Corrosion resistance of praseodymium-ion-implanted TiN coatings in blood and cytocompatibility with vascular endothelial cells

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\textbf{A B S T R A C T}

Praseodymium (Pr) is implanted into TiN coatings to improve the corrosion resistance and cytocompatibility in blood plasma. The corrosion resistance of the Pr-doped TiN coatings in blood plasma is improved based on electrochemical measurements. Pr ion implantation dramatically decreases the hemolysis rate of the TiN coatings suggesting their suitability in cardiovascular applications. The viability of vascular endothelial cells seeded on the untreated TiN coatings and two Pr implanted TiN coatings implanted for different time is assessed. The vascular endothelial cell attach and grow to confluence on the Pr implanted TiN coatings and a network composed of vascular tissues is observed from the 0.5 h Pr implanted coatings. The results suggest that Pr ion implantation can effectively improve the corrosion resistance as well as cytocompatibility of TiN coatings in blood plasma.

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1. Introduction

The essential properties of biomaterials are good corrosion resistance, suitable mechanical properties, and good cytocompatibility [1,2] and the surface properties of biomaterials play an important role in the interactions with tissues and cells. The physical and chemical properties as well as surface morphology are important [3] and biomaterials are often surface modified to meet biomedical and clinical needs [4,5]. Although titanium and titanium alloys are used in biomedical implants, surface modification is frequently needed to improve the corrosion resistance and blood compatibility in the physiological environment [6–12]. In fact, surface modification is an effective way to enhance the surface cytocompatibility without affecting the favorable bulk properties such as materials strength and sturdiness. Transition-metal-based binary or ternary nitride coatings have been fabricated on implants by PVD (physical vapor deposition), CVD (chemical vapor deposition), and ion implantation to improve the cytocompatibility, mechanical properties, and corrosion resistance [13–17].

Titanium nitride (TiN) coatings which can reduce wear damage and improve corrosion resistance of titanium alloys [18–22] are good biomedical materials [23–26], especially as coatings on blood-contacting biomedical implants [27]. An anticoagulant ceramic heart valve comprising a single crystal alumina disk and TiN valve ring has been developed and the heart valve surface does not exhibit platelet aggregation or fibrin deposition [28]. TiN-coated surfaces have been observed to reduce the presence of bacteria significantly [29]. Compared to bare nickel–titanium alloys, TiN coatings improve the physiological activity associated with gene expression of cardiovascular endothelial cells promoting anti-inflammatory and cell adhesion gene expression [30–33]. Generally, TiN coatings have good mechanical properties and chemical inertness, but there are often some inherent small pores and defects such as pinholes in these coatings thereby degrading the corrosion resistance [34]. Ion implantation has been applied to reduce corrosion and wear of many types of biomaterials. In addition to modifying the surface structure and composition, ion implantation can introduce a suitable amount of ions into the near surface of the materials without forming a discrete interface like in the case of a deposited coating, and so the risk of delamination can be minimized. Ion implantation of rare earth elements has been shown to improve the corrosion resistance of materials in aqueous media [35]. For instance, ion implantation of praseodymium (Pr) has been shown to improve the corrosion resistance in aggressive media such as NaCl solutions [36].

Recently there has been a growing interest in science and application of rare earth materials. Pr has been shown to provide levels of corrosion protection to the underlying metal substrate and

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their protective properties have been reported. The corrosion inhibition mechanism of Pr is often attributed to the deposition of an oxide/hydroxide thin film at cathodic domains, facilitated by the alkaline pH which arises from the reduction of water or oxygen [37]. However, under physiological blood condition, may be the thin oxide/hydroxide film is not sufficient for corrosion resistance. For TiN coating, the structural defects such as pores are responsible for the corrosion initiation. Implantation is used to change the surface microstructure of materials without changing the bulk properties in various fields such as biomaterials. Corrosion resistance should be advanced in the TiN coating with the help of Pr ion implantation.

