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TiN coated stainless steel bracket: Tribological, corrosion resistance, biocompatibility and mechanical performance

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ABSTRACT

Multi-arc ion plating was used to deposit TiN films to modify the 316 L stainless steel brackets for orthodontic applications. XRD, SEM, Raman spectroscopy, electrochemical analysis, cell proliferation and enzyme-linked immuno sorbent assay (ELISA) were applied to compare the surface characteristics of TiN coated and uncoated stainless steel brackets. It was found that TiN coating is smooth, hard, well-adherent, biocompatible with super low friction coefficient (<0.03) and pretty good corrosion resistance (pitting potential higher than 600 mV) in artificial saliva. High hardness (about 14.62 GPa) is favored for the low friction coefficient, and great corrosion resistance ascribe to inert nature of TiN reduces the release of toxic elements, which improved the biocompatibility of TiN film. Better comprehension performances make TiN coated stainless steel very suitable for orthodontic applications.

1. Introduction

Wearing braces has gained increasing popularity to orthodontics. Friction between traditional brackets and arch wires causes many problems such as stress corrosion, or even corrosion cracking, the release of toxic elements like Ni and complications such as periodontal lesion and dental root resorption [1]. Considering that a combination of high hardness, low friction coefficient and extraordinary biocompatibility, TiN coatings have been accredited by the Federal Food and Drug Administration (FDA) [2], and have been thought to be good flood contact material [3]. Moreover, beautiful golden color is also a plus for an ideal orthodontic material. Gil et al. [4] tested the friction coefficients of NiTi and TiN coated NiTi arch wire with Ti–6Al–4 V and AISI316L stainless steel (SS), they found that after coated TiN, the coefficient between NiTi and stainless steel reduced from 0.61 to 0.36 and Ti–6Al–4V from 0.55 to 0.25. Similar result has been also acquired by Pappas et al. [2]. Kusy et al. [5–7] did series of researches on the effects of contact angle on friction coefficient, pointing out that while the crossing angle is smaller than the critic angle, surface treatment to the brackets or arch wire like coating diamond-like carbon film and ion planting can be used to reduce friction coefficient. Thorstenson et al. [8] studied 5 different kinds of arch wire, and found that the size and geometric characteristics of arch wire had great effect on friction, and the coefficients of rectangular wires were higher than that of round wires. Hamdan et al. [9] found that different ligation methods also resulted in different friction coefficients. Surface roughness of brackets and arch wire also has influences on friction coefficient to some extent. Friction coefficients between sintered brackets and arch wires are 40%–45% lower than that of conventional brackets for the smoother surface of sintered brackets [10]. In view of the very outstanding properties, fabricating TiN coating is still a popular way to reduce friction. But as orthodontic material, corrosion resistance is also a very important property. There are so many studies on the corrosion resistance of TiN coating [11–14]. Coating TiN on NiTi alloy can significantly improve the corrosion resistance in H_2SO_4 and HCl [15,16]. Endo et al. [17] found TiN coating can improve the corrosion resistance of NiTi in 0.9% NaCl aqueous solution, but when increasing the voltage up to 500 mV, material tends to pitting.

Reducing the friction coefficient is the most concerned factor, the friction coefficient obtained by many researchers was a little lower after coated one or two films, but still higher than 0.1. On the other hand, PVD films can hardly protect substrate well when applied voltage is high. In this study, we mainly focused on further reducing the friction coefficient of TiN and increasing the pitting potential to a more positive voltage. A systematical characterization of TiN coating was conducted to make a comprehensive assessment and to provide all-sided support for the orthodontics application of TiN coating.

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2. Experiment

2.1. Fabrication of TiN coating

First, 15 × 15 × 15 mm^3 316 L SS plates were mirror polished, then ultrasonically cleaned in deionized water, absolute ethanol, and acetone for 10 min respectively, and finally glow discharge cleaned for 30 min with Argon 2.0–2.5 Pa, bias 800–1000 V. TiN films were synthesized by a multi-arc ion planting (AS700DTXBE, ProChina, Beijing). The substrate was fixed on swivel, rotating and revolving. A Ti target (≥99.7%, Φ 100 × 40 mm) was used in N_2 (≥99.999%) atmosphere with a target-substrate separation of 200 mm, pressure of 0.8–1.5 Pa. The arc current was set as 85 A, voltage was 20 V, duty cycles 90%, substrate temperature 350 °C and deposition duration 120 min. A self bias of 100–200 V was applied during deposition. The same condition was applied to deposit TiN on SS brackets. All the samples were ultrasonically cleaned in acetone and deionized water for 15 min respectively, finally dried in air to be tested.

