Anti-corrosion characteristics of nitride-coated AISI 316L stainless steel coronary stents

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Received 17 March 2006; accepted in revised form 22 May 2006
Available online 5 July 2006

Abstract

The corrosion resistance of TiN and TaN coatings deposited on AISI 316L stainless steel thread-coiled coronary stents by pulsed bias arc ion plating is evaluated by electrochemical methods in deaerated Tyrode’s simulated body fluids (37±1 °C). The free corrosion potential of the TaN-coated stents is found to be nobler than that of the TiN-coated and uncoated stents throughout most of the immersion time. The potentiodynamic polarization test results indicate that the TaN coatings offer better passivation stability and anti-breakdown performance. The longer-term 6-month immersion tests disclose slight localized corrosion on the surface of both coatings, but no film delamination or large area pitting can be observed indicating reasonably good corrosion resistance after the long period.
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PACS: 87.68.+z Biomaterials and biological interfaces; 81.15.Jj Ion plating; 77.84.Bw Nitrides; 81.65.Kn Corrosion protection

Keywords: Nitrides; Stent coating; Corrosion tests; Simulated body fluids

1. Introduction

Since the clinical success of implantation of stents into coronary arteries [1], the method has been shown to be effective in the treatment of restenosis. However, in-stent stenosis has become a new clinical problem for metallic stents because of the corrosive environment in the human body. Corrosion of implanted medical devices may result in the potential release of corrosion products with harmful biological consequences. The use of a protective coating is a viable approach to mitigate excessive corrosion and it also combines the desirable characteristics of different materials. There has been extensive research in this area and the coatings can generally be classified as either passive or active [2]. Passive stent coatings that are typically made of carbon [3], silicon carbide [4], or tantalum [5] can reduce surface corrosion and appear to be well tolerated in clinical trials. This is especially true for Ta coatings from the perspective of corrosion resistance, radio opaqueness, and biocompatibility [5].

To be useful in practice, adhesion between the coating and substrate must also be strong in order to ensure a long working life time in the human body. The arc ion plating technique that can provide good film adhesion can satisfy this requirement [6]. Our previous experiments have disclosed that when a pulsed bias is used in this technique, the deleterious macro-particles are charged by electrons due to the oscillation of the sheath and they are repelled by the negative electric field from the substrate. Consequently, fewer macro-particles reach the substrate and the film quality is improved [7]. TiN and TaN are known to have good blood compatibility [8,9]. In this work, the pulsed bias arc ion plating method is used to deposit nitride coatings on AISI 316L stainless steel stents to improve the surface corrosion resistance.

2. Experimental details

AISI 316L stainless steel stents with internal expanded diameters of 2.5 mm were used in our experiments. The chemical composition is shown as follows: Cr: 18%, Ni: 10%, Mn: 2.0%, Mo: 2.5%, Si: ≤1%, P: 0.045%, S: 0.03%, Fe: Balance. The stents were coiled with AISI 316L stainless steel
threads 0.1 mm in diameter. The TiN and TaN coatings were deposited by pulsed biased arc ion plating (PBAIP) [10]. The distance between the samples and cathodic arc targets was about 400 mm. The samples were mounted on a rotating substrate holder. Prior to deposition, the substrate surface was cleaned by argon and metal ion bombardment for 5 min at a working pressure of about 0.4 Pa and a negative substrate bias of \(-900\) V. In TiN deposition, argon and nitrogen were introduced into the vacuum chamber. The nitrogen partial pressure was 0.34 Pa and that of argon was 0.5 Pa. The substrate was pulsed biased to \(-600\) V using a duty cycle of 30% and frequency of 40 kHz. In TaN deposition, only nitrogen gas was bled into the chamber to a working pressure of 0.6 Pa. The substrate pulsed bias was \(-600\) V, duty cycle was 40%, pulsing frequency was 40 kHz, and DC bias was \(-150\) V.