In previous studies of the biological role of rare earth elements such as praseodymium, scandium, and lanthanum, soluble salts (citrate or chloride) were introduced into animals by injection or ingestion [38,39]. Although the direct biological role of praseodymium compounds is still controversial, ion implantation of Pr into artificial biomedical implants is potentially useful. Past investigations indicate that water soluble compounds of rare earth elements are mildly toxic, but insoluble rare earth compounds are nontoxic [40]. Generally, some physiological disorder has been observed. When the elements enter the cell nuclei, a stable complex is formed with the biological macromolecules affecting gene expression and chromosome replication. However, in the case of praseodymium-doped ceramic coatings prepared by ion implantation, whether or not soluble compounds are produced in the human environment requires more research. Although rare earth elements are typically not considered essential to the cellular life cycle, beneficial effects have been observed from crops. Hence, rare-earth-element-enriched fertilizers have been used in China since the 1980s and so far, there have been no reported incidents about toxic effects in humans as a result of uptake through the food chain [41]. In addition, Pr possesses good antibacterial characteristics, does not cause inflammation of human umbilical cord perivascular cells (HUCPV), and is considered nontoxic at the proper concentrations [42,43]. The objective of this study is to study the effects of Pr ion implantation on the corrosion resistance and cytocompatibility of TiN coatings in blood plasma. Real blood is chosen in this study instead of commonly used artificial media such as SBF (simulated body fluid) and PBS (phosphate buffered saline) to better simulate the physiological conditions for cardiovascular devices.

2. Experimental details

2.1. Sample preparation

The TiN coatings were deposited on medical titanium alloy (Ti6Al4V) by DC magnetron sputtering. The substrate was cleaned ultrasonically in acetone and methanol and dried by nitrogen. The sputtering targets were composed of 99.99% pure Ti (5.08 cm in diameter and 5 mm thick) oriented at 45° from each other. The substrate was rotated continuously to face the two Ti targets from a distance of 70 mm. The sputtering parameters used in the deposition of TiN coatings are listed in Table 1. The TiN coatings were ion implanted with praseodymium on the Plasma Technology Ltd. HEMIII-80 cathodic arc plasma ion implanter in City University of Hong Kong. The base pressure in the vacuum chamber was 10⁻⁴ Pa and the important ion implantation parameters are listed in Table 2.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Sputtering parameters for the PVD TiN coatings.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>Base pressure (Pa)</td>
</tr>
<tr>
<td>Ti</td>
<td>6.8 × 10⁻⁴</td>
</tr>
</tbody>
</table>

The sample holder was water cooled during ion implantation to keep the temperature below 30 °C.

2.2. Characterization

The structure of the TiN coatings was characterized by X-ray diffraction (XRD, XRD-7000, SHIMADZU LIMITED) using Cu Kα radiation and the elemental depth profiles and chemical states were determined by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA, KRATOS ANALYTICAL Ltd.). Atomic force microscopy (AFM, SPI3800-SPA-400, Seiko Instruments Inc.) was conducted to examine the surface morphology of the samples before and after Pr ion implantation.

2.3. Corrosion behavior

The corrosion behavior of the control and implanted samples was evaluated by potentiodynamic polarization tests conducted on a Zahner Zennium electro-chemical workstation at 37 °C. A three-electrode cell with the sample as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and platinum electrode as the counter electrode was adopted. The medium was goat blood plasma (RUITE BIOTECH Ltd., Guang Zhou, China) after separating the blood plasma from whole blood by gradient centrifugation. The sample with a surface area of 75 mm² was exposed to the blood plasma. In the potentiodynamic polarization test, the scanning rate was 1 mV s⁻¹. The corrosion potential (Ecorr) was determined by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA, KRATOS ANALYTICAL Ltd.). Atomic force microscopy (AFM, SPI3800-SPA-400, Seiko Instruments Inc.) was conducted to examine the surface morphology of the samples before and after Pr ion implantation.

2.4. Hemolysis ratios

In this hemolysis ratio determination, fresh blood samples were used. Four ml of blood was diluted with 5 ml of 0.9% (w/v) NaCl and 10 ml of 0.9% (w/v) NaCl (negative controls, n = 3) and 10 ml of doubly distilled water (positive control, n = 3) were prepared for antitheses. All the samples were kept at 37 °C for 30 min and incubated in 0.2 ml of whole blood at the same temperature. After 60 min, the samples were centrifuged for 5 min and the supernatant was analyzed at 540 nm to determine the absorbance of cells undergoing hemolysis on a microplate reader (Powerwave XS MQX200R). The hemolysis ratios were calculated by the following relationship: R = (A – C1)/(C2 – C1) × 100% where R was the hemolysis ratio (%), A was the absorbance (%), C1 was the absorbance of the negative controls (%), and C2 was the absorbance of the positive control (%)[44].

