Surface characteristics and corrosion resistance properties of TiNi shape memory alloy coated with Ta

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Abstract

Ti-50.6 at.% Ni alloy samples were coated with tantalum by the arc ion plating method with the aim to improve their radiopacity. Surface characteristics and corrosion resistance properties were investigated in the present study. The results of XRD show that the film as-deposited was composed of a metastable tetragonal \( \beta \)-phase tantalum which can transform into \( \alpha \)-phase tantalum after annealing at 700 °C, 800 °C, 900 °C for 1 h, respectively. TEM observations show that thin nano-structured Ta layers were obtained in the as-deposited samples. Mixture of microcrystallite (approx. 40 nm) and large-size crystal (approx. 150 nm) \( \alpha \)-phase tantalum was formed in the film after annealing at 700 °C. When annealed at 900 °C, the film is composed of dominantly uniform large-size \( \alpha \)-phase tantalum. The results of XPS survey and high resolution spectra show that a thin oxide film with Ta2O5 in the outmost layer and tantalum suboxides in the inner layer, are formed inside tantalum coating as a result of natural passivation of Ta in the atmosphere. The corrosion resistance was determined by electrochemical methods in 0.9% NaCl solution at 37 °C. Both the as-deposited and annealed samples exhibit excellent corrosion resistance property. Compared to the untreated coating samples, the annealed Ta coating samples exhibit higher open-circuit corrosion potential (\( E_{\text{corr}} \)), breakdown potential (\( E_{\text{br}} \)), and lower passive current density (\( I_p \)). The results indicate that the annealing treatment can improve the corrosion resistance property.

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1. Introduction

TiNi shape memory alloys have been found widespread applications in the medical field due to their unique shape memory effect, superelasticity as well as excellent biocompatibility [1–3]. With the miniature of the instruments for minimal access surgery, interventional radiology and flexible endoscopy, such as cardiovascular stent, it is desirable that the materials are more radiopaque [4].

There are a variety of methods to improve radiopacity, such as filling [5], coating [6], banding and addition of contrast agent [7]. Also coating is a simple and feasible method among all this techniques for TiNi alloy. Coatings with high radiopacity eliminate the need for electroplated, crimped, or swaged metal bands that can be abrasive, loosen, crack, or fall off.

For coating applications, a good bonding strength between coating and substrate is required in order to ensure the lifetime service in the implanting environment. The arc ion plating technique, with the feature of high packing density and good adhesion, can satisfy this requirement [8]. Tantalum metal possesses excellent corrosion resistance, chemical stability, high radiopacity and histocompatibility [9–11]. It has been used as a biomedical material in orthopedics since the 1940s and stents made of tantalum, such as Wiktor and Cordis stents possess excellent radiopacity compared to other material stents [12]. Tantalum are previously used to improve the radiopacity of TiNi alloy [5,13].

In this study, Ti-50.6 at.% Ni alloy samples was coated with tantalum by multi-arc ion plating method in order to improve their radiopacity. The aim of the present study is to investigate the surface characteristics and corrosion
resistance properties of TiNi shape memory alloy coated with Ta.

2. Experimental

2.1. Substrate preparation

The experimental alloy have a composition of Ti-50.6 at.% Ni, and all samples were cut into $10 \times 10 \times 2$ mm from the as-received cold rolled TiNi alloy sheet. For all samples one $10 \times 10$ mm surface was polished down to 1600 grit specification, mirror polished with $1 \mu m$ diamond paste and then cleaned ultrasonically in acetone.

2.2. Deposition and annealing treatment

The apparatus of the arc ion plating for surface modification is schematically shown in Fig. 1. The arc plating target was pure tantalum (99.99%). The purity of Ar gases used was 99.99%. The base pressure of the vacuum chamber before operation of the system was approximately $6.67 \times 10^{-5}$ Pa. Prior to the deposition, the surface of the substrates was further cleaned by Ar ion bombardment with a negative bias voltage of 1100 V for 10 min. Also the temperature of the substrates was gradually raised up to $300 ^\circ C$. Subsequently, deposition of Ta began at a desired substrate negative bias voltage 300 V, with an arc current of 75 A, deposition pressure at 1.5–2.0 Pa, and deposition time for 20 min. Some of the as-deposited samples were vacuum annealed ($1.3 \times 10^{-3}$ Pa) at 700 °C, 800 °C, 900 °C for 1 h, respectively, followed by quenching into water.