Phase identification of the coatings was conducted by X-ray diffraction (XRD) using a SHIMADZU XRD-6000 diffractometer with Cu K\(_\alpha\) irradiation (\(\lambda = 0.154060\) nm) and the morphology of the coatings was characterized using scanning electron microscopy (SEM) with a JEOL-JSM-5600LV. The corrosion and electrochemical behaviors of the coated and uncoated stents were studied in 37±1 °C Tyrode’s simulated body fluids (SBF) with the following composition (mmol L\(^{-1}\)): NaCl: 100.0, KCl: 10.0, KH\(_2\)PO\(_4\): 1.2, MgSO\(_4\): 5.0, glucose: 20.0, taurine: 10.0 and MOPS: 10.0, and the solution was maintained at the normal physiological pH at 7.2. The specimens were affixed onto a holder as described in reference [11] and the procedures followed the ASTM G5 corrosion test protocol in a 0.5 l well-capped electrochemical cell. The solution was purged with nitrogen for half an hour prior to immersion. The apparatus consisted of a conventional three-electrode cell comprising a working electrode, a saturated calomel electrode (SCE), a platinum sheet as the counter electrode, as well as an M273 EG&G potentiostat. The changes in the free corrosion potential (\(E_{corr}\)) were monitored as a function of time under open circuit conditions for approximately 30 h. After 0.5 h immersion in the test solution, a fairly stable potential could be achieved, and then the potentiodynamic polarization measurement was carried out at a scanning rate of \(1\) mV s\(^{-1}\). The initial potential was 100 mV below \(E_{corr}\). In order to determine the long-term anticorrosion characteristics, the TiN- and TaN-coated stents were immersed in the Tyrode’s simulated body fluids (37±1 °C) for 6 months, after which time SEM was employed to detect any surface pitting.

3. Results

3.1. Coating characteristics

The SEM micrographs of both the TiN- and TaN-coated stents depicted in Fig. 1 do not show any cracks. However, there are some macro-particles on the surface of the TiN coating while the TaN coating has a smoother surface. It should be noted that both coatings cover the entire surface of the stents more completely than TiNO\(_x\) previously reported [12]. The phases of both coatings were evaluated by X-ray diffraction and the results are displayed in Fig. 2. TiN and Ti phases can be detected in the TiN coating whereas cubic TaN and hexahedral TaN\(_{0.8}\) phases are observed in the TaN coating.

3.2. Corrosion properties

The evolution with time of the free corrosion potentials (\(E_{corr}\)) obtained from the coated and uncoated stents is presented in Fig. 3. Initially, the potentials of the specimens are different.

![Fig. 1. SEM micrographs showing the morphology of the surface of the coated stents: (a) TaN coated; (b) TiN coated.](image1)

![Fig. 2. XRD patterns obtained from the two types of nitride coatings.](image2)
Throughout the entire immersion period, the $E_{\text{corr}}$ values of the coated specimens are much more positive than those of the uncoated stent. After immersion of approximately 12.5 h, the $E_{\text{corr}}$ value of the TiN-coated specimen decreases abruptly, and subsequently, the potential fluctuates substantially up to 25 h, indicating that the test solution has reached the substrate and has caused pitting corrosion as well as rapid repair. The stability of $E_{\text{corr}}$ after 25 h of immersion is evidence of post-passivation. In contrast, the $E_{\text{corr}}$ values measured from the TaN-coated specimen do not vary as much. After an initial decrease, the $E_{\text{corr}}$ value increases slightly with immersion time as a sign of strong surface passivation and less porosity.