2.2. Characterization of coating

X-ray diffraction (XRD, D/max2500) was used to characterize the crystalline structure of the film with Cu Kα irradiation, scanning rate 4°/s, scanning range 20–90°. The stoichiometric ratio of the film was tested by laser Raman spectrum (LabRAM ARAMIS) with 532 nm excitation laser, laser power 21 mW and a spot size of 1 μm. Film thickness was measured by scanning electron microscopy (SEM, Nova NanoSEM 230). Surface roughness of the film was measured by using atomic force microscopy (AFM, Solver P47) with tap mode and 2 × 2 μm^2 in area. Corrosion resistance was tested by CHI 660e electrochemistry station (CH Instrument, Austin, TX) with a 3 electrodes system, pure titanium as counter electrode, Ag/AgCl as reference electrode, the smooth TiN film surface with the rest of it encapsulated in silica as working electrode. All these electrodes were cleaned by ultrapure water (>18 M Ω, 25 °C) and then immersed in artificial saliva for 24 h to reach an equilibrium state, and finally tested in artificial saliva at 37 ± 0.5 °C. Friction and wear performance were acquired using a ball-on-disk tribometer (UMT3, USA) with a chrome steel ball (d = 9.5 mm, Hardness 62 HRC) as counterpart and electronic balance (BSA224S-CWmax220g, sartorius, Beijing, d = 0.1 mg). The applied normal loads were 5 N and 10 N, respectively, cycle frequency was 15 Hz, sliding distance of a half cycle was 10 mm, and testing duration was 3600 s. The specimens and counter ball were immersed in artificial saliva during the test to simulate oral environment. The measurement of hardness and elastic modulus and film-substrate adherence was carried out by nano-mechanical properties comprehensive instrument (UNHT + MCT, CSM, Switzerland). The ultranano-indentation part has a maximum load of 10 mN, loading and unloading rate of 10 mN/min and the interval of 15 s. The micro-scratch part has a maximum load of 30 N, loading rate of 30 N/min, and data acquisition rate of 30 Hz, and a Rockwell diamond indenter of 200 nm in radius. To characterize the biocompatibility of specimens before and after coating TiN, cell proliferation and ELISA were applied. Cell proliferation test was performed with an original mononuclear macrophage cell number of 1×10^5, cell number was calculated after cultured 2 and 3 days, 5 specimens were tested for every culture duration. Mononuclear macrophages (THP-1 monocytes) were cultured in RPMI 1640 with 10% FBS, 50 $\mu mol \cdot L^{-1}$ of β-mercaptoethanol, 100 $units \cdot mL^{-1}$ penicillin, 100 $\mu g \cdot mL^{-1}$ streptomycin, and 2 $mmol \cdot L^{-1}$ glutamine. Samples were sterilized and placed in culture flasks with a nutrient solution and sample ratio of 10 mL/g after sterilized by ultraviolet, and stored in germfree fridge with a temperature of 4 °C for one week. All the samples were cultured in an incubator with CO_2 concentration of 5% at 37 °C for 48 h and 72 h. And then count the cell number with THP-1 cell suspension concentration of 1×10^5/2 mL by fluorescence microscopy. And conducted ELISA of nutrient solution with Human TNF-α kits (PEPROTECH, USA).

2.3. Statistical analysis

Data from experiments characterizing TiN coated and uncoated specimens are presented as the mean ± one standard deviation (SD) of the cell proliferation test and ELISA test perform on five different samples. Statistical analysis was calculated by SPSS using a Student's *t*-test, and the level of significance was set at $p < 0.05$.

3. Results and discussion

3.1. Composition and structure

Raman spectrum reflects the polarization changes resulted from electronic vibration. Due to its O_h symmetry of NaCl B1 structure of TiN, Raman scattering is forbidden [18]. Because of the existence of defect-induced distortions in TiN synthesized by PVD, Raman spectrum can sensitively detect these distortions. And Raman spectrum is very popular in the field of hard coatings. Fig. 1 shows the Raman spectrum of TiN coating, from which we can see that the coating has three strong peaks at 213 cm^{-1}, 323 cm^{-1}, 557 cm^{-1} respectively, included in two bands at 200–350 cm^{-1} and 400–600 cm^{-1}, namely acoustic transitions at a range of 200–350 cm^{-1} (LA and TA) mainly caused by the vibration of Ti ion vacancies and optic model at 400–600 cm^{-1} (LO and TO) mainly caused by N ion vacancies vibration. W. Spengler et al. [19] studied the Raman spectra of different stoichiometric TiN_x films, and found that first order Raman scattering intensity of TiN_x film increased with the number of N vacancies. Compared with W. Spengler's results, we can see that the TiN_x films in this study are very close to stoichiometry ratio ($x \geq 0.95$).