2.5. Vascular endothelial cell culture

The endothelial cell line (EAhY926) was provided by Shanghai cell bank (catalog number GNHu39) of The Chinese Academy of
Sciences. They served differentiated endothelial cell functions, namely angiogenesis, homeostasis, thrombosis, blood pressure, and inflammation. Furthermore, they could be cultured to high passages without appreciable changes in the growth rate and phenotype, thus avoiding the diversity of primary isolated endothelial cells from different individuals, limitation of replication potential, and senescent tendency in cultures. The cells were cultured in high-glucose DMEM supplemented with 10% fetal bovine serum (FBS) and 1% (v/v) penicillin/streptomycin on culture dishes and incubated in a humidified atmosphere of 5% CO₂ at 37 °C [45].

2.6. Cell proliferation

After sterilization with 75% alcohol, the samples were placed on a 12-well culture plate and 1 ml of the DMEM medium was introduced. The concentration of endothelial cells was 5 × 10⁴ cells/ml. Endothelial cell proliferation was investigated by the CCK-8 kit (Biotime, China) after incubation for 1 and 6 days. After removing the medium, the samples were washed twice with PBS. The fresh medium containing the CCK-8 reagent was added to each sample and incubated at 37 °C for 3 h under standard culturing conditions. Afterwards, 100 μl of the blue solution were transferred to a 96-well plate. The absorbance was measured at 450 nm on a microplate reader and all the proliferation experiments were performed in triplicates [46].

2.7. Cell morphology and spreading

5 × 10⁴ Endothelial cells were seeded on the surface of the samples and cultured for 1 and 6 days in an incubator to study cell spreading. The CFDA SE kit and FITC kit (Beyotime China) was used for endothelial cells staining and the staining method was based on the manufacturer’s instructions. After staining was completed, each sample was put in 1 ml of fresh medium and cultured for 24 h to ensure that all cells were stained. A fluorescence microscope was used to examine the samples afterwards.

3. Results and discussion

3.1. Coatings characteristics

Fig. 1 presents the XRD results of the TiN coatings with Pr implanted at different duration. The primary phases of the Pr implanted TiN coatings were approximately identical to those of the un-implanted TiN coating and the (1 1 1) plane was the preferred orientation. However, after Pr implanted, the intensity of (2 2 0) peak increased slightly, and (2 0 0) peak decreased. For TiN coatings, (2 2 0) peak with a higher surface energy absorbs more plasma protein [47]. With increasing the implantation duration, the relative diffraction intensities ratio of I(1 1 1)/I(2 0 0) increased. It was suggested a change of the partial microstructural after ion implantation, although it could not change the preferred orientation.

After Pr ions were implanted into the TiN coating, some PrN peaks appear in the XRD spectrum. Some literatures have shown that the TiN and PrN have the same cubic structure [48, 49]. From the XRD results, chemical state of Pr is dominated present in the nitride state. Some studies report, in the TiN coatings, the new exogenous nitride phases were formed by ion implantation treatment [50, 51]. There may be complex compounds such as Ti–Pr–N in the Pr ion-implanted TiN coatings although more work is needed to elucidate the phenomenon clearly. In addition, after the ion implantation, [2 0 0] peak decreased, may be due to the effects of ion bombardment.

