



Microstructure and tribocorrosion performance of nanocrystalline TiN graded coating on biomedical titanium alloy

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Abstract: A nanocrystalline TiN graded coating was prepared on Ti6Al4V alloy by DC reactive magnetron sputtering method. The microstructure and mechanic properties of the coating were investigated. The electrochemical corrosion and tribocorrosion of the coated specimens in physiological environment were compared with those of Ti6Al4V substrate. The results show that the gradient distribution of nanocrystalline TiN is favorable for releasing the inner stress in the coating, which increases adhesion strength to 90 N. The compact structure and refined-grains of the coating result in the surface nanohardness of 28.5 GPa. The corrosion protection efficiency of the nanocrystalline TiN coating reaches 96.6%. The tribocorrosion resistance of the coating increases by 100 times in comparison with that of Ti6Al4V substrate. The high chemical stability and H^3/E^2 ratio (where H is hardness, and E is elastic modulus) of the nanocrystalline TiN coating are responsible for good corrosion and wear resistances.

Key words: TiN coating; nanocrystalline; hardness; adhesion; tribocorrosion performance

1 Introduction

Over the past decades, the artificial joints have been successfully applied for the treatment of the patient's joint failure resulting from disease or trauma. However, the metal materials used in these procedures, such as stainless steel, titanium alloy and cobalt chromium alloy, still do not satisfy the demands of a durable functioning joint. Because of the frequently relative movement of the prosthesis part in physiological environment, various mechanical and chemical processes will damage the long term stability of the implants. The surface properties of implant materials are particularly important because the generation of debris particles or dissolution of metal ions and fatigue cracking occur on the surface of prosthesis. They can cause toxicity to periprosthetic tissues, loosening and fracture of the prosthesis, which pose a serious threat to human health [1–4].

Metal matrix ceramic coating material, which combines the properties of a ceramic with a bulk metal, can provide a ceramic-like surface replacement with improved wear and corrosion resistances. Nitride

ceramic coatings, such as CrN, TiN and TiCN, have been proved to effectively decrease the release of Cr, Co, V and Al ions from CoCrMo and Ti6Al4V alloys, and the size and amount of the debris during the abrasion. The biological, chemical and mechanical performances of the artificial joint are thus improved [5–7]. Among them, TiN coating is of good biocompatibility with human tissue. It can improve cell adhesion as well as inhibit bacterial adhesion [8,9]. In 1980s, TiN coating has been accepted as a candidate material by US Food and Drug Administration for medical application of cardiovascular, dental and orthopedic implants [10].

Up to date, many publications have reported that the main limitation of the clinical application for the TiN coated artificial joints is low adhesion and surface scratch resistance [11,12]. Because of high internal stress resulting from the abrupt changes of chemical compositions and mechanical properties between coating and metal substrate, TiN coating is prone to early debonding or cracking [13]. The lack of sufficient hardness and compactness also causes a number of scratches on the coating surface. High surface roughness of the coating also aggravates the wear performance of

the implant. In the past decades, nano- or sub-micron scale multilayer coatings, such as TiN/AlN, TiN/TiCN, and TiN/CrN, have been designed to improve hardness and fracture toughness [14]. But these hard-hard composite coatings on the relatively compliant substrate behave spallation or high friction of coefficient in many tribological situations [15,16]. The hard-soft coating, such as TiN/Ti multilayer coating, offers a simple approach to control residual stress, which not only improves adhesion strength, but also produces a toughening response because of the stress buffer effect of Ti interlayer [17]. But the interface debonding between TiN and Ti layer was found to occur on the surface of the coating. The situation is more serious with the reduction of TiN layer thickness [18].

Recently, our research group has reported a newly developed TiN graded coating with high adhesion, low friction and good anti-wear performances [19]. It consists of nanocrystalline TiN and small amount of TiN_x transitional phase with variable composition, and exhibits more compact structure and smoother surface than the traditional TiN coating with columnar crystal structure. However, the chemical stability and tribocorrosion mechanism of the nanocrystalline TiN coating in physiological environment are still unclear. Moreover, the mechanical properties of the nanocrystalline TiN coating are expected to be further increased through improving preparation processing. In this work, the electrochemical corrosion and tribocorrosion performances of the TiN coating on titanium alloy were investigated so as to deeply evaluate the suitability as surface modification material on orthopedics implant in physiological environment.

2 Experimental

The nanocrystalline TiN graded coating was deposited on medical grade Ti6Al4V alloy by DC reactive magnetron sputtering method with high pure titanium target (99.95%). High purity argon (99.99%) and high purity nitrogen (99.99%) were introduced into the chamber. The substrate plates were firstly ground up to 2000 grit SiC paper, polished with alumina powder (0.2 μm in particles size), and then ultrasonic-cleaned in acetone. Prior to deposition, the chamber was pumped down to a pressure of 4×10^{-3} Pa. Titanium target was pre-cleaned via Ar^+ bombardment for 10 min in order to remove surface impurities. The working pressure was 0.38 Pa. The substrate plates were preheated to 300 °C. Ti interlayer was firstly deposited on the substrate plate for 10 min to increase the adhesive strength of the coating. The TiN graded coating was obtained by gradually increasing N_2 flow rate from 1 to 14 mL/min while maintaining constant Ar flow rate of 30 mL/min.