Fig. 2 shows the XRD patterns of TiN film and stainless steel, the inset image of which is the magnified pattern at the 2 theta range of 41°–45°. In standard PDF card of TiN, the heights of three peaks of TiN, i.e. (111), (200) and (220), are 72.3, 100.0 and 44.4 respectively, that is to say that (200) plane at 42.7° possesses the highest peak, and nearly 1.5 times the height of (111) at 36.6°. From Fig. 2 we can see that the intensity of (111) at 36.6° is far stronger than any other peak, which indicates that TiN film has a (111) preferred orientation. The distortion caused by deficiency of N results in the shrink of interplanar spacing, which gives rise to the shift to low angle of XRD patterns. The similar phenomenon has also been observed in Raman spectrum, namely that the increase of first order of Raman spectrum implies the increasing of N vacancy.

From the results above we can conclude that stoichiometric TiN films with (111) preferred orientation were synthesized.

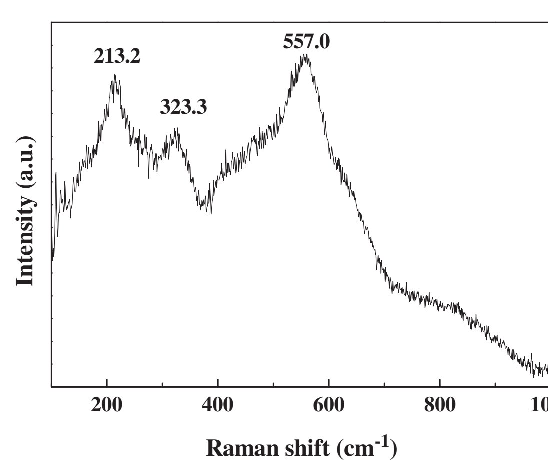

Fig. 1. Raman spectrum of TiN film.

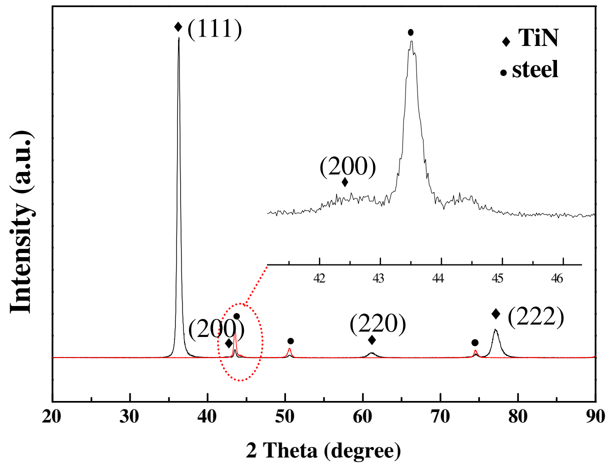

Fig. 2. XRD patterns of TiN film and stainless steel substrate.

3.2. Tribological performance

Considering that surface roughness has great influence on friction coefficient, AFM was performed firstly to characterize the roughness of TiN films. Fig. 3 shows the AFM results of TiN film, from which we can see that the crystal is homogenous and dense, which acts as a protection outer layer. And the film possesses a smooth surface with a root-mean-square roughness of 32.6 nm, which is beneficial to reduce friction coefficient.

Fig. 4 is the fluctuation of friction coefficients with time of TiN films and substrates under different normal loads in artificial saliva. We can see that friction coefficients decrease with the increasing of applied normal load. And the friction coefficients of TiN are lower than that of substrates, even when the load is 5 N for TiN and 10 N for substrate. This indicates that friction coefficients reduced significantly after coated TiN films, which is more favorable to orthodontic applications. The average coefficients are 0.079, 0.035, 0.028 and 0.023 from high to low, which is shown in Fig. 5. Friction coefficients increase inversely with applied normal loads can be explained by non-Amontonian phenomenon [20]. With the increase of applied normal load, the asperity number of specimens contacted with counterpart increases, which enlarges the contact area, and makes the increase ratio of contact stress at large load smaller than that at small load, thus the increase ratio of tested frictional force becomes smaller than that of load, so the friction coefficients decrease. Due to the fact that TiN is harder than counterpart, transfer film will form on TiN surface to make TiN smoother, and the friction coefficients will decrease. While the hardness of substrate is close to the counterpart's, there will be no transfer film but wear debris forming in the friction testing process, which will accelerate wear. Moreover, countered with a material with similar hardness (especially when the hardness is not so high) will cause viscous friction, so the friction coefficients of stainless steel substrate are higher than that of TiN. No significant wear was detected by the electronic analytical balance after friction test, implying satisfied wear resistance for orthodontic applications of these specimens.