To investigate the surface properties of the TiN coatings implanted with praseodymium for different time and determine the amount of Pr in the coatings, XPS is conducted on two samples, one implanted for 0.5 h and the other for 1 h. The XPS depth profiles and high-resolution Ti 2p and Pr 3d spectra obtained from the praseodymium-implanted TiN coatings are depicted in Fig. 2. The sputtering rate during the XPS analysis was 4 nm/min. The praseodymium concentration reaches about 50 at% in the 1 h sample and about 25 at% in the 0.5 h sample. Fig. 2b and e shows the Pr 3d3/2 and Pr 3d5/2 peaks in the two samples allowing unambiguous identification even without exact knowledge of the peak positions. The intensity of the peaks increases with implantation time and the chemical state changes as well. Fig. 2b reveals characteristic shoulders on the low-energy side of both Pr 3d peaks and Pr may be present in the Pr³⁺ in accordance with the Pr 3d⁵/₂ binding energy range [52]. Due to this peak position different with Pr oxide binding energy range, indicate some other Pr compound formed not only oxide. In spite of there were a small amount of Pr oxide on the surface of the coatings as a result of air oxidation, but few small, so not the main reason for the performance impact. Pr in PrN compound is in the Pr³⁺ state. This inference is reliable and in agreement with the XRD result. The details not yet clear, more work need to do in the future.

Fig. 2e shows that the peak position of Pr 3d changes with ion implantation duration. The peak shift may arise from the different praseodymium chemical states such as metallic ones (binding energy between 931 eV and 932 eV) and other species. Due to PrN lattice parameter larger than TiN, may easily integrate the lattice of PrN, which can subsequently alter the electron field of Pr, and hence decrease the binding energy of Pr³⁺. In the view of the analysis above, TiN should be the main components in both un-implanted and Pr implanted TiN coatings and the PrN could be found after Pr ion implantation.

The AFM images in Fig. 3 show the surface morphology of the untreated TiN coatings and Pr-implanted coatings. The morphology is obviously altered by ion implantation. The surface of the untreated TiN coatings shows large and uniformly distributed cones (Fig. 3a) with a root-mean-square (RMS) roughness of 3.25 nm. In comparison, the surface after ion implantation is smooth (Fig. 3b and c) with root-mean-square (RMS) roughness values of 0.21 nm [Pr(0.5 h)] and 0.17 nm [Pr(1 h)]. This smoothing effect may be due to ion beam sputtering during ion implantation. However, there is no significant difference in the surface roughness between the two Pr implanted TiN coatings.
According to previous reports, ion implantation of Pr and other rare earth elements can reduce the friction coefficient of the materials, make the surface smooth, and increase the microhardness \[53\]. In this study, surface morphology improvement is believed to stem from the Pr ion bombardment as well as surface atomic mobile due to Pr ion implantation.

Our AFM results are consistent and a smooth surface bonding well for blood cells and consequently cardiovascular implants. Blood cells are broken down after exposure to the implant in a process called hemolysis. Ion implantation is an effective means to reduce damage to blood cells and the hemolysis rate is an objective indicator whether the surface roughness affects the blood cells.

After implanted with Pr, the crystal TiN mixed with crystal PrN is better suited for the biological application. The Pr implanted TiN surface topography is generally island-like and the size of these islands in the crystal depends on the volume entrapped. The changes in the island dimensions may also affect the functions of the vascular endothelial cells.

**3.2. Corrosion behavior**

The potentiodynamic polarization curves acquired from the untreated and implanted samples in blood plasma at 37 °C are displayed in Fig. 4 showing that the corrosion potential of the untreated TiN coatings is lower. After Pr ion implantation, the corrosion potential is significantly improved while the corrosion current density decreases. A possible reason is the protection offered by the barrier provided by the Pr implanted TiN coatings and another one may be that inter granular corrosion is suppressed by implantation of praseodymium into the TiN coatings \[54\]. Nitride of Pr existed around TiN grain boundaries, both them had the same crystal structure, which might be beneficial to the compact coating formation of PrN and TiN. Because the poor corrosion properties of TiN coating are dependent on the structural defects. The TiN coatings exhibit the columnar structure with pores between the intergranular column, forming a direct path for the corrosive medium to pass through the coating defects. The crystalline particles located...
at the boundaries of the pores are weakly bonded. The pores may be the most possible spots for corrosion initiation [55]. When the TiN coatings were immersed in blood, the corrosion initiates at some structural pores, which will easily filled in by blood plasma or corrosive medium.

After implanted with Pr, the coatings corrosion resistance is enhanced. From the XRD result, the reason maybe was that formed crystalline PrN phase or the ternary Ti—Pr—N complex compounds plug the transport path for the corrosive medium, which could restrain the penetration and diffraction of corrosive medium into the inner of TiN coatings.