The total deposition time was 180 min and the final coating thickness was about 6 μm .

The phase composition of the coating was characterized using X-ray diffractometer (Smart Lab, Japan) with $\text{Cu K}\alpha$ radiation at a scanning speed of 8 (°)/min. In order to accurately analyze the phase compositions at different layers in the coating and rule out the influence of the titanium alloy substrate on the diffraction peak, three kinds of thin films that employed the same deposition parameters as inner layer (N_2 flow rate of 1–5 mL/min), intermediate layer (N_2 flow rate of 6–10 mL/min) and external layer (N_2 flow rate of 11–14 mL/min) of the graded coating were deposited on silicon substrates. High resolution transmission electron microscope (JEM-2100, Japan) was used to observe the morphology of nanocrystalline TiN. 2D and 3D surface profiles were observed by atomic force microscope (EasyScan2, Switzerland).

An in-situ nanomechanical testing system (Hysitron Triboindenter, USA) was used to measure indentation hardness and elastic modulus of coatings with different layer depths at the maximum load of 9 mN. The adhesion strength of the coating was tested by a micro-scratch tester (WS-2005, China) with a diamond stylus of 0.2 mm in radius. The load progressively increased up to 150 N with a loading rate of 100 N/min. The critical loads (L_c) representing adhesion to the substrate were determined by a sudden increase of acoustic emission signal. In order to ensure the reproducibility of the results, the nanoindenter and scratch tests were repeated three times on each coated specimen.

Three-electrode electrochemical working station (Zennium, Germany) was used to perform the electrochemical tests with saturated calomel electrode as reference electrode, platinum plate as counter electrode and specimens as working electrode (1 cm^2 exposure area to the solution). The potentiodynamic polarization curves were recorded over the potential range from -1.5 to 1.5 V at a scan rate of 1 mV/s in the naturally aerated Hank's solution. The electrochemical impedance spectra (EIS) were measured by applying a sinusoidal potential perturbation of 5 mV with a frequency from 1×10^{-2} to 1×10^5 Hz in logarithmic increment at the open circuit potential. Before the tests, the specimens were immersed in the electrolyte for 1 h to attain stable open circuit potential.

Linear reciprocating ball-on-disc wear tests were performed using a tribometer (CSM, Switzerland) with d_6 mm Si_3N_4 ball rubbing against the specimens in Hank's solution at 37 °C. The compositions of Hank's solution were: 8 g/L NaCl, 0.4 g/L KCl, 0.1 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.14 g/L CaCl_2 , 0.154 g/L NaH_2PO_4 and 0.06 g/L KH_2PO_4 . The duration of the rubbing experiment was 180 min. The applied

normal force was 5 N and the stroke length was 10 mm. The oscillation frequency was 1 Hz. The Hertzian average contact pressure (assuming elastic moduli of Si_3N_4 and TiN are 350 GPa and the contact radius is 0.05 mm) was 672 MPa. The worn volume of the TC4 substrate specimen was measured by laser scanning confocal microscope (LSCM 510 system, Germany) and the worn volume of the coated specimen was measured by probe-type surface profiler (Dektak 150, USA). The surface morphologies of the worn specimens were observed by SEM (SSX-550).

3 Results

3.1 Microstructures

Figure 1(a) shows a XRD pattern of the TiN coating deposited on TC4 substrate. It shows that the TiN coating exhibits strong (200) orientation texture. The small amount of Ti (N) solid solution ($\text{TiN}_{0.26}$) and transitional phase (Ti_2N) are found from the XRD pattern. It is known that TiN crystal deposited by sputtering generally prefers to nucleating on (100) crystal plane with low surface energy and growing up along (111) orientation with low strain energy. (200)_{TiN} orientation texture for the present coating is evidently influenced by the continuous change of N_2 flow rate during deposition. Figure 1(b) shows the XRD patterns of three films at different N_2 flow rates which correspond to different depths of the TiN graded coating. The strong (111)_{TiN} diffraction peak and almost negligible (200)_{TiN} diffraction peak are seen from the XRD pattern of the inner layer at N_2 flow rate of 1–5 mL/min. No Ti diffraction peak is found even at such a low N_2 flow rate. It is inferred that the surplus Ti atoms possibly exist in an amorphous form. With the stepped increase of N_2 flow rate, (111)_{TiN} diffraction peak gradually becomes weakened and (200)_{TiN} diffraction peak begins to strengthen. This is because the increased supply of N_2 enhances TiN nucleation rate. The randomly distributed TiN crystal nucleus interrupts the orientation growth of the primary TiN grains. This means that the stepped increase of N_2 flow rate can inhibit the formation of the coarse column crystal with (111) preferred orientation.

Figure 2 shows TEM images of the intermediate layer and external layer in the TiN coating. In the intermediate layer, TiN grain size is comparatively uniform in the range of 2–9 nm. In the external layer, TiN grains begin to coarsen, and the maximum size reaches 20 nm. Meanwhile, a number of small grains with the size less than 2 nm can also be observed. Evidently, the continuous change of N_2 flow rate not only multiplies the number of TiN nucleation but also accelerates the growth of TiN grains. The whole TiN coating exhibits the gradual increase in grain size and

volume fraction from inner layer to external layer. The special microstructure will cause the gradual change of the mechanical properties including elastic modulus, hardness and toughness, as demonstrated by nano-indentation tests.

