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Corrosion Behavior of Ag-doped TiO_2 Coatings on Commercially Pure Titanium in Simulated Body Fluid Solution

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Abstract

TiO_2 films including different amounts of Ag obtained by sol-gel method on commercially pure titanium (CP-Ti) and the corrosion properties of Ag-doped TiO_2 films were investigated by potentiodynamic polarisation and Electrochemical Impedance Spectroscopy (EIS) tests in Simulated Body Fluid (SBF) solution. The results were compared with untreated and un-doped samples. Surface characterizations before and after the corrosion tests were performed by the Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) analysis. It was observed that Ag-doping for TiO_2 films improved the corrosion resistance when compared with untreated and un-doped TiO_2 film coated samples. The highest corrosion resistance was obtained from Ag-doped samples coated with a solution of 0.05 M Ag.

Keywords: TiO_2 coating, Ag-doping, corrosion, CP-Titanium, simulated body fluid

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1 Introduction

Titanium and its alloys are the very important and widely used metallic materials because of their high strength to weight ratio, good static and dynamic loading, excellent corrosion resistance, and easy fabrication[1,2]. Owing to their superior properties, titanium-based materials are frequently used in many industrial applications such as sports tool manufacturing, chemical, food, biomedical and aerospace industries. Among titanium-based materials, commercially pure titanium (Grade 2) is widely used as implant material, especially in hard tissue replacements such as hip and knee joints, fixation screws and dental implants in the body. Although titanium materials have many advanced properties, their hardness is insufficient and tribological properties are poor. Therefore, they are subjected to some problems in the service conditions and consequently, the service lives are restricted[3]. Hence, it is inevitable to apply a suitable surface treatment to reach desired surface properties. There are many surface modification methods such as plasma assisted thermo-chemical treatment, ion implantation, anodic chemical treatment, sol-gel coating and thin film deposition, which were performed to improve the surface properties of metallic materials in scientific literature[4–9].

Good mechanical and tribological properties along with desirable chemical inertness and high corrosion resistance are expected from the coatings for biomedical applications. Among these coatings, ceramic-based coatings are potential candidates for implant materials because of their high chemical stability and low permeability. Also, a bioactive coating can be used as a good binding interface between implant and bone. Kokubo and Takadama[10] pointed out that patite forms on suitable material surface in Simulated Body Fluid (SBF). Thus, this material bonds to living bone through this apatite layer. This relationship holds as long as the material does not contain a component that induces toxic or antibody reactions. Also, Cheng *et al*.[11] investigated the corrosion behavior of a biocompatible material as dicalcium phosphate dihydrate (DCPD) coating on AZ91D magnesium alloy in SBF. They determined the corrosion resistance by acid drop, electrochemical polarization, electrochemical impedance spectroscopy and immersion tests. They obtained that the DCPD coating

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on AZ91D magnesium alloy evidently slowed down the corrosion rate of the alloy in SBF. Also, it was determined that the hydrogen evolution rate decreased significantly after coating. High durability, low friction coefficient and self-lubricant properties of TiO_2 coatings endow their popular applications for various environments where the wear resistance is essential, for example artificial joints and dental implants[12–14]. TiO_2 films can be deposited with many coating methods such as Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), Micro Arc Oxidation (MAO), anodizing and sol-gel dip coating. Sol-gel coating is a very advantageous method because of its low cost, easy operation and rapid coating. There are some studies related to un-doped TiO_2 coatings and it was suggested that the calcination temperature was the most important coating parameter. R. Mechiakh *et al*.[15] indicated that TiO_2 crystallize structure transformed from anatase to rutile with increasing calcination temperature. Comakli *et al*.[9] stated that as calcination temperature increased, the structure of TiO_2 film changed and tribological properties improved. In recent years, doping has been an attractive method to gain some advanced properties of films. Wang *et al*.[16] proposed that the nitrogen-doped TiO_2 coatings could achieve higher corrosion polarization resistance and a more stable corrosion potential in the SBF environment than the uncoated samples. In another study, Arman *et al*.[17] prepared un-doped and S-doped TiO_2 thin films on titanium substrate through the sol–gel method. The photoelectrochemical behavior of S-doped TiO_2 thin film was studied and the results showed that S-doped TiO_2 thin film has better corrosion resistance. Fu *et al*.[18] applied Ag-containing TiO_2 films on surface roughened biomedical NiTi alloy and they showed that Ag-doping increased the surface hydrophilicity of the coated NiTi samples by reducing the contact angles. Ag has long been known as an effective antimicrobial and antibacterial material as well as low toxicity towards cells[19–21]. Wu *et al*.[22] investigated antibacterial effects and corrosion resistance of Cu-TiO_2 films deposited with MAO. They found that the Cu–TiO_2 coatings exhibit excellent antibacterial activities, and the antibacterial rate gradually rise with the increase in Cu concentration in the films. The Ag ion-implanted TiO_2 films would provide a new possibility to be good candidates for anti-bacterial materials due to their unique structures. Also, the TiO_2 films would protect Ag ions and stabilize them against chemical corrosion[23].

Although the good anti-bacterial and anti-microbial properties were reported, the film integrity and structure, amount of doped material and corrosion resistance which are of importance for their biomedical applications have been rarely studied. In practical applications, commercially pure titanium (CP-Ti) material is especially preferred for dental implants. Longer service lives for implant materials are important because of both cost and patient physiology. Therefore, in this study, the efficiency of hard and wear resistant Ag-doped TiO_2 ceramic-based coatings was investigated on corrosion resistance of this implant material. Moreover, the effect of doped Ag amounts on corrosion performance of TiO_2 films was investigated using potentiodynamic polarisation and Electrochemical Impedance Spectroscopy (EIS) tests, in SBF solutions.

2 Experimental details

2.1 Material

The chemical composition of CP-Ti used as substrate is given in Table 1. Prismatic samples with dimensions of 25×25×5 mm^3 were polished using SiC emery paper with 600–1200 mesh grit and then polished with 0.3 μm and 0.5 μm alumina powder. Finally, the surfaces of samples were cleaned by ethanol.

2.2 Manufacturing of un-doped and Ag-doped TiO_2 films and coating method

The chemicals were titanium tetraisopropoxide (TTIP) as precursor, isopropanol as solvent and Ag nitrate ($AgNO_3$) as doper. For un-doped TiO_2 solution, the ratio of TTIP: isopropanol was 1:81. Isopropanol was set in a beaker. TTIP was added in this beaker by dropwise with strong stirring under vacuum in nitrogen atmosphere and at room temperature. The solution was stirred continuously with magnetic stirrer approximately an hour. Then, the solution was left in vacuum without stirring for 24 hours. For Ag doped TiO_2 solution; the above method was used exactly. 0.5 g, 1.0 g and 1.5 g of $AgNO_3$ were dissolved in 9 ml of distillated water respectively. Then this solution was added into above

Table 1 Chemical composition of CP-Ti (wt%)

Substrate	Ti	C	Fe	H	N	O
CP-Ti (Grade2)	99.2	Max. 0.1	Max. 0.3	Max. 0.01	Max. 0.03	Max. 0.25