Generally, a pore-free coating gives the substrate greater passivity than a coating with pores [56]. From the AFM result, the coating surface morphology is obviously altered by ion implantation. This smoothing effect may be due to Pr ion bombardment which leads to change microstructural, result in pores reduce or vanish.

On the other hand, plasma protein adsorption also influences the corrosion process of cardiovascular implants when surface coverage by blood components occurs. In case of surface coverage the layers formed may act as a diffusion barrier leading to reduced corrosion. After Pr ion implantation, the coatings exhibited increased surface energy due to enhanced TiN (2 2 0) plane intensity, with a higher surface energy adsorbs more plasma proteins.

It has been shown that magnetron sputtered TiN coatings improve the corrosion resistance of hard coatings such as Ti—Si—N and Ti—Al—N and that ion implantation of Pr and other rare earth elements promotes the wear and corrosion resistance due to the formation of surface barriers [57]. In this work, the TiN coating is treated as the control. The purpose of the experiment is to determine whether the Pr-implanted TiN coatings possess enhanced corrosion resistance in blood. The corrosion potential of the un-coated Ti6Al4V alloy in artificial saliva is −0.3 V which is smaller than that of the TiN coating under the same conditions [58]. The composition of blood is more complex than that of artificial saliva and the TiN coating shows better corrosion resistance than the uncoated Ti6Al4V alloy in blood. In biomedical applications, many different types of coatings have been proposed to protect titanium alloys. With respect to biodegradable implants made of polymers or magnesium alloys, extensive corrosion can create mechanical problems prior to tissue healing [59].

After ion implantation, the implanted samples exhibited increased surface hardness, and improve corrosion property [35]. The improvement is believed to stem from the implantation induced smoothing of the surface as well as surface hardening due to ion implantation. In this study, Pr implanted TiN coatings are better than un-implanted TiN coating corrosion resistance.

All in all, our experiments corroborate that Pr ion implantation indeed improves the corrosion resistance of TiN coatings in a real blood environment.

3.3. Hemolysis rate

The hemolysis rate is an important indicator of the effectiveness of biomaterials in the blood environment and a smaller hemolysis rate translates into better blood compatibility. The surface roughness is indirectly related to the hemolysis rate. A hemolysis rate below the threshold of 5% means little harm to red blood cells [60]. Fig. 5 shows the hemolysis rate of the untreated and Pr implanted TiN coatings and the hemolysis rates of two different Pr implanted TiN coatings are significantly smaller than that of the control which shows a hemolysis rate larger than 5% possibly due to the surface roughness. The Pr implanted materials show that a hemolysis rate of less than 3% is more suitable clinically.

From the AFM results, Pr implanted TiN coatings surface roughness decreased, may be due to the effects of ion bombardment. A smoother surface may induce less damage to blood cells in flowing blood. The blood components are blood cells and plasma. Rapid movement of blood cells in a blood vessel does not rupture endothelial tissues and a smoother surface can also reduce the mechanical friction loss.

3.4. Cell proliferation

Vascular endothelial cells in the inner walls of blood vessels are in direct contact with blood and implants and vascular endothelial cell proliferation is an important index gauging the cytocompatibility of the implants [61]. The effects of Pr ion implantation on endothelial cell proliferation are investigated by a CCK-8 viability assay after incubation for 1 and 6 days, respectively. Fig. 6 shows the amount and proliferation of endothelial cells on the surface of the three samples. The absorbance is proportional to the amount of cells. That is, the more the cells on the surface, the larger is the absorbance. After 1 and 6 days, increased proliferation is observed and the two kinds of Pr samples show more prominent
proliferation together with the TiN coatings. Pr ion implantation changes the chemical properties of the coatings and tends to adsorb more extracellular matrix that is conducive to cell adhesion and proliferation.

The surface characteristics of the materials such as surface chemistry, roughness, and other topographic features play important roles in cell proliferation and also the internal environment inside the organism [62,63]. It has been shown that Pr does not inhibit proliferation of human umbilical cord perivascular cells (HUCPV) [43] and our data further demonstrate that Pr ion implantation does not inhibit proliferation of vascular endothelial cells rendering the materials desirable in the blood environment.

