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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 ultrananо-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 μmol·L^{-1} of β-mercaptoethanol, 100 units·mL^{-1} penicillin, 100 μg·mL^{-1} streptomycin, and 2 mmol·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.

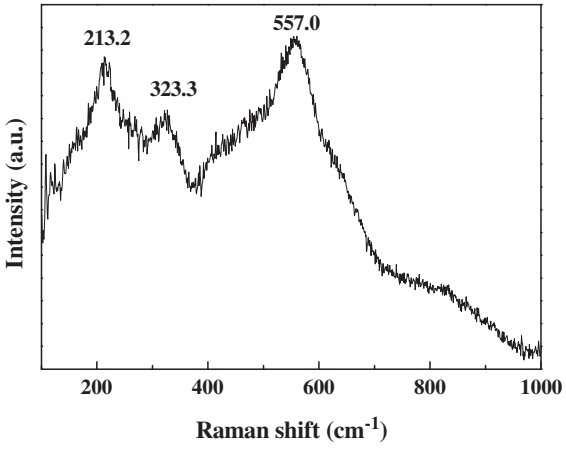

Fig. 1. Raman spectrum of TiN film.