by PIIID, with a relatively smooth surface morphology. Zirconium and non-stoichiometric $Zr_3O_{1-X}$ phase appear as the composition phases in the prepared film. The open circuit potential for zirconium film coated sample keeps a steadier and higher value than the uncoated substrate. The current density in the anodic region for zirconium film coated sample is very low at the scanned potential range, and the current density keeps almost unchanged with the increase of the anodic potential, exhibiting the excellent corrosion resistance. The zirconium film can also effectively reduce the Ni ion concentration released from the substrate in the Hank's solution.

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