After implanted with Pr, TiN coatings [2 2 0] plane intensity increased, and this crystal plane with a higher surface energy absorbs more extracellular matrix proteins. Extracellular matrix proteins are known to both maintain cellular morphology and act as conduits between extracellular stimuli and cells by regulating proliferation, migration, differentiation, and survival. The protein adsorption is the key determinant of cell proliferation on the material surface.

Numerous clinical studies with bare metal implants showed several limitations under cardiovascular condition. Especially, in-stent stenosis, late stent thrombosis and problems with revascularization are still unsolved major critical issues. Therefore, the ideal cardiovascular implants should prevent smooth muscle cell hyperplasia, and support a fast healing of the endothelial tissue [64]. In this study, Pr implanted TiN coating promote endothelial cell proliferation due to coatings micro-structural adjustment by Pr ion implantation, which consistent with the clinical requirements. Anti-carcinogenic properties of Pr have been shown in number of studies [65,66]. This also indicated that, Pr implanted TiN coatings should be adjustable in the normal range of cell cycle gene expression, rather than the malignant proliferation.

3.5. Cell morphology and spreading

The morphology and arrangement of the vascular endothelial cells on the samples are determined by immunofluorescence staining for the actin expression. Fig. 7a–c depicts the cytoskeleton of the vascular endothelial cells after incubation for 1 day. The vascular endothelial cells on all the samples are similar exhibiting an elliptical or round morphology.

The cell morphology and functions are related. The morphology changes after cell necrosis, aging, damage, and so on and so the cell morphology is an important index of cytocompatibility [67]. Our cell proliferation experiments show that the two Pr implanted samples do not harm vascular endothelial cells that can adhere and proliferate on the surface. The observed cytoskeleton and morphology of the vascular endothelial cells are normal indicative of normal physiological functions. Vascular endothelial cells have many important physiological functions such as anticoagulation, blood clotting, vasodilatation, etc [68]. Our results indicate the Pr
implanted TiN coatings maintain the normal functions of the blood vessel inner wall while the corrosion resistance is improved.

One of the important requirements for cytocompatibility is the formation of a dense layer of cells on the materials surface. The vascular endothelial cells also show good spreading and proliferation on the TiN coatings and two Pr implanted TiN coatings. Almost confluent coverage of vascular endothelial cells with ellipsoidal morphology is observed after culturing for 6 days. Fig. 7d shows that after 6 days, the cells spread on the TiN coatings, but there are still gaps between the endothelial cells. In comparison, the endothelial cells are very dense on the 0.5 h Pr sample (Fig. 7e) and a vascular tissue-like network is observed in vitro implying good cytocompatibility. Good cell spreading is also observed from the 1 h Pr implanted TiN coating (Fig. 7f).

The surface morphology containing micro/nano scale features should be designed to enhance the cell functions [69]. The tissue structure is a part of the endothelial cell property that is necessary for proper cell morphology, attachment, and secretion. The coating topography with a mixture of micro-/nano-scale features is an important factor for enhancing cellular responses. The Pr implanted TiN coatings with a micro-/nano-scale crystals’ surface topography provided an excellent substrate for cell adhesion. The cell adhesion morphology with better tissue structure, cell spreading, and cell-cell interaction on the Pr implanted TiN coatings clearly suggests that the Pr implanted TiN coatings had favorable surface characteristics for cell property. The experimental results are consistent with cell proliferation data demonstrating that Pr ion implantation enhances the cytocompatibility of TiN coatings.

4. Conclusion

In this study, the Pr ion implantation was used to improve the corrosion resistance and cytocompatibility of TiN coatings. From the XRD and XPS result, it was found formed Pr nitride in Pr implanted TiN coatings. May be the corrosion path is blocked in the Pr implanted TiN coatings. The implantation treatment enhances the corrosion resistance of the TiN coating in blood condition. The change of TiN crystal (2 2 0) plane intensity and formation of smooth surface produce a relatively stable and biofriendly interface for red blood cell intact and endothelial cells growth, resulting in enhanced cytocompatibility in vitro.

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