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Electrochemical corrosion behavior of magnetron sputtered TiN coated steel in simulated bodily fluid and its hemocompatibility

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Abstract

Titanium nitride (TiN) films were deposited on AISI 316L stainless steel substrates by reactive magnetron sputtering using a Ti target. With the aim to improve the corrosion resistance an additional interlayer of about 5 μm thick brush plated nickel was deposited onto these substrates. Coatings were characterized by X-ray diffraction, which showed the presence of face centered cubic structure. Columnar growth of the film was observed from cross section SEM analysis. Platelet adhesion experiments were done to examine the interaction between blood and the materials in vitro. The low corrosion current density (I_{corr}) and rather high corrosion potential (E_{corr}) value implied that the TiN with Ni interlayer coated specimen in simulated bodily fluid displayed a good resistance to the tested condition.

Keywords: Thin films; Titanium nitride; Magnetron sputtering; Corrosion; Oxidation

1. Introduction

Hard coatings such as titanium nitride (TiN) and titanium aluminum nitride (TiAlN) coatings have been widely developed in many application fields such as cutting, forming tools, semiconductor devices, optical instruments, compressor blade of aero engines, diffusion and biocompatible barriers [1–5]. The TiN-coated Ti with sufficient biocompatibility compatible to Ti is promising as an implant material [6]. The TiN/Ti_2N containing layer provides new possibilities for producing non-toxic, human fibroblast — compatible surface layer on Ti alloy [7]. Fibroblast cells adhere more intimately to the surface of a TiN coated Ti substrate compared with an untreated Ti substrate [8]. Titanium aluminum nitride films were deposited on special dental alloys by reactive RF sputtering to modify the characteristics of nickel-based and chromium-based dental material [9].

TiN coatings are stable in aqueous solutions at anodic potentials considerably higher than their thermodynamic oxidation potential due to the formation of an N-riched layer on the surface [10]. However, the corrosion behaviour of thin PVD coating is often unsatisfactory as the hard layer is often not completely dense due to the defects in the coatings (such as pores, pin holes and cracks), which may be formed during deposition. These defects may create channels for the aggressive medium to attack the substrate, thus affecting the electrochemical behaviour of the coatings [11–13].

In this investigation, electrochemical corrosion behavior and hemocompatibility of DC magnetron sputtered TiN films with brush plated Ni interlayer on AISI 316L stainless steel substrates are reported.

2. Experimental

The layers of TiN were deposited on well cleaned AISI 316L stainless steel substrates using a dc magnetron sputter deposition unit HIND HIVAC. The purity of titanium target used for the reactive sputtering was 99.95%. The base vacuum of the chamber was below 1×10^{-6} Torr and the substrate temperature and power were kept at 400 °C and 300 W respectively. A high purity argon was fed into the vacuum chamber for the plasma

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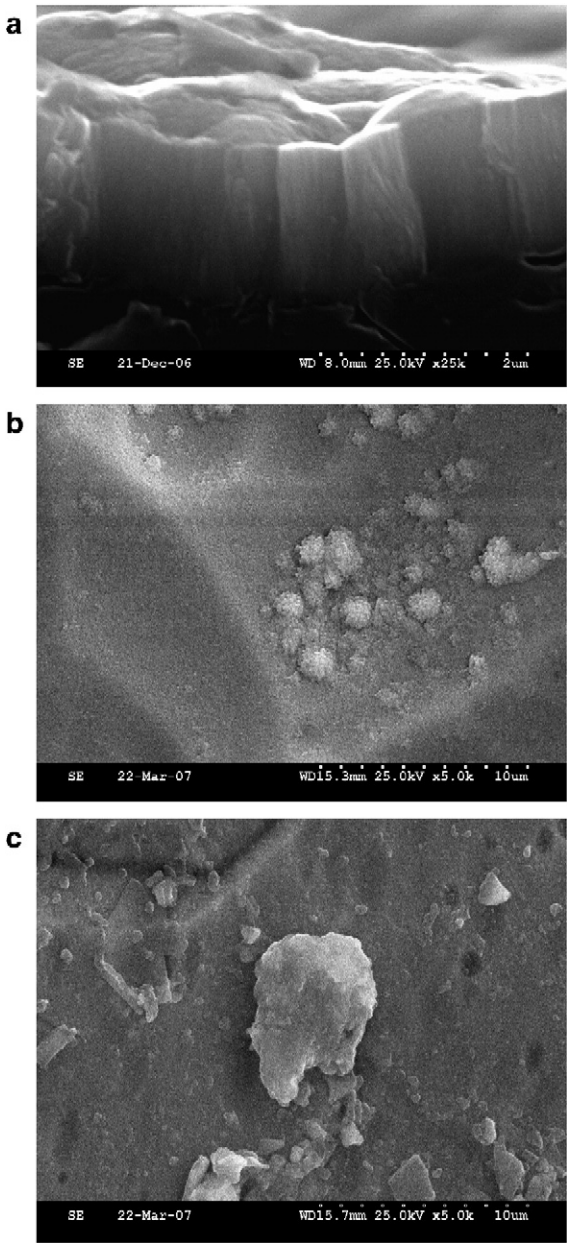