3.3. Corrosion resistance

The surface oxidation of transition metal nitrides has great impacts on their wear resistances, and once the molar ratio of oxide to nitride is large, the stress of the films will increase sharply, which will result in cracking or flaking [18]. Moreover, the corrosion of films will lead to the release of toxic substrate elements, which gives rise to poisoning or allergy. So it is never too essential to study corrosion resistance.

Open-circuit test of TiN and substrate in artificial saliva at 37 °C was curried out prior to linear sweep test. Testing duration was set as 200 s, and when the potential difference was lower than 2 mV, the average potential was set as self corrosion potential. The open-circuit potential of TiN is about −0.016 V, while substrate is −0.105 V. Just from the perspective of open-circuit potential, open-circuit potential of TiN is more positive, and close to 0 V, so the tendency to corrosion is smaller for TiN without applied current. It is not solely open-circuit potential that matters, the requirement is rather severe for the application to orthodontics due to the complex bio and chemistry environment of oral cavity. The corrosion performance at higher potentials must be studied. Linear sweep test can be conducted to study the corrosion performance at a range of applied potentials.

Fig. 6 is the anodic polarization plots of TiN and substrate in artificial saliva at 37 °C. The initial potentials were set as the open-circuit potential acquired by open-circuit technique, from which to a positive 2 V was the testing range, and the scan rate was 1 mV/s. We can see that the currents of TiN and substrate are steady at the beginning of the curves (usually define it as passivation range), and can hardly see the activation process, indicating that the surfaces of these specimens were totally passivated after immersed in artificial saliva for 24 h. Currents started to rise at a certain potential, which is called transpassivation potential, indicating that pitting starts at this potential. The transpassivation potential of substrate is 0.75 V, while the passivation range of TiN is not so steady, the cross point (about 0.7 V) of tangent with potential axis was set as the transpassivation potential of TiN as the blue dashed line showed. Then the passivated range of TiN can be defined as 0–0.7 V. As mentioned above, oral cavity is a complex environment, but the potential in it is not exceeding 0.6 V [21] as the green dash line shows. Though the transpassivation potential of TiN is a litter lower than that of stainless steel substrate, it still satisfies the requirements of orthodontic applications.

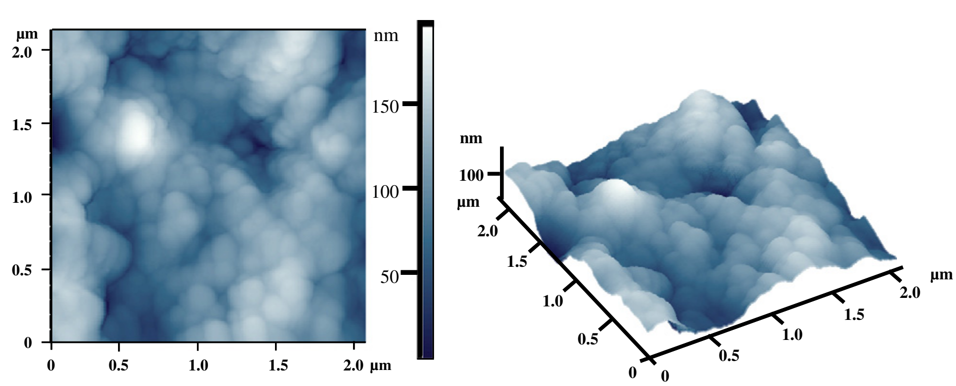

Fig. 3. AFM results of TiN film.

