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Synthesis and electrochemical characteristics of Ta–N thin films fabricated by cathodic arc deposition

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Abstract

Ta–N thin films were deposited on AISI 317L stainless steel (SS) substrates by cathodic arc deposition (CAD) at substrate biases of −50 and −200 V. The as-deposited films were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDX). The results show that stoichiometric TaN with hexagonal lattice (3 0 0) preferred orientation was achieved at the bias of −200 V. On the other hand, Ta-rich Ta–N thin film deposited at −50 V shows amorphous nature. According to the XPS result, Ta element in the films surface exist in bonded state, including the Ta–N bonds characterized by the doublet (Ta $4f_{7/2}$ = 23.7 eV and Ta $4f_{5/2}$ = 25.7 eV). Electrochemical properties of the Ta–N coated stainless steel systems were investigated using potentiodynamic polarization and electrochemical impedance spectroscope (EIS) in Hank's solution at 37 °C. For the Ta–N coated samples, the corrosion current (i_{corr}) is two or three orders of magnitude lower than that of the uncoated ones, indicating a significantly improved corrosion resistance. Growth defects in the Ta–N thin films produced by CAD, however, play a key role in the corrosion process, especially the localised corrosion. Using the polarization fitting and the EIS modelling, we compared the polarization resistance (R_p) and the porosity (P) of the Ta–N coatings deposited at different biases. It seems that Ta–N film with comparatively lower bias (−50 V) shows better corrosion behavior in artifical physiological solution. That may be attributed to the effect of ion bombarding, which can be modulated by the substrate bias.

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Keywords: Tantalum nitride; Cathodic arc deposition; Microstructure; Corrosion

1. Introduction

Due to their comparatively low corrosion resistance in physiological environments, biomedical metals such as stainless steel, Co–Cr alloys, titanium and titanium alloys limit the longevity and the efficiency of prosthesis, especially the artificial joints [1]. Surface modification, as well as film deposition, has been proven as successful way to improve surface properties of biomedical metals such as hardness, coefficient of friction, wear resistance, corrosion resistance and biocompatibility [2,3].

For the last decade, tantalum nitride has been intensively investigated as a protective coating material in a wide variety of applications due to its high thermal stability, mechanical hardness, chemical inertness, stable electric resistivity and good corrosion resistance [4–7]. Previous attention has been focused on its applications in the mechanical and microelectronic industries. However, it may be of potential value in biomedical field. Leng and his group reported that tantalum nitride film showed better hemocompatibility than low-temperature isotropic pyrolytic carbon (LTIC), and asserted that it was a viable substitute for LTIC in artificial heart valves [8]. Concerned with its potential use, however, information about the corrosion properties of tantalum nitride in

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physiological solutions is still scarce. In this paper, we studied the in vitro corrosion resistance of tantalum nitride coated stainless steel in Hank's solution at 37 °C to evaluate its potential for use as a biomaterial.

Tantalum nitride has been successfully synthesized by several methods such as reactive sputtering [6], ion beam assisted deposition [7], low energy ion implantation [9] and chemical vapor deposition [10]. Cathodic arc deposition (CAD) is an effective technique to fabricate transition metal nitride films (TiN, CrN, ZrN, etc.) owing to its high ionization rate and plasma density [11]. Nevertheless, few attempts were released on the tantalum nitride films produced by CAD. In the present work, we have achieved tantalum nitride thin films on 317L stainless steel (SS) substrates utilizing this technique. Negative substrate biases (−50 and −200 V) were applied, which could not only ensure superior bonding strength between coatings and substrates, but also overcome the line-of-sight shortcoming.

2. Experimental procedures

A stainless steel (SS) AISI 317L was selected as the substrate in the present work. The chemical composition of the material is list in Table 1. The substrates were ground with silicon carbide papers, and finally polished to mirror-like with Al_2O_3 powders. Then they were ultrasonically cleaned in a bath in distilled water and ethanol for 15 min, respectively.