Fig. 1. SEM micrograph a) cross sectional view of sputtered TiN film on steel, b) morphology of the adherent blood platelets on the substrate, and c) morphology of the adherent blood platelets on TiN coating.

generation. The substrates were etched for 5 min at a dc power of 50 W and an argon pressure of 10 mTorr (1.33 Pa). Microprocessor controlled Selectron Power Pack Model 150A — 40 V was used to perform brush plating of Nickel onto the substrate. The schematic of the brush plating system is presented elsewhere [14]. The deposited films were analyzed for crystallographic structure with a X Pert Pro diffractrometer. The microstructure was examined using a Hitachi S 3000H scanning electron microscope. Platelet adhesion experiments were done to evaluate 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 60 min at 37 °C. After incubation, the specimen were fixed in glutaraldehyde and critical point dried before gold sputtering and then the specimens were prepared for examination in the Scanning Electron Microscope.

Electrochemical polarization studies were carried out using BAS IM6 Electrochemical analyzer. Experiments were conducted using the standard three-electrode configuration, with a platinum foil as a counter electrode saturated calomel electrode as a reference electrode and the sample as a working electrode. Specimen (1.0 cm^2 exposed area) was immersed in the test solution of modified Fusayama simulated bodily fluid [15]. Experiments were carried out at room temperature (28 °C). In order to establish the open circuit potential (OCP), prior to measurements, the sample was immersed in the solution for about 60 min. The anodic dissolution was determined by polarization electrochemical test, sweeping from −600 mV below the corrosion potential up to 2000 mV. The electrolyte used for the corrosion tests was 3.5% NaCl (pH 6). The tests were performed at room temperature. The scan rate was 50 mV s^{-1}. Saturated calomel electrode was used as reference electrode. Impedance measurements were conducted using a frequency response analyzer. The spectrum was recorded in the frequency range 10 mHz–100 kHz. The applied alternating potential had a root mean square amplitude of 10 mV on the open circuit potential. After getting the stable OCP the upper and lower potential limits of linear sweep voltammetry were set at +/−200 mV with respect to OCP. The sweep rate was 1 mV s^{-1}. The Tafel plots were obtained after the electrochemical measurements.

3. Results and discussion

3.1. Materials properties

The X-ray diffraction pattern obtained for the reactive magnetron sputter deposited titanium nitride films on AISI 316L SS with the Ar/N_2 ratio of 1:1 indicated a successful formation of TiN which have a face centred cubic crystal system with the lattice parameter of a=4.231 nm

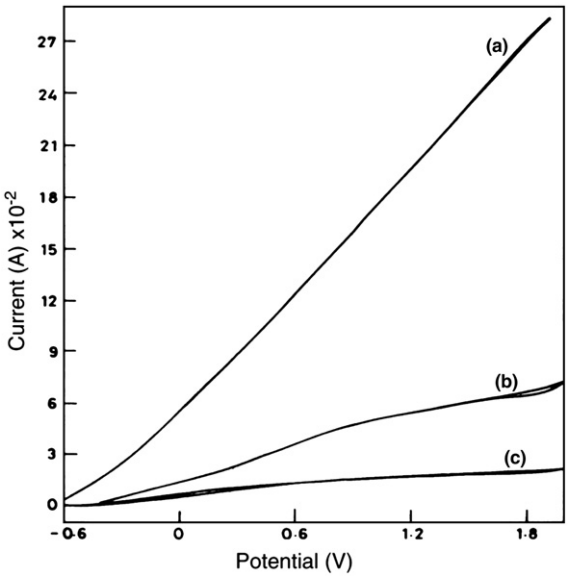

Fig. 2. Cyclic voltammetry of a) blank substrate, b) TiN, and c) TiN/Ni in simulated bodily fluid.

The observed d values are in very good agreement with the values reported by other investigators [16]. The cross sectional scanning electron micrograph of TiN film is shown in Fig. 1a. It is evident that the TiN film has a columnar structure with voids and boundaries throughout the film thickness. The morphology of the adherent blood platelets observed from SEM analysis is shown in Fig. 1b and c.

On the AISI 316L SS surface at 60 min incubation, the number of the adherent platelets is higher, with a higher degree of spreading and mutual interaction (Fig. 1b). Whereas the adherent platelets on the surface of TiN coating is fewer (Fig. 1c). The results indicate that the TiN coated specimen resulted in less activation of platelets and showed improvement of the hemocompatibility than the bare substrate.