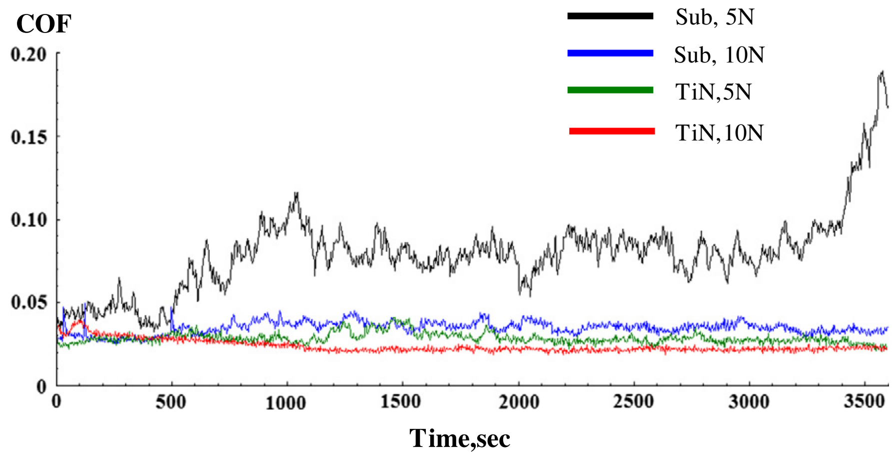

Fig. 4. The COF — time plot of TiN and substrate in artificial saliva under 5 N and 10 N.

Another important factor is the adsorption property of the orthodontic materials for the sake of hygiene. The adsorption of food debris will on one hand dramatically change the pH value near the brace, and on the other hand bring about bacterial growth, which will accelerate the corrosion of the brace and the demineralization of teeth. Electrochemical impedance spectroscopy (EIS) was carried out to assess the adsorption performance.

Fig. 7 shows the Nyquist plot of bare substrate and TiN coated SS, and Fig. 8 is the corresponding Bode plots. Similar to anodic oxidation plot, larger semi-circle radii of bare substrate indicates larger electric resistance than TiN coated substrate, which can be ascribed to the porous characteristic of PVD TiN film. Only one circle can be seen in the figure, indicating no obvious adsorption of particles in artificial saliva, which is considerably suitable for orthodontic applications. The Bode plot shows that there were two time constants in TiN coated bracket, while only one time constant can be visibly defined in bare substrate, indicating the porous surface character of TiN and a closed stacked outer layer of bare substrate.

3.4. Biocompatibility

Fig. 9 shows the average cell number of these specimens, from which we can see the cell number on each surface differed slightly due to the fact that most cells were still in dormant state in the first 2 days' culture. Cell number on TiN surface was more than other samples after 3 days, but there were no significant difference ($p > 0.05$). This result implied that there were no obvious promotions for cell proliferation for each specimen.

Fig. 10 shows the TNF-α mass detected in nutrient solution after cultured for 72 h. The data acquisition interval is 5 min, and started at 25 min. By detecting TNF-α mass, we can characterize the activity and anti-allergic performance of cells. As shown in Fig. 11, the mass of TNF-α increased with time. The mass of TNF-α detected in nutrient solution culturing TiN is the largest and commercial stainless steel the second. Significant difference was observed between them ($p < 0.05$), implying that TiN contributes to the excellent activity of cells. Scarano et al. [22] claimed that TiN can prevent the adherence of bacteria to decrease bacteria-induced tissue lesions. Meanwhile, Enamel demineralization and white spot lesions (WSL) also stem from bacteria accumulation around braces and the decrease of pH value. These two complications can be significantly reduced by coating TiN film [23,24].

3.5. Mechanical properties

Through all these tests, we can find that the corrosion resistance, wear performance and biocompatibility meet the acquirements for orthodontic applications. But some mechanical properties such as adherence, hardness and elastic modulus, are also of great importance to orthodontic applications. Great adherence is the premise of any application, and appropriate hardness and elastic modulus serves as a guarantee to an ideal lifespan. Ultranano-indentation was used to characterize hardness and elastic modulus. Considering that TiN film is far harder than stainless steel substrate, to reduce substrate effect,

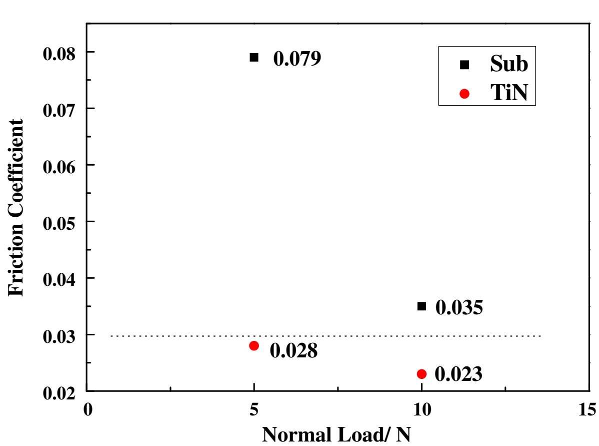

Fig. 5. Average friction coefficients of TiN and substrate.