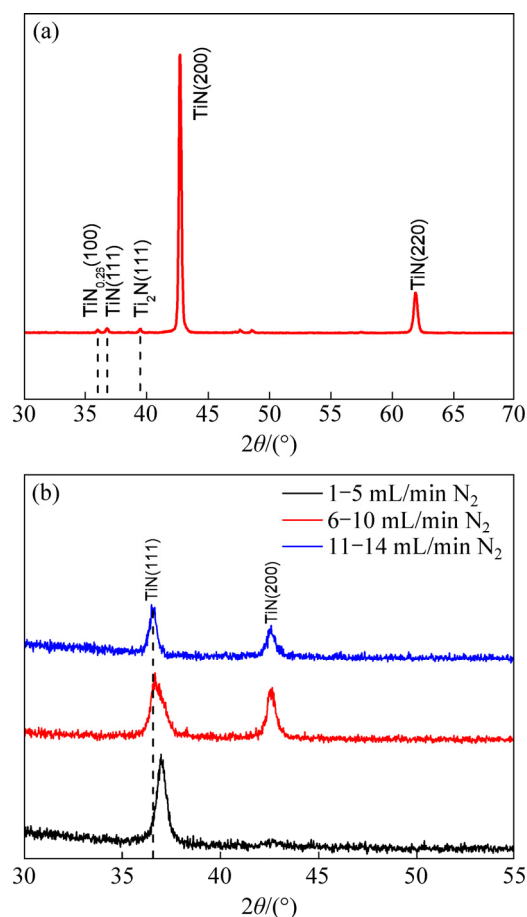


Fig. 1 XRD patterns of TiN graded coating: (a) Phase analysis of whole coating deposited on TC4 substrate; (b) Phase analysis of different layers in coating deposited on silicon substrate at different N_2 flow rates

3.2 Mechanical properties

Nanoindentation tests were used to measure nano mechanics at different depths of the coating. Figure 3(a) shows the cross-sectional image of the coating. The dense and well adhesive coating was seen on the TC4 substrate. The load–displacement curves tested at three positions in the coating are shown in Fig. 3(b). The calculated mechanical properties are given in Table 1. Nanohardness and elastic modulus synchronously increased from inner layer to outer layer of the coating. The H/E ratio (H is the hardness, and E is the elastic modulus), a measurement representing resistance to plastic deformation, is higher than 0.05 that is exhibited by general TiN coating. The H^3/E^2 ratio, which represents the resistance to cracking [20] and wear [21], reaches maximum of 0.2 GPa. The value doubles over that of the general TiN coating. This indicates that the

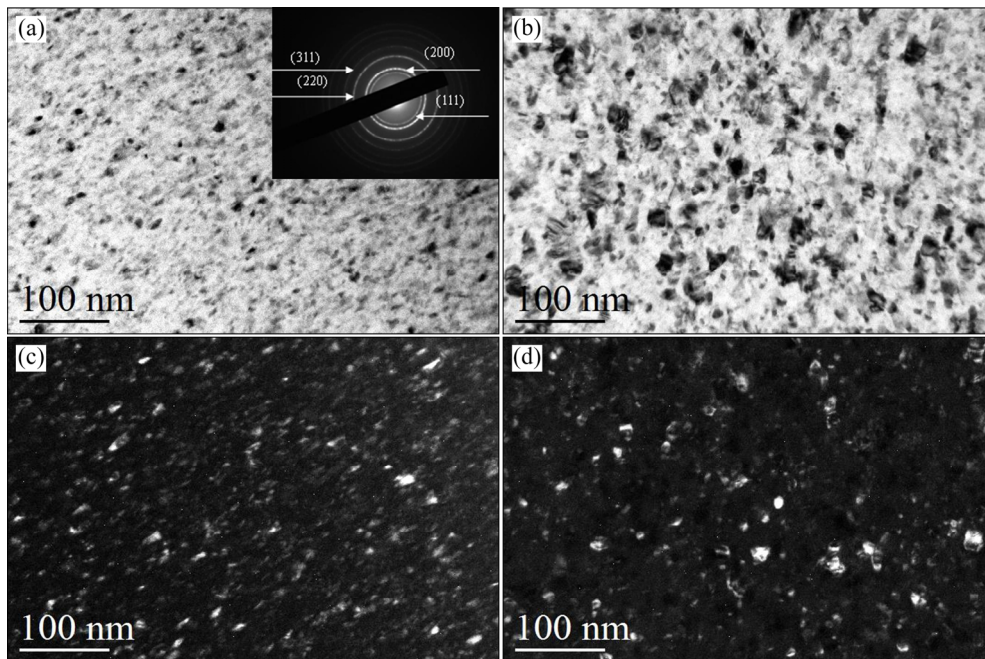


Fig. 2 TEM bright (a, b) and dark (c, d) field images of nanocrystalline TiN at intermediate (a, c) and external (b, d) layers of coating at different N_2 flow rates: (a, c) 6–10 mL/min; (b, d) 11–14 mL/min