2.3. Characterization of the deposited films

The microstructure of the as-deposited and annealed samples were analyzed using a glancing angle X-ray diffractometer (Philips X'pent) with filtered CuKα radiation. Transmission electron microscopy (TEM) specimens of the Ta-coated TiNi alloys were cut by electrospark method and then thinned on the uncoated surface until the perforation occurred, and JEM-200CX TEM was used to investigate the influence of annealing on the microstructure of Ta coated TiNi alloys.

Surfaces of the air-exposed coating samples were characterized using a ESCA PHI500 spectrometer with a Mg Kα X-ray source. The ion sputter profiling was performed with a 1 keV Ar⁺ ion beam over a $5 \times 5$ mm area at an angle of 50° with respect to the surface of the coating.

2.4. Electrochemical tests

Electrochemical experiment was carried out using a computer-controlled potentiostat (EG&G Princeton Applied Research, model 273) in 0.9% NaCl solution at $37 \pm 0.5 ^\circ C$ (pH 7.4) in order to study the corrosion resistance property. The solution was deoxygenated with nitrogen gas while carrying out the electrochemical studies. Polarization experiments started after the specimen immersed in the experimental solution for half an hour under open-circuit conditions and performed at a rate of 20 mV/min.

3. Results and discussion

3.1. Structure of the TiNi alloy coated with Ta

Phase is the most important factor controlling coatings performance. As the Ta coating thickness ($3 \mu m$) is thinner than the depth ($10–30 \mu m$) penetrated by X-ray, we use glancing angle X-ray diffraction (GAXRD) pattern to study the structure of coating. Fig. 2 is X-ray diffraction patterns at different glancing angles and normal angle of the as-deposited Ta coating on TiNi alloys. It can be seen from Fig. 2a that the broad and low-intensity peak appears at a 2-theta value of approximately $42^\circ$, which indicates that the outermost layer of the specimen is amorphous.

Increasing the angle of incidence, several diffraction peaks appears, which indicates the existence of $\beta$-Ta phase as shown in Fig. 2b. When the angle of incidence is raised to $5^\circ$, the diffraction peaks corresponding to $\beta$-Ta phase become strong and sharp. Fig. 2d is the normal tetragonal XRD spectra of the specimens from which both B2 structure TiNi parent phase and $\beta$-Ta phase diffraction peaks can be identified.

It is well known that titanium has a higher affinity for oxygen than nickel, this will be of great benefit to surface oxide films formed spontaneously in an oxygenated environments. Consequently, oxide films are present on the metal surface of TiNi alloy [15]. In addition, tantalum has two kinds of depositing forms according to the deposition condition: a body-centered cubic $\alpha$-phase, and a metastable tetragonal $\beta$-phase. It is reported by Feinstein and Hutteman that the $\beta$-phase Ta always resulted on substrates, which contain oxygen or have a surface oxide. In our
study, we found that the film as-deposited was composed of a metastable tetragonal $\beta$-Ta, similar to the work by Feinstein and Hutteman conclusion.

As the film as-deposited was composed of a metastable tetragonal $\beta$-Ta which is hard, brittle, thermally unstable, and can transform into $\alpha$-phase tantalum through annealing [16]. In order to gain $\alpha$-Ta which possesses good chemical, thermal, and mechanical properties, the samples were annealed at 700 °C, 800 °C, 900 °C for 1 h, respectively.

The effect of annealing temperatures on the microstructure of as-deposited films is shown in Fig. 3. XRD results reveal that all the metastable tetragonal $\beta$-Ta transform into body-centered cubic $\alpha$-Ta with body-centered cubic structure after annealing.

