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Sputtered nanocrystalline ceramic TiC/amorphous C thin films as potential materials for medical applications

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Abstract

The relationship between structural behaviour of sputtered TiC/amorphous C (TiC/a:C) thin films and corrosion properties was measured in three various pH solutions (0.5 M NaCl (pH=6); 0.1 M HCl (pH=1); and 0.1 M NaOH (pH=13)). The ~400 nm thick nanocomposites were deposited by DC magnetron sputtering on different substrates (Ti6Al4V alloy and CoCrMo alloy) in argon at 25 °C and 0.25 Pa with 150 W input power of carbon target and 50 W input power of titanium target. The structure and composition of nanocomposites were investigated by Transmission and Scanning Electron Microscopy. In both samples the structural investigations confirmed columnar structure of TiC/a:C films with 25–50 nm sized cubic TiC. These columns were separated by 2–3 nm thin amorphous carbon layers. TiC/a:C /Ti6Al4V alloy implant material showed better corrosion resistance than the TiC/a:C/CoCrMo alloy in 0.5 M NaCl solution based on results of the Electrochemical Impedance Spectroscopy. For both samples, the 0.1 M NaOH solution was the most corrosive media.

Keywords: B. Nanocomposite; Ceramic TiC; Corrosion resistance; Structure

1. Introduction

CoCrMo and Ti6Al4V alloys are widely used as medical implants. These alloys exhibit excellent corrosion resistance, biocompatibility, high durability and strength [1–3]. Pure titanium undergoes an allotropic transformation from the hexagonal close-packed (HCP) alpha phase structure to the body-centered cubic (BCC) beta phase structure at a temperature of 882 °C [4]. Due to this structural change titanium alloys fall into three classes: α alloys, $\alpha+\beta$ alloys and β alloys. Different alloying elements can stabilize either the α (for example aluminium) or β phase (for example vanadium) [4–5].

The release of V, Al, Ti, Co, Cr or Mo into adjacent tissue has been detected based on several previous studies [6–8]. Research on Ti6Al4V alloy showed corrosion problems [9]. This problem can be solved with proper pretreatments before implantation. There are several methods to modify the surface of implant materials including ion implantation [10], sandblasting [11], the application of micro-rough Ti surfaces via Al_2O_3 sandblasting and acid etching (SLA), heat treatment and alkali treatment (SMART), hydrogen peroxide and heat treatment (SAOH), and potentiostatic anodization in sulphate electrolytes through constant electric current supply (ECH) [12]. Wen et al. [13] also used a simple chemical treatment, namely incubation in diluted alkali at 140 °C, while Hanawa [14] examined the effect of calcium ion implantation into titanium. In both cases, Ca–P deposition or precipitation was observed on the substrates.

Biomaterials must be nontoxic, non-carcinogenic, chemically inert, stable and mechanically strong enough to withstand the repeated forces during their lifetime. These conditions are achievable with producing a protective film or surface coating on metal devices [15]. Nanocomposite coatings consisted of nanocrystalline grains and amorphous matrix promises possibility of synthesizing a surface protection layer with an

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unusual combination of mechanical properties [16]. Titanium carbide (TiC) may be a potential candidate for such a surface protection coating which serves as a barrier layer because of its high mechanical hardness, excellent corrosion resistance and good biocompatibility [17–19]. The corrosion behaviour can be studied by potentiodynamic measurements and by Electrochemical Impedance Spectroscopy (EIS). EIS is a non-destructive and also one of the most appropriate techniques to characterize the corrosion behaviour of our materials [20].

In this work, the investigation of the composition and corrosion behaviour of the TiC/a:C coated and uncoated CoCrMo and Ti6Al4V alloys was studied by three solutions with different pHs applied at room temperature: acidic hydrogen chloride with pH of 1, basic sodium hydroxide with pH of 13 and close to neutral sodium chloride with pH of 6. The comparison of structural changes before and after corrosion tests was examined.

2. Material and methods

2.1. Purchased materials

The commercial Ti6Al4V and CoCrMo substrates were purchased from Protetim Ltd. with diameter 20 mm and thickness 2 mm. They were applied in this paper in "uncoated" (pristine) and "coated" forms. The coating procedure is described below. The commercial CoCrMo substrate is composed of 58.9–69.5% Co, 27.30% Cr, 5.0–7.0% Mo and limits on other important elements such as Mn, Si, less than 1% Fe, Ni and C [21]. One side (the one to be coated) of the samples was roughened using a sandblasting procedure with a 180 grit aluminium oxide media for better cell adhesion.