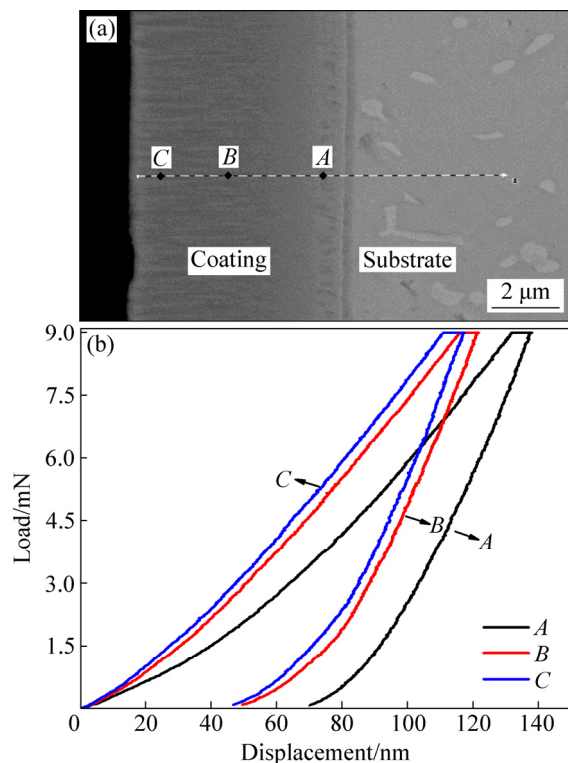


Fig. 3 Cross-sectional image of TiN graded coating (a) and load–displacement curves measured at different positions of A, B and C in (a) by nanoindentation tests (b)

nanocrystalline TiN graded coating simultaneously obtains high strength and high toughness. The scratching test further proves that the critical cracking and rupture forces of the graded coating are 74 N (L_{c1}) and 90 N (L_{c2}),

Table 1 Mechanical properties measured at different depths of TiN coating by nanoindentation test

Position	Nanohardness, H /GPa	Elastic modulus, E /GPa	Pressed depth/nm	H/E	$(H^3/E^2)/$ GPa
A	21.6	281.4	138.1	0.077	0.13
B	27.7	332.3	121.8	0.083	0.19
C	28.5	343.7	117.4	0.083	0.20

respectively, as shown in Fig. 4. Whereas, the adhesion strength of the general TiN coating on TC4 alloy is only at the level of $L_{c1}=15\text{--}20$ N or $L_{c2}=40\text{--}60$ N [22,23]. The above results indicate that the mechanical properties of the new-type TiN coating have been comprehensively improved by the gradient distribution of nanocrystalline.

3.3 Electrochemical corrosion and tribocorrosion performance

The tribocorrosion behavior of artificial joints in vivo environment has attracted more and more attention because the combined action of wear and corrosion accelerates the failure of the metal implants. Although TiN coating can effectively stop the release of metal ions from metal implant, the chemical stability of the nanocrystalline TiN coating in physiological environment needs to be determined due to the high chemical activity of nanocrystalline material. In this work, the electrochemical corrosion behavior of the nanocrystalline TiN coating and TC4 alloy substrate was compared in order to ascertain the protective effect of the

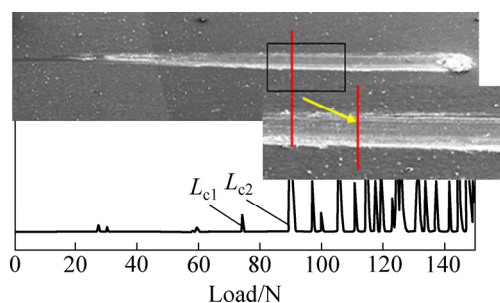
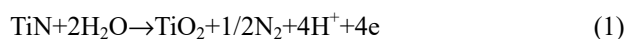


Fig. 4 Acoustic emission signal pattern during scratching showing critical forces representing cracking ($L_{c1}=74$ N) and rupture ($L_{c2}=90$ N) of coating, respectively

coating on the TC4 alloy substrate in static corrosion and tribocorrosion process. Figure 5 shows the potentiodynamic polarization curves of the coated and TC4 substrate specimens. The coated specimen has lower self-corrosion tendency than the TC4 substrate, which is reflected by the nobler corrosion potential (ϕ_{corr}) and lower corrosion current density (J_{corr}). In anodic polarization zone, the TC4 substrate exhibits wide passivation potential range until 1.5 V (vs SCE). But the passive potential of the coated specimen is below 0.24 V (vs SCE). After that, the corrosion current density gradually increases. This indicates that the passivation of the coated specimen is limited within narrow potential range (as indicated by dotted lines in Fig. 5). TiO_2 may play a major role in the passivation area, which results from the following oxidation reaction:



Then, the passive film of the coated specimen is

destroyed with increasing anodic potential. In spite of this, the corrosion rate of the coated specimen is much smaller than that of the TC4 substrate. Table 2 shows that the corrosion current densities of the coated specimen at self-corrosion potential and passivation potential are almost two orders of magnitude lower than those of the TC4 substrate. Since in-vivo potential of the implant materials is in the range of 0.1–0.3 V (vs SCE) [24], the corrosion resistance of the nanocrystalline TiN coated implant is superior to that of the TC4 substrate in physiological environment. Particularly, the pitting corrosion of the coated implant can be completely avoided.