Fig. 4 shows the typical potentiodynamic polarization curves of the coated and uncoated specimens. It can be observed that the coated specimens are unstable under a lower corrosion current density in the beginning. The current densities within the passive range for a potential of 0.4 V are $1.55 \times 10^{-7}$ A cm$^{-2}$ for the TiN-coated specimen and $1.43 \times 10^{-7}$ A cm$^{-2}$ for the TaN-coated sample. These values are about three orders of magnitude smaller than those of the uncoated stents. With further anodic polarization, the corrosion current increases suddenly at potentials above 0.49 V for the TiN-coated specimen, indicating the onset of pitting corrosion. In contrast, the breakdown potential observed from the TaN-coated specimen is 1.31 V, which is approximately three times greater than that of the uncoated stent. The electrochemical values derived from the polarization curves are also listed in Table 1 in which the differences indicate changes in the corrosion resistance of the different samples.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>$i_{\text{corr}}$ (A cm$^{-2}$)</th>
<th>$i_{0.4 \text{ V}}$ (A cm$^{-2}$)</th>
<th>$E_{\text{brk}}$ (V)</th>
<th>$E_{\text{pr}}$ (V)</th>
<th>$\Delta E$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare stent</td>
<td>$1.47 \times 10^{-7}$</td>
<td>$1.26 \times 10^{-4}$</td>
<td>0.47</td>
<td>0.11</td>
<td>0.36</td>
</tr>
<tr>
<td>TiN-coated stent</td>
<td>$3.78 \times 10^{-9}$</td>
<td>$1.55 \times 10^{-7}$</td>
<td>0.49</td>
<td>$-0.21$</td>
<td>0.70</td>
</tr>
<tr>
<td>TaN-coated stent</td>
<td>$6.21 \times 10^{-9}$</td>
<td>$1.43 \times 10^{-7}$</td>
<td>1.31</td>
<td>0.89</td>
<td>0.42</td>
</tr>
</tbody>
</table>

$\Delta E$: $E_{\text{brk}} - E_{\text{pr}}$; $i_{\text{corr}}$: corrosion current density; $i_{0.4 \text{ V}}$: passive current density at a potential of 0.4 V; $E_{\text{brk}}$: breakdown potential; $E_{\text{pr}}$: protective potential.

Fig. 5 exhibits the SEM micrographs of the TiN- and TaN-coated stents after 6-month immersion in the Tyrode’s SBF. The specimens show a slightly corroded surface. Although substantial micro-pitting occurs, coating delamination and large area pitting are not observed indicating good long-term corrosion resistance offered by the coatings, which is in agreement with the $E_{\text{corr}}$ values.

Fig. 3. Evolution of the free corrosion potential for the uncoated and coated stents in deaerated Tyrode’s simulated body fluids.

Fig. 4. Typical polarization curves acquired from the uncoated and coated stents in deaerated Tyrode’s simulated body fluids.

Fig. 5. SEM micrographs showing the surface morphologies of the coated stents after a 6-month SBF immersion: (a) TaN; (b) TiN.
4. Discussion

The objective of this study is to investigate the improvement in the corrosion resistance offered by the nitride coatings on coronary stents using the SBF immersion test that mimics the corrosive environment in the human being. First of all, our results demonstrate that the nitride films can be effectively plated onto the stent surface using pulsed biased arc ion plating (PBAIP). Secondly, the corrosion test data show that the TaN coatings can offer better corrosion resistance than the TiN coatings.

The evolution of the $E_{\text{corr}}$ values reflects the surface passivation and activation of the samples in the test solution whereas the magnitude illustrates the thermodynamic stability [6]. The $E_{\text{corr}}$ values determined from the coated specimens are very different from those of the uncoated stainless steel stent. For the bare stent, the initial decrease indicates strong surface activation and then the $E_{\text{corr}}$ value becomes stable with increasing immersion time. This may be caused by dissolution and growth of the oxide film at equal rates [13]. In contrast, the $E_{\text{corr}}$ values of the coated specimens decrease with immersion time initially and then increase after about 1 h of immersion. It is believed that the oxidized layer on the nitride coating [6] formed by exposure to air or during deposition plays an important role in the electrochemical stability of the coating. Dissolution and self-repair may cause the observed changes in the free corrosion potential. Meanwhile, these variations can also result from metastable pitting reactions on the stainless steel surface. The $E_{\text{corr}}$ values observed from the TaN-coated sample are more stable at $−0.08\,\text{V}$ throughout most of the 30 h immersion with the exception of the initial variation. On the other hand, the $E_{\text{corr}}$ values determined from the TiN-coated specimens vary more significantly during immersion. The emergence of pitting corrosion is indicated by the sharp decrease in the potential before recovery to a more stable value caused by the penetration of water molecules and ions through the defects in the coatings [14]. The results show that the TaN coating is nobler and more effective in protecting the stent from corrosion.