3.2. Microstructure of the TiNi alloy coated with Ta

Fig. 4 shows the TEM bright field images and corresponding diffraction patterns of Ta coating under the as-deposited and annealed conditions, respectively. It can be seen that thin nano-structured $\beta$-Ta layers exist in the as-deposited samples, as shown in Fig. 4a. Through observation of the microstructure of the sample annealed at 700 °C, we found that small part of the film consists of a mixture of microcrystallite (40 nm) and large-size crystals (150 nm) of $\alpha$-phase tantalum indicating the microstructure is inhomogeneous. The coating annealed at 800 °C has relatively uniform grain. When annealed at 900 °C, the film is composed of dominantly uniform large-size $\alpha$-phase tantalum. The results of TEM of the samples after annealing can be verified by XRD patterns illustrated in Fig. 3.

3.3. XPS analysis of the surface of Ta coatings

3.3.1. Surface chemical composition of the Ta coatings

Fig. 5a is the XPS survey spectrum of the surface of the TiNi sample coated with tantalum without annealing after 3 min argon sputtering. Four major tantalum peaks observed in the spectra at 24.1 eV, 230.6 eV, 240.3 eV and 459.1 eV positions are corresponding to Ta4f, Ta4d3, Ta4d5 and Ta4p1/2, respectively. O signals are also detected at the
surface. This result indicates that a thin tantalum oxide film is formed on the outmost surface of the Ta coating as a result of natural passivation of Ta in atmosphere, as expected. The survey spectrum of Ta coating after 10 min sputtering is showed in Fig. 5b. It can be seen that only Ta peaks appear at different binding energies which correspond to Ta4f, Ta 5p, Ta4d5/2, Ta4d3/2, Ta4p1/2, etc. These results show that pure tantalum layer is reached beneath the tantalum oxide layer.

Fig. 4. TEM images and corresponding SAED patterns of TiNi alloy with Ta coating (a) as-deposited specimen; (b) annealed at 700 °C for 1 h; (c) 800 °C; (d) 900 °C.

Fig. 5. Typical XPS survey spectra of TiNi alloys coated with Ta after argon sputtering for (a) 3 min; (b) 5 min.
3.3.2. Surface chemical state of Ta coating

Fig. 6 shows the Ta 4f and O 1s XPS high resolution spectra of tantalum coating for different sputtering time, indicating the in-depth chemical structure of the coatings. Fig. 6a illustrates the Ta 4f and O 1s photoelectron spectra at the surface of a coated sample. For the Ta 4f spectra, the two peaks are located at 28.2 eV and 26.3 eV, respectively, with energy separation of 1.9 eV and an area ratio of 1.3–1.4 for Ta 4f\(_{7/2}\) compared to Ta 4f\(_{5/2}\). The Ta 4f\(_{7/2}\) line position at 26.3 eV is a typical of Ta chemical state in Ta\(_2\)O\(_5\) [14]. The shape of the doublet shows no evidence for the presence of non-stoichiometric oxide. This is also confirmed by the spectra of O 1s with the line position at 530.7 eV. These results indicate that the film at the outmost surface of the coating is fully oxidized stoichiometric Ta\(_2\)O\(_5\). As the sputtering process proceeds, the Ta 4f doublet changes its typical form to a broad peak and the position of the main peaks corresponds to the energies lower than that of Ta–O doublet arose from Ta\(_2\)O\(_3\) and higher than that of the metallic Ta 4f doublet (Fig. 6b), indicating that tantalum suboxides exist in the coating surface. As based on the literature [15], tantalum can oxidized according to the following reaction:

\[
\begin{align*}
4\text{Ta} + 5\text{O}_2 &\rightarrow 2\text{Ta}_2\text{O}_5 \\
\text{Ta} + \text{O}_2 &\rightarrow \text{TaO}_2 \\
2\text{Ta} + \text{O}_2 &\rightarrow \text{TaO} \\
2\text{Ta} + x\text{O}_2 &\rightarrow 2\text{TaO}_x \quad (x < 1)
\end{align*}
\]

It can be conjectured that a passive tantalum oxide layer composed of Ta\(_2\)O\(_5\), TaO\(_2\), TaO and TaO\(_x\) (\(x < 1\)) be formed on the sub-surface of the tantalum coating when the samples are exposed to air.