The corrosion protection properties of the nanocrystalline TiN graded coating can be further evaluated through measuring electrochemical impedance spectra (EIS). As shown in Fig. 6, the coated and TC4

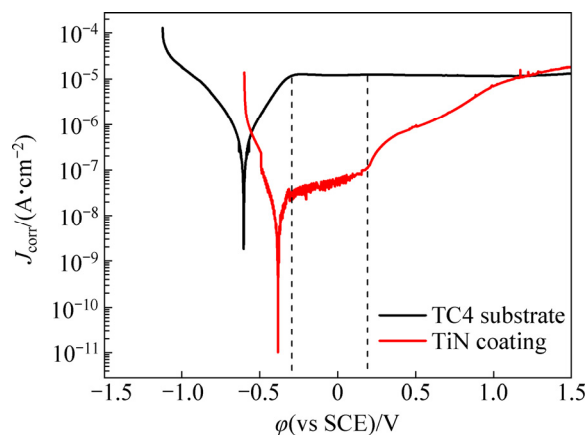


Fig. 5 Potentiodynamic polarization curves of coated and TC4 substrate specimens in Hank's solution

Table 2 Electrochemical corrosion parameters of coated and TC4 substrate specimens in Hank's solution

Specimen	$\phi_{\text{corr}}/\text{mV}$	$J_{\text{corr}}/(\text{A} \cdot \text{cm}^{-2})$	$J_{\text{pass}}/(\text{A} \cdot \text{cm}^{-2})$	$R_s/(\Omega \cdot \text{cm}^{-2})$	$R_{\text{ct}}/(\Omega \cdot \text{cm}^{-2})$	n
Coated TC4 alloy	-468.2	6.5×10^{-8}	9.0×10^{-7}	23.05	6.17×10^5	0.89
TC4 substrate	-600.8	1.9×10^{-6}	2.0×10^{-5}	20.39	9.01×10^4	0.90

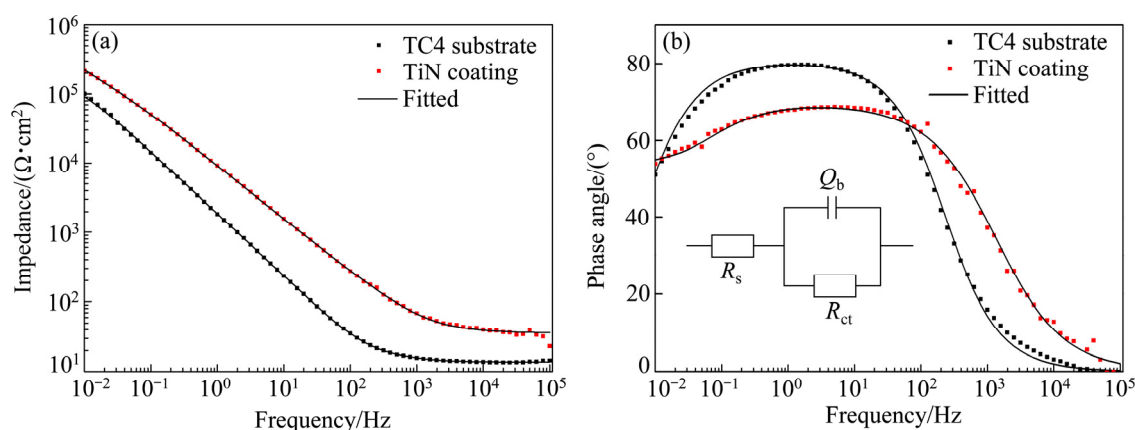


Fig. 6 Bode-impedance (a) and Bode-phase angle (b) plots of coated and TC4 substrate specimen (The proposed equivalent electrical circuit is superimposed in (b))

substrate specimens behaved the similar Bode-impedance and Bode-phase angle plots and the same equivalent electrical circuit mode, suggesting that the nanocrystalline TiN coating has good compactness as natural oxide film formed on the TC4 substrate. The difference between them is that the coated specimen has higher impedance in low frequency range. Table 2 shows that the charge transfer resistance (R_{ct}) of the coated specimen increased by about six times in comparison with that of the TC4 substrate specimen, which indicates that the thicker and denser coating decreases the adsorption capacity of ions and suppresses the transportation of the carriers. Based on the above results, it is concluded that the nanocrystalline TiN coating not only has high chemical stability, but also plays an important role of inhibiting the adsorption, penetration and erosion of the corrosive ions from body fluid.