The potentiodynamic polarization test can detect the relative susceptibility to localized corrosion on the samples. The corrosion rate is normally proportional to the corrosion current density ($i_{\text{corr}}$) measured in the polarization tests [8]. In our analysis, the corrosion current density is estimated by linear fitting and Tafel extrapolation to the cathodic part of the polarization curve. The $i_{\text{corr}}$ values determined from the nitride-coated stents are approximately two orders of magnitude lower than that of the bare stent. Spikes are observed in the anodic current in the region of passivation at potential close to $0.12\,\text{V}$, indicating initiation and repassivation of the metastable pits. When the potential exceeds $0.12\,\text{V}$, the bare stent shows a characteristic inflexion point that resembles a secondary passivation region, where pitting corrosion is possibly inhibited by chemical anions in the Tyrode’s SBF. The TiN-coated stent shows a passive region but with a different shape than that of the bare stent extending to a similar potential range. That is to say, when the potential is under $0.49\,\text{V}$, the Ti–O films formed on the TiN surface or in the defects cannot impede the penetration of the test solution [15]. In comparison, the breakdown potential of the TaN-coated stents is significantly higher, indicating more effective inhibition of localized corrosion. However, when the potential is above $1.31\,\text{V}$, a sharp current increase is observed indicating development of active pits. The back scan part of the polarization curves reveals that the coated stents suffer pitting attack due to defects in the coatings. $\Delta E (E_{\text{brk}}\,−\,E_{\text{pr}})$ represents the corrosion resistance of the materials and the smaller the $\Delta E$ value, the better is the anti-corrosion property. The polarization test results consistently record better corrosion resistance for the TaN-coated specimen followed by the TiN-coated specimen ($0.42\,\text{V}$ vs. $0.70\,\text{V}$) as shown in Table 1. Compared to pure Ti, due to the higher melting point of pure Ta, the formation of Ta macro-particles is more difficult and the deposition rate of the TaN coating is lower. Consequently, the quality of the TaN coating is better than that of the TiN coating. Owing to the lesser amount of imperfections, diffusion of the test solution to the interface between the coating and the substrate diminishes. As a result, the TaN coating has better electrochemical stability and corrosion resistance in the simulated body fluid environment.

In our long-term immersion test, the surface morphology of the TiN- and TaN-coated stents displayed in Fig. 5 indicate slight local corrosion on the coatings after 6 months but there is no major pitting or film delamination. A small amount of corroded debris can be observed near the pits (shown by an arrow). The EDS (energy-dispersive X-ray) results show that the white micro-particles are mainly composed of sodium compounds which precipitate from the solution. Our long-term test indicates reasonable corrosion resistance, although further improvement may still be necessary before the coated stents can be used clinically.

5. Conclusion

TiN and TaN coatings are deposited on AISI 316L stainless steel coronary stents by means of pulsed biased arc ion plating. The technique can effectively coat the entire surfaces of the stents. In the immersion test conducted in deaerated Tyrode’s simulated body fluids at human body temperature, the TiN and TaN coatings are observed to reduce the overall dissolution rate and enhance the corrosion resistance of the coated stents. Comparing the two coatings, the more compact TaN coating offers better electrochemical stability and corrosion resistance. Long-term immersion tests indicate a slight degree of local corrosion but large scale pitting and layer delamination are not observed.

Acknowledgments

The project was jointly supported by the National Natural Science fund of China under the contract No. 50081001 and NAMCC 863 (No. 2002AA326010) as well as the Hong Kong Research Grants Council (RGC) and the National Science Foundation of China (NSFC) Joint Research Scheme No. N_CityU 101/03.
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