2.2. Thin film preparation

DC magnetron sputtering was used for deposition of ~400 nm thin TiC/a:C nanocomposite films on the above substrates at room temperature in argon 0.25 Pa (Fig. 1). The detailed preparation steps were described in our previous works [22]. The input power applied on the carbon target (99.999%, Kurt and Lesker) was 150 W, while that applied for the titanium target (99.995%, Kurt and Lesker) was 50 W. The sample–target distance was ~70 mm.

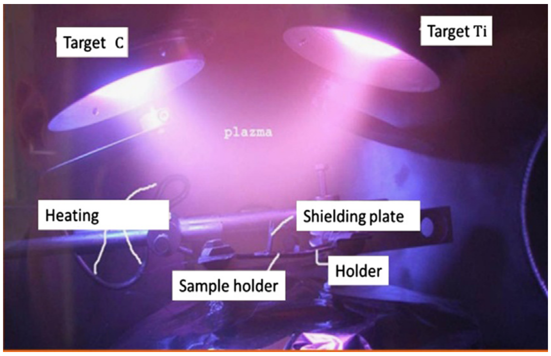

Fig. 1. Real image of DC magnetron sputtering equipment used for TiC/a:C thin films.

2.3. Structural characterization

All thin films were first mechanically thinned to ~50 μm. Then, they were further thinned till perforation by 6 kV Ar^+ ions from both sides. The thin damaged layer was removed by 2 keV Ar^+ ions. This procedure minimized the thermal load during sample preparation. Transmission Electron Microscopy (TEM, Philips CM-20, 200 kV) and High Resolution Electron Microscopy (HREM, JEOL 3010, 300 kV) equipped with an Electron Energy Loss Spectroscopy (EELS) were used for cross-sectional structural investigations of films and substrates. Surface morphologies of coated and uncoated substrates before and after corrosion tests were studied by Scanning Electron Microscopy (SEM-LEO 1540 XB). Selection Area Electron Diffraction (SAED) was used for the phase analysis.

2.4. Electrochemical tests

The potentiodynamic and electrochemical impedance measurements were carried out with Zahner IM6e electrochemical workstation (Zahner, Germany). The electrochemical potentiodynamic polarization tests were performed in a standard three-electrode-cell, at a potential scanning rate of $0.5\ \mathrm{mV\ s^{-1}}$ initiated at −200 mV below the open-circuit potential. During all measurements the atmosphere was open to air. The working electrodes were the metallic implant discs Ti6Al4V (ISO5832-3) and CoCrMo (ISO5832-12) with $1.37\ \mathrm{cm^2}$ active surface area with ("coated") and without ("uncoated") TiC/a:C coating. Platinum net electrode was used as counter electrode. Ag/AgCl/KCl_{sat} electrode was used as reference electrode. The electrolyte was 0.5 M NaCl solution (pH=6), 0.1 M HCl solution (pH=1) and 0.1 M NaOH solution (pH=13). The tests were started after a steady state open-circuit potential was attained (not more than ±5 mV drift within 5 min). The polarization curves were recorded after 30 min immersion time and they were characterized by the Tafel extrapolation method.

EIS was measured by open circuit potential of the working electrode in 0.9 wt% NaCl solution at room temperature by applying a 10 mV AC sine wave perturbation. During the EIS measurements, the frequency span was changed from 100 kHz down to 10 mHz. The investigated samples were initially immersed into solution and left at open-circuit for 30 min to stabilize the surface of specimen. EIS spectra were represented in both complex impedance diagrams (Nyquist plot) and Bode amplitude and phase angle plots. The imaginary component of the impedance is plotted as a function of the real component in the Nyquist graph, whereas the Bode representation shows the logarithm of the impedance modulus $|Z|$ and phase angle ϕ as a function of the logarithm of the frequency (f). All impedance data were fitted and analyzed using Zview2 software. In each case, it was necessary to set up an appropriate equivalent circuit to estimate the values of charge transfer resistance (R_{ct}). For this purpose, the impedance spectra were analysed using electrical equivalent circuit model which is shown in Fig. 2a.