The Ta–N films were deposited by a self-made cathodic arc deposition system. Details of the deposition apparatus were presented in Ref. [12]. The cathode is 99.999 wt.% pure Ta, from which tantalum plasma was generated via the arc spot. The arc was operated at a current of 120 A. High purity (99.99 vol.%) N_2 gas was introduced into the deposition chamber through filament hollow cathode ion source. The substrates and silicon wafer (1 1 1) were mounted on a rotary sample holder in the vacuum chamber. The base pressure was 1×10^{-2} Pa. Prior to deposition, Ar ions sputter cleaning was performed with a negative dc substrate bias of 600 V. The deposition pressure were kept at 6×10^{-1} Pa and the substrate bias was maintained at −50 and −200 V. The film thickness was kept at 80–100 nm.

The crystallographic structures of the as-deposited Ta–N films were examined by X-ray diffractometer (XRD) (D/MAX-2400) using Cu Kα radiation. The composition and binding state of the films were analyzed by X-ray photoelectron spectroscope (XPS) (MKZ-VG, Al Kα 1486.6 eV) and energy dispersive X-ray analyser (EDX) (XL30 S-FEG). The scanning electron microscope (SEM) (XL30 S-FEG) was applied to observe the corrosion morphology of the sample after potentiodynamic polarization.

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were carried out in a conventional three-electrode cell, where three were a test sample as working electrode, a platinum sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode. And both tests were performed in unstirred Hank's solution without aerating. In order to simulate the physiological medium environment, Hank's solution was used as electrolyte and the temperature during the electrochemical measurements was kept at 37 °C. The ingredient of the electrolyte is shown in Table 2. The specimens were masked with epoxy in order to expose a constant surface area of 1 cm^2. The potentiodynamic polarization tests were behaved using an EG&Par PC controlled potentiostat/galvanostat system (Model 283) and M270 software. The potential of the electrode was swept at a rate of 2.0 mV s^{-1} from −1000 to 1500 mV versus SCE. With an ac sine wave amplitude of 5 mV applied to the electrode at its corrosion potential, impedance spectra were collected over frequency ranging from 10^{-2} to 10^5 Hz, using another EG&Par frequency response detector (Model 1025) and Eis M398 software. Prior to EIS tests, the samples were immersed in Hank's solution at 37 °C for 72 h.

Table 1
Chemical composition of the substrates (wt.%)

Steel	Element							
	C	Mn	P	S	Si	Cr	Ni	Mo
AISI 317L	0.03	2.00	0.045	0.03	1.00	18.0–20.0	11.0–15.0	3.0–4.0

Table 2
The ingredient of the Hank's solution used in the electrochemical tests

Component	Concentration (mol/L)
NaCl	0.1369
KCl	0.0054
$MgSO_4 \cdot 7H_2O$	0.0008
$CaCl_2 \cdot 2H_2O$	0.0013
$Na_2HPO_4 \cdot 2H_2O$	0.0003
KH_2PO_4	0.0004
$NaHCO_3$	0.0042
$C_6H_{12}O_6H_2O$	0.0050
pH	7.2

3. Results and discussion

Fig. 1 presents the XRD patterns of the as-deposited samples. For clarity, the curves have been offset vertically.

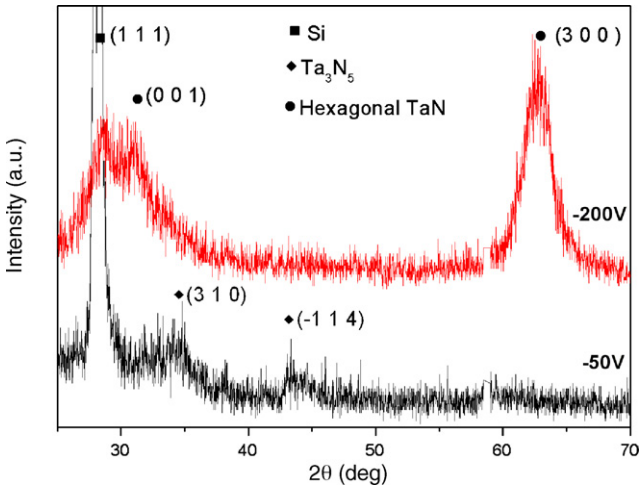

Fig. 1. XRD patterns of Ta–N films deposited at substrate biases of −50 and −200 V.