In the tribocorrosion tests, the coated and the TC4 substrate specimens exhibited totally different friction and wear behaviors. The differences were associated with the chemical activity, surface energy and mechanical properties of the TiN coating and TC4 substrate. Figure 7 shows the change of the open circuit potential (OCP) and the coefficient of friction (COF)

with sliding time for the coated and TC4 substrate specimens. The OCP of the TC4 substrate shifted towards negative potential from the beginning and then started to sharply fluctuate after 50 min. The maximum potential difference reached 80 mV. In contrast, the OCP of the coated specimen slightly shifted towards positive potential at the beginning and then maintained almost the constant value as before wear test. It has been reported that the OCP of TiN coating during abrasion always shifted towards negative potential [25,26]. In this work, the almost unchanged OCP reflects the higher chemical stability of the nanocrystalline TiN coating than coarse crystalline TiN coating. It is worth noting that the change tendency of the OCPs for both specimens just coincides with the COFs, as shown in Fig. 7(b). For the TC4 substrate, the reduced and fluctuated OCP just corresponds to the increased and undulated COF. The phenomenon can be explained by the repeated removal and formation of the oxide film. For the coated specimen, the constant OCP correlates with the stable and low COF (almost one third of TC4 substrate), indicating that less damage occurs on the worn surface of the TiN coating. The results further prove that good chemical stability and high resistance to plastic deformation and cracking of the nanocrystalline TiN coating are responsible for the improved friction and wear performance.

The worn surfaces of the TiN coating and TC4 substrate were observed by SEM, as shown in Fig. 8. Only slight worn track can be seen on the TiN coating. No cracks and breakage are found within or at the edges of the worn track. This presents an obvious contrast against the worn surface of the TC4 substrate specimen, on which furrows, adhesive scars and cracks are clearly seen. The EDS analysis to some special areas on the worn surface was performed, as denoted by Zones A and B in Figs. 8(a) and (b), respectively. The black area on the worn surface of the TiN coating is proved to be Ti–N–O compound. The gray area is primary TiN coating. This indicates that only a few protuberant or defective areas have suffered from slight tribocorrosion. The formation of Ti–N–O compound does not degrade the friction performance, instead, plays a lubrication role in decreasing COF. Area B on the worn surface of the TC4 substrate specimen in Fig. 8(b) was analyzed to be phosphate-containing titanium oxide. The brittle composite oxide film easily cracks and peels off in tribocorrosion, which leads to rougher surface and higher COF. Because of lower hardness, the plastic deformation on the surface layer of the TC4 substrate not only results in the separation of material, forming deep furrows and adhesive scars, but also enhances corrosion tendency and corrosion rate. The synergistic effect of wear and corrosion seriously degrades the wear performance of the TC4 substrate. The exfoliated oxide debris also promotes

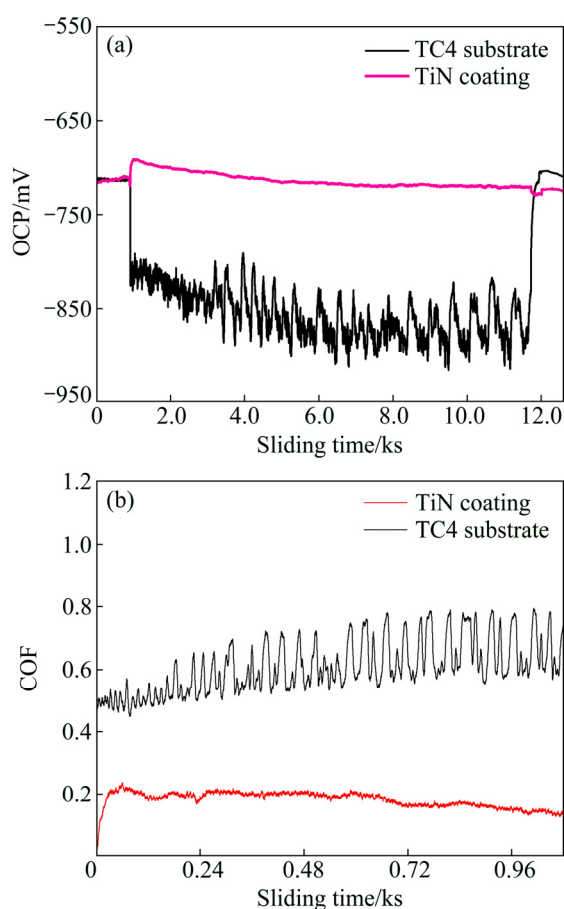


Fig. 7 OCP (a) and COF (b) versus sliding time curves of coated and TC4 substrate specimen under load of 5 N in Hank's solution