3.2. Cyclic voltammetry, polarization and AC impedance spectroscopy

Anodic cyclic voltammetry curves of uncoated AISI 316L SS substrate, titanium nitride coatings on substrate and titanium nitride coatings with brush plated in interlayer on substrate are shown in Fig. 2a, b, and c. For the uncoated substrate, a continuous increase of the current density for the entire range of potential studied has been observed. A lesser rate of dissolution was showed by sample TiN with brush plated Ni interlayer showing the lowest current density for the entire range of potentials studied.

Typical polarization curves obtained for the corrosion behavior of the samples are shown in Fig. 3. Table 1 shows the results of corrosion testing for the AISI 316L stainless steel substrate, TiN, TiN/Ni (interlayer) in simulated bodily fluid. The corrosion potential of the AISI 316L SS substrate is about −0.291 V. The corrosion current I_{corr} of steel substrate is greater than those of TiN, TiN/Ni. For the TiN, the corrosion current is reduced to 0.01 A cm^{-2}, as indicated in Table 1. Impedance measurements were made at open circuit potential (OCP) applying an AC signal of 10 mV in the frequency range 10 Hz to 1 MHz.

The double layer capacitance C_{dl} value is obtained from the frequency at which Z imaginary is maximum

$$\omega\left(Z_{(im)}\ \max\right) = 1/C_{dl}R_{ct} \quad (1)$$

At higher frequencies the interception of real axis in the Nyquist plot is ascribed to the solution resistance (R_s) and at the lower frequencies, the interception with the real axis is ascribed to the charge–transfer resistance (R_{ct}). When the sample is immersed in the electrolyte the defects in the coating provide the direct diffusion path for the corrosive media. In this process the galvanic corrosion cells are formed and the localized corrosion dominates the corrosion process. R_{ct} and C_{dl} are related to the charge–transfer reaction at the electrolyte/substrate interface. The R_{ct} increases (Table 1) in the following order: steel substrate < TiN < TiN/Ni/substrate, which shows that TiN/Ni/substrate coating on steel substrate has higher corrosion resistance.

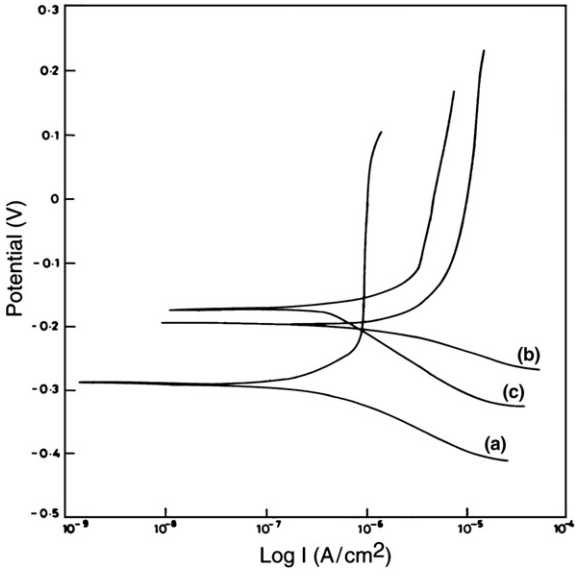

Fig. 3. Polarization studies of a) blank substrate, b) TiN, and c) TiN/Ni in simulated bodily fluid.

Table 1
Potentiodynamic polarization and electrochemical impedance data

Sample	E_{corr}	b_a	b_c	I_{corr}	Corrosion rate	R_{ct}	C_{dl}
	mV	V/dec	V/dec	A/cm^2	mpy	Ω cm^2	μF/cm^2
AISI 316L SS (substrate)	−0.291	1.4	−0.09	7.7×10^{1}	1.77	6.61×10^{3}	1210
TiN/substrate	−0.196	1.1	−0.11	6.9×10^{0}	1.21	2.03×10^{4}	1160
TiN/Ni/substrate	−0.174	0.2	−0.06	1.2×10^{-1}	0.21	2.64×10^{4}	530

4. Conclusions

In this study, we investigated the corrosion resistance and hemocompatibility of TiN coated AISI 316L SS for clinical applications. The structural analysis using XRD reveals that the films are polycrystalline in nature possessing face centred cubic structure. A dense columnar structure was observed from SEM analysis. The TiN/Ni/AISI 316L SS had better hemocompatibility than the bare substrate. Tafel plots in simulated bodily fluid showed that the corrosion rate for the specimens ranked as: AISI 316L SS (substrate) > TiN/substrate > TiN/Ni/substrate. The TiN/Ni coating on AISI 316L SS has improved the corrosion resistance, and had weaker tendency towards corrosion and lower passivation current density.

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