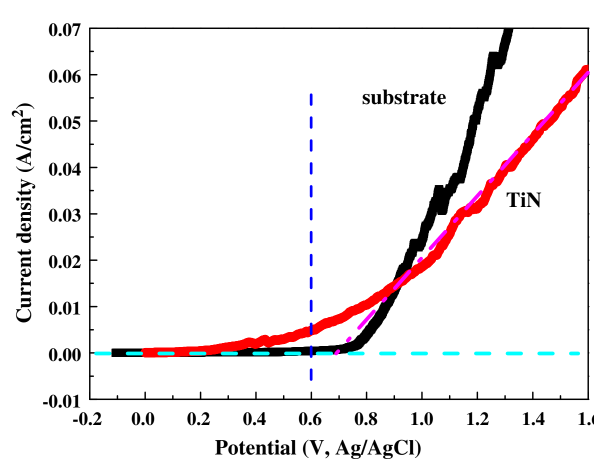

Fig. 6. Anodic polarization plot of TiN and substrate in artificial saliva at 37 °C.

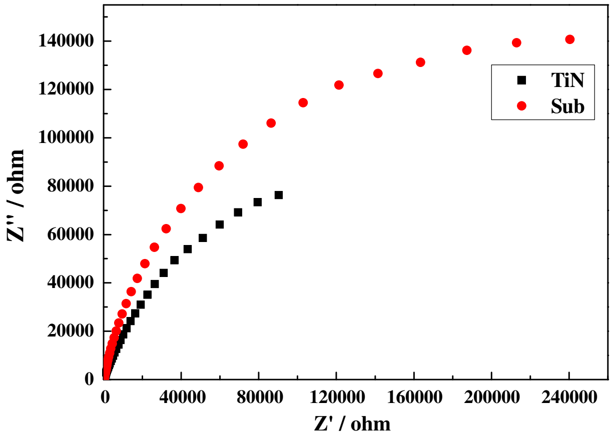

Fig. 7. Nyquist plots of bare substrate and TiN coated stainless steel.

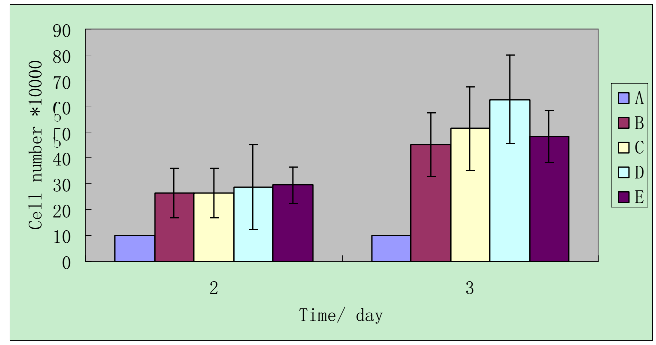

Fig. 9. Cell number on different surface after cultured for 2 and 3 days: A) original cell number, B) rough stainless steel bracket, C) commercial bracket, D) TiN coated bracket, and E) Cu.

indentation displacement should not exceed 1/10 the thickness of film, so cross-section SEM was applied to observe the thickness of TiN film previous to ultranano-indentation test. Cross-section SEM (Fig. 11) shows that dense, homogeneous TiN film (as demonstrated in Fig. 3) with a thickness of about 2 μm was obtained by this means, which is in the best thickness range of Hai et al. [25]. Fig. 12 shows the displacement change with applied load. The maximum displacement at maximum applied load of 10 mN is 150 nm, which is smaller than 1/10 the thickness of TiN film, guaranteeing substrate effect can be negligible. The hardness and elastic modulus figured out by this method was 14.62 GPa and 95.69 GPa respectively. Micro-scratch test shows the critical load was 11.08 N, which is big enough for orthodontic applications.