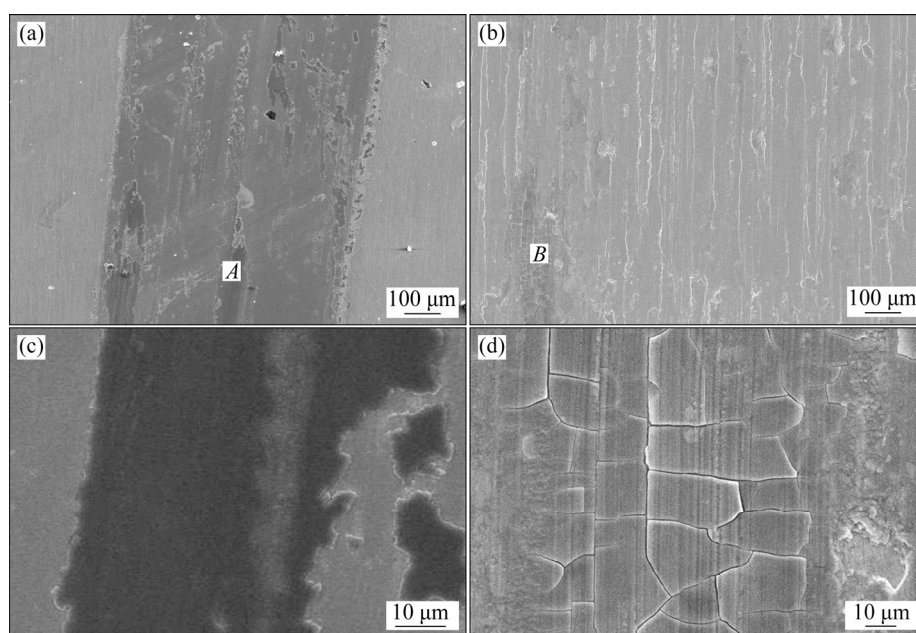


Fig. 8 Worn track morphologies (a, b) and local magnified images (c, d) ((c) for Area A and (d) for Area B) at sliding distance of 150 m in Hank's solution: (a, c) TiN coated specimen; (b, d) TC4 substrate

the increase of the COF as the third body abrasion. Furthermore, large number of debris is prone to damage tissue surrounding the implant and cause periprosthetic bone loss [27,28].

4 Discussion

The service life of the biocoating on the surface of the artificial joints for corrosion and wear protection depends on some chemical and mechanical factors, e.g. adhesion strength, hardness, coefficient of friction and corrosion rate. In the present work, the nanocrystalline TiN coating on titanium alloy is obviously superior to the traditional TiN coating in these aspects. The gradient distribution of the nanocrystalline TiN in the coating constitutes a special microstructure with the characteristics of inner layer “soft” and outer layer “hard”, which is favorable for releasing growth stress and thermal stress between substrate and coating. And the adhesion of the coating to Ti alloy substrate is thus greatly improved. The layer-by-layer deposited nanocrystalline TiN eliminates micropore defects as frequently seen in columnar crystal coating and enhances the compactness of the coating. A few or tens of nanometers size TiN grains strongly limit dislocation movement as the coated material is subjected to external load. Meanwhile, small amount of TiN_x transitional phases around TiN grains contain a lot of defects (vacancies, dislocations or lattice distortion) [19]. They act as an auxiliary reinforcement or a hindrance of crack propagation. As a result, the hardness and fracture toughness of the nanocrystalline TiN graded coating are

improved simultaneously. Furthermore, the surface roughness of the TiN coating decreases due to the refined microstructure. Figure 9 shows the 2D and 3D surface profiles of the nanocrystalline TiN coating observed by

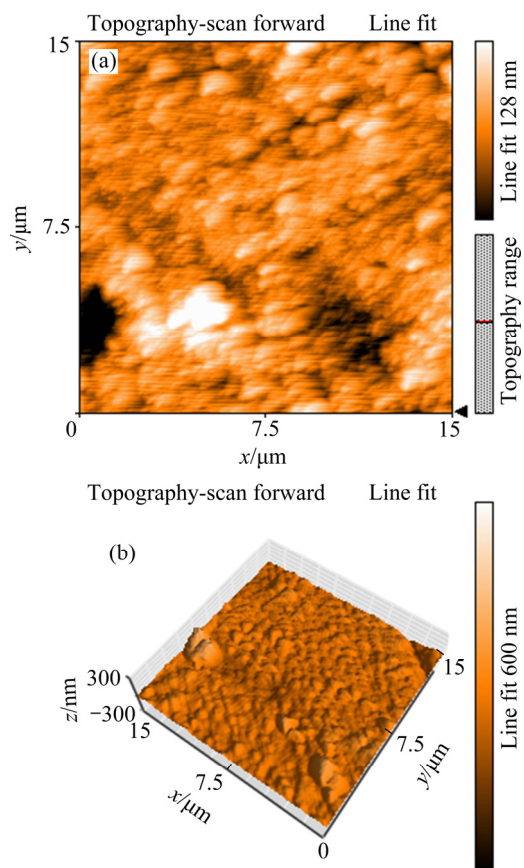


Fig. 9 2D (a) and 3D (b) surface profiles of nanocrystalline TiN graded coating observed by AFM

atomic force microscope (AFM). The mean square roughness within the area of $15\ \mu\text{m} \times 15\ \mu\text{m}$ is only 20 nm. The smooth surface lowers the surface energy of the coating and tendency to adhesive wear.

The corrosion protection efficiency P of the coating on titanium alloy can be calculated by the following equation [29]:

$$P = (1 - J_{\text{corr}} / J_{\text{corr}}^0) \times 100\% \quad (2)$$

where J_{corr} and J_{corr}^0 indicate the corrosion current densities of the coated and TC4 substrate specimens, respectively. The P values of the nanocrystalline TiN coating at self-corrosion potential and passivation potential reach 96.6% and 95.5%, respectively. The values are higher than those of general TiN coating that has been reported in Refs. [30–32]. The excellent corrosion resistance of the nanocrystalline TiN coating is attributed to the dense structure, rapid passivation capability and high chemical stability.

