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Materials Letters 59 (2005) 3813 – 3819

materials letters

www.elsevier.com/locate/matlet

Corrosion resistance and hemocompatibility of multilayered Ti/TiN-coated surgical AISI 316L stainless steel

Liu Chenglong [a,b], Yang Dazhi [a,b,*], Lin Guoqiang [b,*], Qi Min [a,b]

[a] *Department of Materials and Engineering, Dalian University of Technology, Dalian Linggong Road 2, 116024, PR China*

[b] *State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian University of Technology, Dalian 116024, PR China*

Received 1 March 2005; accepted 27 June 2005
Available online 2 August 2005

Abstract

Ti/TiN-multilayered films were prepared on surgical AISI316L stainless steel by arc ion plating. The crystallographic orientation and surface morphology were studied using XRD and SEM. The corrosion resistance of the coated specimen was evaluated by open-circuit test and potentiodynamic polarization test. It was found that the multilayered Ti/TiN-coated specimen had a weaker tendency towards corrosion and higher corrosion resistance in simulated bodily fluid than the bare substrate and the TiN-coated specimen. Additionally, in vitro hemocompatibility of the multilayered film and AISI316L was evaluated by dynamic clotting time and platelet adhesion experiments. The results indicated that for the multilayered Ti/TiN-coated specimen, the clotting time was lengthened and the adhesion and mutual interaction of platelets on its surface was also restrained.

Keywords: Ti/TiN-multilayered film; AISI316L stainless steel; Corrosion resistance; Hemocompatibility

1. Introduction

AISI316L stainless steel (AISI316L) has been widely used for biomedical implants, such as orthopedic, cardiovascular and dental devices. The success of implants in the human body depends on their biosafety, biocompatibility and biofunctionality in the environment where implants are placed in. But the body environment is rigorous, which may result in corrosion of implants, releasing particulate matter into the surrounding tissue, and causing malignant body reaction [1].

In recent years, the application of protective coatings for implants has been attracting considerable attention [2]. TiN film is an interesting choice for implants due to its useful properties, including chemical stability, high hardness, excellent wear properties, electrical properties and intrinsic biocompatibility. However, the difference of the deposition methods can have a marked effect on the chemical and physical characteristics of TiN films, including variations in preferred crystal orientation, mechanics, corrosion resistance, and also the biocompatibility of TiN [1]. Due to the presence of particles and pinholes in thin TiN films by arc ion plating, TiN coatings on orthodontic bracket in AISI316L as a corrosion-protective film could not provide good protection in acidic and neutral salt solution containing the chloride ion [3–5].

Many efforts have been devoted to solving these deficiencies by modifying the microstructure and morphology of TiN films. The surface of the TiN coating became smooth and the amount and size of the particles were also decreased by use of pulsed bias [6]. With a Ti intermediate layer, the corrosion resistance may be markedly improved [7]. Ti/TiN-multilayered coatings by a reactive magnetron sputtering have found many virtues, e.g., higher hardness, toughness, wear properties and good adhesion strength [8].

In this paper, we investigated Ti/TiN-multilayered coatings on surgical AISI316L stainless steel. The effect of multilayered coatings on improving the corrosion resistance in simulated bodily fluid and hemocompatibility of

* Corresponding authors. State Key Laboratory of Materials Modification by Laser, Ion and Electron Beams, Dalian Linggong Road 2, 116024, PR China. Tel.: +86 411 84708441; fax: +86 411 83638137.

E-mail addresses: dzyang@dlut.edu.cn (Y. Dazhi), gqlin@dlut.edu.cn (L. Guoqiang).

0167-577X/$ - see front matter
doi:10.1016/j.matlet.2005.06.058

AISI316L stainless steel was evaluated. In addition, the relationships between the hemocompatibility of Ti/TiN-multilayered film and its surface characteristics were discussed briefly.