3.6. Discussion

As for orthodontic materials, many performances should be taken into consideration besides biocompatibility. In a complex environment like oral cavity, more or less relations may exist among each property. Superficially, corrosion resistance only affects the stability of the material, but toxic elements will gradually released once corroded, imperiling health. In the same way, wear resistance also has influences on lifespan and orthodontic effect, as well as biosafety. Once worn, the wear rate would be accelerated, and toxic element released. Moreover, as mentioned above, too great friction coefficient will also cause many periodontal complications. Meanwhile, hardness and elastic modulus as well as surface roughness are the main factors related to friction performance. Adherence also affects biosafety due to its influence on stability of the film. In a whole, what matters is not only a single factor, but a series of properties. Considering the integration of perfect corrosion resistance and biocompatibility, high hardness, modulus and wear resistance, TiN film was chosen to be deposited on stainless steel, and satisfied results were acquired. In fact, many of the properties above have been discussed, but no systematic research was found to study the feasibility of TiN used to orthodontic applications. Inert as TiN is, the porous character of PVD TiN films dramatically deteriorates the corrosion resistance, as anodic polarization plots and EIS plots shows (Figs. 7 and 8), the open circuit potential of TiN coated specimen was more positive than uncoated one, indicating the inert nature of TiN film. But from the perspective of the total impedance, corrosion current density and break potential, TiN coated one was inferior to the uncoated one in corrosion resistance due to the penetration of aggressive electrolyte through the defects of TiN film. One effective way to reduce the penetration is to add transition layers between active substrate and TiN outer layer. Metallic or metallic nitride transition layers are of great popularity. Titanium and chromium are preferred as transition layer for their superior corrosion resistant dense oxide layer formed on the surfaces. Chenglong Liu et al. [26]. compared the corrosion resistance of bare NiTi, multilayered Ti/TiN and single layered TiN in artificial saliva, and multilayered Ti/TiN exhibited the best corrosion resistance and single layered TiN the worst, which shows the similar results to the present work, and can be ascribed to the permeable porous surface character of PVD TiN film, thus occluded cells forming. While the multilayered coating could redistribution of corrosion current due to mild interphase corrosion and reduce current concentration at the pinholes. Nevertheless, nitride coatings formed on the Ti–6Al–4V shows the better corrosion resistance than bare substrate [27–29], and even better than TiAlN/TiAlCrN multilayer [27], which may due to the less aluminium content of monolayered TiN. Moreover, many researches also found that TiN layer can effectively protect the metallic substrate from corroding in aggressive solutions [30]. It seems that a controversial conclusion can be drawn. Or rather, nitride layer with different structure was obtained. Different deposition parameter makes the film different in porosity and crystallite size, which will dramatically affect the corrosion performance of TiN coating. In present study, TiN coatings with kinds of defects such as cavities, pinholes, droplets and clusters were deposited,

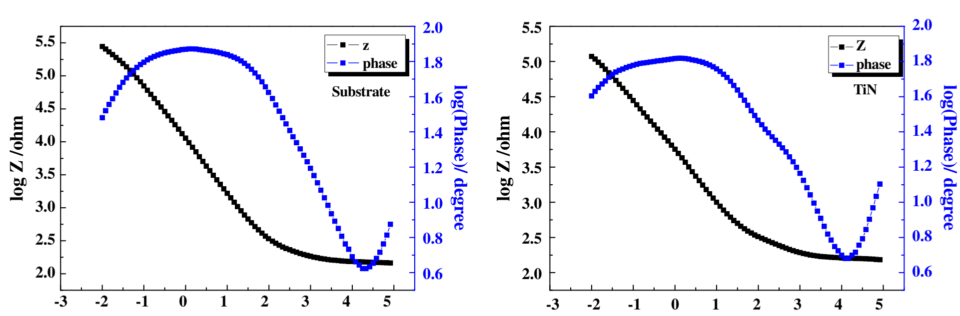

Fig. 8. Bode plots of bare substrate and TiN coated stainless steel.

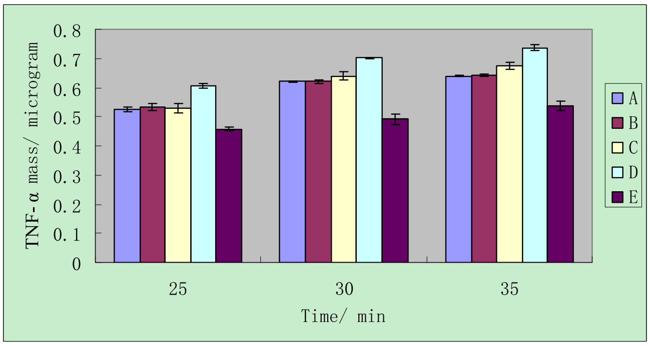

Fig. 10. TNF-α mass detected in nutrient solution after cultured on different materials for 72 h: A) blank control, B) rough stainless steel bracket, C) commercial bracket, D) TiN coated bracket, and E) Cu.