The lost volume (ΔV_T) of the material in tribo-corrosion process can be divided into three items [33]:

$$\Delta V_T = \Delta V_W + \Delta V_C + \Delta V_{\text{Syn}} \quad (3)$$

where ΔV_W is pure mechanical wear volume, ΔV_C is the lost volume caused by corrosion in the absence of wear, which can be calculated by using Faraday's law, and ΔV_{Syn} incorporates two components: the effect of wear on corrosion (C_w) and the effect of corrosion on wear (W_c). Table 3 gives the ΔV_T and ΔV_C of the coated and TC4 substrate specimens.

It can be seen that the ΔV_T and ΔV_C values of the TC4 substrate specimen are nearly 120 times and 30 times higher those of the coated specimen, respectively. $\Delta V_C/\Delta V_T$ ratios for the substrate and coated specimens were 6.9×10^{-4} and 2.7×10^{-3} , respectively. These data indicate that the tribocorrosion of the TC4 substrate can be greatly improved by applying nanocrystalline TiN graded coating. The lost volumes (ΔV_C) caused by pure corrosion are negligible for both specimens. Pure mechanical wear (ΔV_W) and synthetic effect of corrosion and wear (ΔV_{Syn}) become dominant factors to the total lost volume. For the TC4 specimen, the chemically active regions can be immediately created within the worn track because plastic deformation results in the drastic reduction of the OCP. The cracking and exfoliation of the titanium oxide film incorporated with phosphate promote the loss of the material. Owing to the strong interaction between corrosion and mechanical wear, ΔV_{Syn} item accounts for the important proportion in ΔV_T . By comparison, the nanocrystalline TiN coated specimen has higher surface hardness and corrosion resistance. The ΔV_W , ΔV_C and ΔV_{Syn} are significantly reduced. Especially, ΔV_{Syn} item gives less contribution to the ΔV_T . In this case, human fluid possibly plays a role of

lubrication, which is favorable to reducing wear rate. To summarize, the increased surface hardness, toughness and smoothness of the TiN coated titanium alloy can effectively improve the tribocorrosion performance of the implant in physiological environment.

Table 3 Lost volumes in tribocorrosion tests at OCP for coated and TC4 substrate specimens

Specimen	$\Delta V_T/\text{cm}^3$	$\Delta V_C/\text{cm}^3$	$\Delta V_C/\Delta V_T$
TC4 substrate	6.67×10^{-5}	4.62×10^{-8}	6.9×10^{-4}
Coated TC4 alloy	5.45×10^{-7}	1.45×10^{-9}	2.7×10^{-3}

5 Conclusions

(1) Nanocrystalline TiN graded coating has strong (200) preferential orientation. The microstructure and mechanical properties exhibit gradual increase along deposition direction. In the top layer of the coating, the TiN grain size is 20 nm, surface nanohardness is 28.5 GPa and H^3/E^2 ratio is 0.2 GPa. The adhesion force of the coating to the TC4 substrate is as high as 90 N.

(2) The electrochemical corrosion protection efficiencies P of the nanocrystalline TiN coating at self-corrosion potential and passivation potentials are larger than 95%. The dense structure, rapid passivation capability and high chemical stability of the nanocrystalline TiN are responsible for the improved corrosion resistance.

(3) In tribocorrosion test, the TC4 substrate exhibits fluctuated and decreased OCP in accompanying with the fluctuated and increased COF. The phenomena are associated with the repeated removal and formation of the brittle phosphate-containing titanium oxide film. The synthetic effect of corrosion and wear significantly increases the wear rate of the titanium alloy substrate.

(4) The coated TC4 alloy behaves almost constant OCP and COF in tribocorrosion test, which is attributed to good smoothness and high resistance to plastic deformation and corrosion of the nanocrystalline TiN coating. Mechanical wear is the main tribocorrosion mechanism of the coated TC4 alloy. The COF and wear volume loss of nanocrystalline TiN coating are 0.15 and $5.45 \times 10^{-7}\ \text{cm}^3$, respectively.

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医用钛合金表面纳米晶 TiN 梯度涂层的 显微组织及腐蚀磨损性能

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摘 要: 采用磁控溅射方法在 Ti6Al4V 钛合金表面制备纳米晶 TiN 梯度涂层, 研究涂层的显微组织和力学性能, 并对涂层和 Ti6Al4V 合金基体在生理环境中的电化学腐蚀行为和腐蚀磨损性能进行比较。结果表明: 纳米晶 TiN 的梯度分布有利于释放涂层中的内应力, 使粘附强度增加到 90 N。致密的结构和细化的晶粒使涂层表面纳米硬度达到 28.5 GPa, 纳米晶 TiN 涂层的防腐蚀效率达到 96.6%。与 Ti6Al4V 合金基体相比, 纳米晶 TiN 涂层的耐腐蚀磨损性能提高了 100 倍。纳米晶 TiN 梯度涂层具有良好的化学稳定性和较高的 H^3/E^2 比(H 为硬度, E 为弹性模量), 是改善耐腐蚀性能和抗磨损性能的主要原因。

关键词: TiN 涂层; 纳米晶; 硬度; 结合性; 腐蚀磨损性能

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