2. Materials and methods

2.1. Preparation and characterization of coatings

The substrate material used in this study is surgical AISI316L stainless steel, which was cut into standard samples with the size of ϕ 12 mm $\times$ 2 mm. The substrates were grounded and polished to obtain a mirror-like surface, and then cleaned using an ultrasonic cleaner; first in acetone, and then in ethanol. TiN and Ti/TiN-multilayered coatings were deposited in a Bulat-6 AIP system using two 99.9% pure titanium targets [9]. The distance between samples and cathodic arc targets was about 240 mm. Prior to deposition, the substrate surface was cleaned by argon and titanium ion bombardment for 5 min under a vacuum at about 0.4 Pa and a negative substrate bias of 900 V. For the TiN deposition, argon and nitrogen were introduced in the vacuum chamber with a suitable flux. For the Ti/TiN-multilayered coating, the first layer deposited on the substrate was Ti and the last TiN. Argon plasma was used for the Ti layers and a mixture of argon plus nitrogen for the TiN layers. The deposition was performed under nitrogen partial pressure of 0.34 Pa and argon partial pressure of 0.5 Pa. The change from the Ti deposition to the TiN deposition was achieved by controlling the nitrogen flow, without plasma interruption. The following notation is used to identify the sample: multilayered Ti/TiN-coated AISI316L (composed of 22 layers of Ti and 22 layers TiN) and TiN-coated AISI316L.

The coating structures were analyzed by X-ray diffraction (XRD) using Cu Kα radiation. The cross section and planar morphology of the coatings were observed by JEOL-JSM-5600LV scanning electron microscopy (SEM) attached with EDX analyzer. The root mean square (RMS) roughness of the multilayered Ti/TiN-coated and uncoated AISI316L specimen was investigated by atomic force microscopy (AFM) on an equipment from Digital Instruments Inc., USA (Model Nanoscope IIIa), and scanning for recording topographical details was carried out in a force constant mode. Surface hydrophilicity was evaluated by measuring the contact angle using the sessile drop method by a JJC-1 contact angle geniometer. There, measurements were made and the average value had a standard deviation of $\pm 0.3°$ in θ.

2.2. Corrosion tests

Corrosion tests were carried out in the Tyrode's simulated bodily fluid (TSBF, pH = 7.4) at a temperature of 37 $\pm$ 1 °C. A sheet copper was attached onto the uncoated side of the specimen, which was cold-mounted by olefin with a 1-cm^2 monitoring area of the coatings. The testing process was carried out either with aeration or without aeration. The experimental setup consisted of a conventional three-electrode cell containing the working electrode, a saturated calomel electrode (SCE) and a platinum sheet as the counter-electrode.

The tests were performed by monitoring the free corrosion potential (E_{op}) as a function of time for specimens exposed to TSBF under open-circuit conditions for 6 h.

After 0.5 h immersion in TSBF, a fairly stable potential could be achieved, and then potentiodynamic polarization test was carried out at a scan rate of 1 mV/s. The initial scan potential was 100 mV below E_{corr}. The corrosion current density (i_{corr}) was estimated by linear fit and Taffel extrapolation to the cathodic part of the polarization curve.

2.3. In vitro hemocompatibility tests

The in vitro hemocompatibility was investigated by dynamic clotting time measurement and blood platelet adhesion tests.

For clotting time measurement, a dynamic method similar to the work described by Liu was used [10]. First, 0.1 ml of human blood anticoagulated by acid citrate dextrose was dripped on the specimen surface in an open atmosphere at room temperature (25 °C). Clotting was initiated by the addition of 10 μl of 0.2 M $CaCl_2$ solution. After 10, 20, 30, 40 and 50 min, each specimen was transferred into a breaker containing 50 ml distilled water. Then the optical density of the supernatant was measured at 540-nm wavelengths using a UV–Vis spectrometer. For each specimen, average optical density was obtained for three measurements. The relationship between the optical density and time was plotted as the clotting time curves, which would indicate the relative clotting time for each specimen.

Platelet adhesion experiments were conducted to evaluate the surface thrombogenicity of the materials and to examine the interaction between blood and the materials in vitro. The specimen was washed and then incubated in human platelet-rich plasma (PRP) for 30 and 60 min at 37 $\pm$ 1 °C, respectively. After incubation, the specimens were fixed in glutaraldehyde and critical point dried before gold sputtering, and then the specimens were prepared for examination in the scanning electron microscope. The morphology, aggregation and pseudopodium of the adherent platelets were examined to investigate the surface thrombogenicity. Ten fields of view were chosen at random to obtain good statistics.

3. Results and discussion

3.1. Coating characterization

The X-ray diffraction patterns of the TiN and Ti/TiN-multilayered coatings are shown in Fig. 1. The Ti and TiN peaks can be distinguished clearly.

Fig. 2 indicates the planar and cross section SEM morphology of the Ti/TiN-multilayered coating, respectively. There are many