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Fig. 6. Ta 4f and O 1s XPS spectra of tantalum coating sputtered with argon for (a) 1 min; (b) 3 min; (c) 5 min; (d) 10 min.
Samples after argon sputtered for 5 min (Fig. 6c) and 10 min (Fig. 6d) show a purely metallic feature in the Ta 4f photoelectron spectrum. The 4f\(\frac{7}{2}\) peak is located at a binding energy of 21.9 eV, with the 4f\(\frac{5}{2}\) peak located at 23.76 eV, consistent with metallic Ta spectra [14], which indicates that the pure tantalum coating has been reached. The change of the peaks with sputtering time shows as follows: with increasing sputtering time, composition of the coating evolves from Ta\(\text{2O}_5\) to the suboxide of tantalum, then to the metallic tantalum, which demonstrate that the formation of relative thin oxidations layers presented on the Ta coatings.

3.4. Corrosion resistance property of TiNi alloy coated with Ta

Fig. 7 plots the typical anodic polarization curves for TiNi alloy coated with tantalum under the unannealed and annealed condition in 0.9% NaCl solution. As we know that the breakdown potential \(E_{br}\) represents the potential above which a pre-existing passive film breaks down and pits originate on the free surface of the specimen. \(E_{br}\) for the as-deposited sample is approximately 810 mV, approximately 300 mV lower than that of the annealed sample. The values of \(E_{br}\) are close for the samples annealed of different temperature. The passive current density \(I_p\) for the unannealed is approximately \(7.5 \times 10^{-7}\) A/cm\(^2\), higher than the corresponding values for the annealing specimen. Furthermore, the passive range of the annealing samples is wider than that of the unannealed sample. For the annealed sample, it is worth noting that the numerous spikes of anodic current are observed in the region of passivity indicating initiation and repassivation of metastable pits, while the anodic polarization curves of the annealing samples are smooth implying stable passive film are formed in the passive range.

As discussed above, we can come to the conclusion that annealing treatment can improve the corrosion resistance of TiNi alloys coated with Ta in the 0.9% NaCl solution. The reason for the improvement of corrosion resistance of annealed samples may be closely related to the change of the surface characteristics. As for the as-deposited sample, the coating is composed of metastable β-Ta which has lower chemical stability compared to α-Ta obtained after annealing. Furthermore, both the as-deposited and annealing samples exhibit excellent corrosion resistance property. As tantalum metal possesses excellent corrosion resistance, chemical stability, although the metal is thermodynamically very reactive [16], it presents an exceptional resistance to corrosion, arising from the tantalum oxide which naturally covers its surface, which forms spontaneously in air conditions, exhibits excellent anti-corrosion properties than the other reactive metal protective oxide films [11]. The formation of tantalum oxide can be verified by the above XPS analysis.

4. Conclusions

1. The film as-deposited was composed of a metastable tetragonal β-phase and which can transforms into α-phase tantalum after annealing at 700, 800 and 900 °C for 1 h individually.
2. Thin nano-structured Ta layers were obtained in the as-deposited samples. Mixture of microcrystallite (40 nm) and large-size crystal (150 nm) α-phase tantalum were formed in the film after annealed at 700 °C. When annealed at 900 °C, the film is composed of dominantly uniform large-size α-phase tantalum.
3. The results of XPS survey and high-resolution spectra show that a thin oxide film with Ta\(\text{2O}_5\) in the outmost layer and tantalum suboxides in the inner layer is formed inside tantalum coating on TiNi substrate.
4. Both the as-deposited and annealing samples exhibit excellent corrosion resistance property. Compared to the untreated coating samples, the annealed Ta coating specimens exhibit higher breakdown potential \(E_{br}\), lower passive current density \(I_p\) and wider passive range in 0.9% NaCl solution at 37 °C indicating that the annealing treatment can improve the corrosion resistance property of TiNi alloys coated with Ta.

References