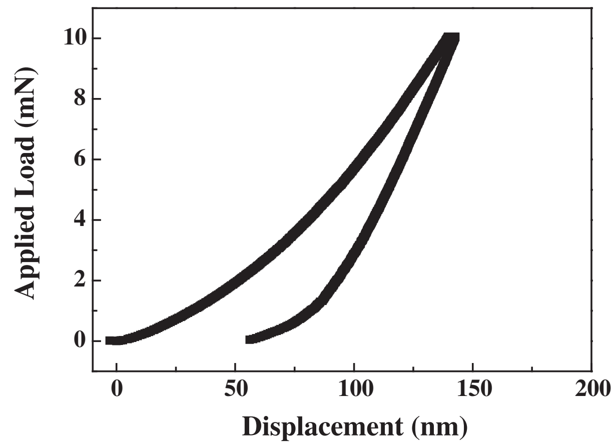

Fig. 12. Nanoindentation curve of TiN film.

the porosity of which was pretty large, resulting in less corrosion resistant. One thing must be pointed out is that the corrosion resistance of TiN coating is quite well, though a little inferior to substrate. Researches on the friction performance of TiN pointed out that a TiN layer can significantly reduce the friction coefficient and wear rate of stainless steel. In this work, super low friction coefficient and wear rate was detected, which makes it fairly suitable for orthodontic applications. Though DLC have lower friction coefficient than TiN [31], the beautiful golden color of TiN will win the choice of patients. The stress corrosion will also reduce under low applied load because of low friction coefficient.

On the other hand, high hardness and elastic modulus can reduce wear in friction process, thus reducing the release of toxic elements in substrate, prolonging the lifespan and ensuring the safety. Great adherence ensures the stability of TiN coated brackets, and it can be ascribed to the rough substrate surface and proper fabrication method. Rough surface, on the one hand, improves the surface energy of substrate, resulting in higher nucleate rate and denser TiN film, on the other hand, enhances the mechanical adherence of film and substrate. Meanwhile, low deposition temperature can also reduce the thermal stress induced by the mismatch of thermal-expansion coefficient of film and substrate, reducing cracking and flaking of films. What is more, the adoption of pulse-bias also enhanced the adherence. Most importantly, TiN synthesized in this work can also serve as prosthesis or other artificial joint for its low friction and high hardness.

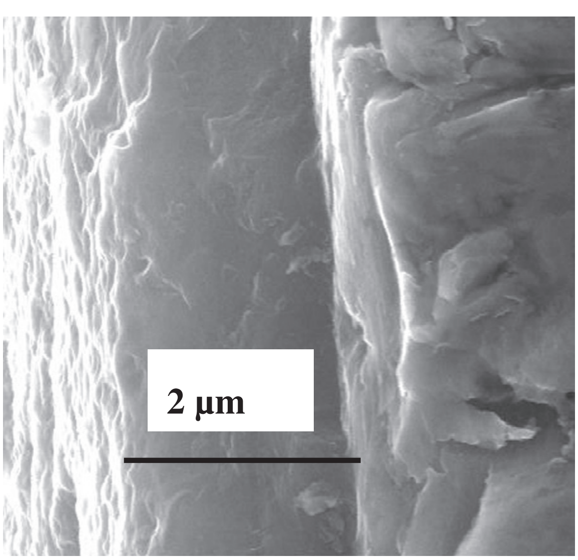

Fig. 11. Cross-section SEM of TiN film.

4. Conclusion

TiN films with (111) preferred orientation and a thickness of about 2 μm were fabricated on 316 L SS plates and brackets using multi-arc ion planting method. Super low friction coefficients (<0.03) of the samples were detected in artificial saliva. Cell proliferation test showed no significant promotion between TiN coated and uncoated SS. TNF-α amount tested by ELISA was far more than that of stainless steel, indicating better biocompatibility, especially anti bacterial property of TiN coated samples, and there were statistical differences. Though the corrosion resistance of TiN is not so great as stainless steel substrate, it still meet the requirements for orthodontic applications. Ultrananoindentation test indicated that the hardness and elastic modulus of TiN film are 14.62 GPa and 95.69 GPa respectively. The adherence obtained form micro-scratch was 11.08 N, which provided a solid guarantee for its stability. And TiN film has absorbing golden color. Overall, it is an ideal coating material to modify SS used in orthodontics.

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