Journal of Materials Science & Technology 31 (2015) 873–880

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Corrosion Behavior of Reactive Sputtered Al_2O_3 and ZrO_2 Thin Films on Mg Disk Immersed in Saline Solution

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ARTICLE INFO

Article history:
Received 25 March 2015
Received in revised form
5 May 2015
Accepted 16 June 2015
Available online 30 July 2015

Key words:
Magnetron sputtering
Magnesium
Aluminum oxide
Zirconium oxide
Porosity

Magnesium has attracted a lot of attention over the last few decades due to its light weight and potential use as biomaterial. However, the poor corrosion resistance of magnesium restricts its practical use for application where exposure to aggressive aqueous media is unavoidable. This paper describes the growth, characterization and corrosion analyses of Al_2O_3 and ZrO_2 thin film coatings aimed at slowing down the fast degradation of Mg in saline solution. In this study, different thicknesses of Al_2O_3 and ZrO_2 were deposited on pure magnesium (99.95%) disk using pulsed-DC reactive sputtering process. The microstructure and phase analyses were performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The corrosion protection behavior of the Al_2O_3 and ZrO_2 coated magnesium samples immersed in 0.9 wt% NaCl solution were evaluated using electrochemical measurement techniques, such as open-circuit potential (OCP), potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS). The microstructural analyses showed that the Al_2O_3 thin film coatings have circular grains between 5 and 25 nm, while the ZrO_2 coatings have bigger ellipsoidal grains. The results from the electrochemical corrosion analyses showed that the Al_2O_3 coated Mg disk had corrosion resistance of approximately 3 times that of ZrO_2 coated Mg disk. It was also observed that increasing the thickness of the Al_2O_3 coating improved the corrosion resistance of the Mg disk. These results suggest that Al_2O_3 and ZrO_2 coating can be used to effectively control the fast degradation of magnesium for medical implant applications.

1. Introduction

Biodegradable metallic implants are beginning to breakdown the paradigm of using only highly corrosion-resistant metallic implants for surgical procedures[1,2]. They eliminate the need for revision surgeries and enable post-operative diagnostic imaging[3]. However, the corrosion rate of magnesium is very high, seriously limiting its use as metallic implants[4,5]. Over the last few decades, several efforts have gone into developing various alloying and coating techniques to control the degradation of magnesium[6]. So far, a number of studies have been reported about identifying the potential alloying elements that can improve the corrosion resistance, mechanical and biological properties of magnesium[7–9]. In recent years, various surface modification techniques are also being explored[10–13]. Some of the most common techniques include plasma electrolytic oxidation (PEO)[10,11], sputtering[14], plasma spraying[15], sol-gel[16] and organic coating[17]. While PEO is one of the most popular methods among these techniques[11], sputtering is gaining reputation due to the control over thickness, porosity and quality of coating in submicron level[18].

The main purpose of magnesium based implant is to provide temporary structural support[2]; therefore, slowing down its degradation rate may require a degradable protective coating whose survivability can be accurately predicted. Although much progress has been made in the application of coating for controlling the degradation of magnesium, there are no reports on the predictability of the degradation of these coatings. Most researchers report improved corrosion properties of coated compared to uncoated magnesium[17,19] without necessarily predicting how long the coating will stay on the magnesium substrate. Wu et al.[20] showed that Al_2O_3 and TiO_2 developed using electron beam evaporation can significantly improve the corrosion resistance of AZ31. They showed that the films' compositions deviated from the standard stoichiometric ratios. Their results suggested that Mg diffused into films and existed as magnesium oxide in the TiO_x film as well as the AlO_x film[20]. Xin et al.[21] also reported an improved corrosion resistance of AZ91 using 1 μm thick Al_2O_3/Al bilayer coatings developed by filtered arc cathodic deposition. They reported 2 orders of improvement in corrosion current density and also showed improvement in the polarization resistance over 18 h[21]. This suggests that Al_2O_3 coatings are

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http://dx.doi.org/10.1016/j.jmst.2015.07.020

excellent candidates for long term protection of biodegradable Mg implants.

While much progress has been made in developing protective coating for preventing the corrosion of biodegradable magnesium, there are increasing concerns about the coating survivability and the size of the corrosion products generated after its degradation. Previous studies have shown that corrosion resistance coatings that do not dissolve in simulated body fluids can cause foreign body reaction and/or inflammation which may ultimately lead to implant failure[22]. In the present study, we are exploring the thin film coatings with well controlled thickness and porosity whose corrosion products are small enough to prevent any foreign body reaction by the body. It is also worth mentioning that, there are some applications that require improved corrosion properties during handling and a couple of hours after installation. These thin film coatings can control the initial high local concentration of Mg^{2+} ions and hydrogen evolution a few hours after Mg implantation.

In this study, Al_2O_3 and ZrO_2 thin film coatings were fabricated on pure magnesium disk using pulsed DC reactive sputtering technique. The aim of these thin film coatings is to control the initial degradation of magnesium devices during handling and installation. Electrochemical corrosion techniques were employed in evaluating the degradation rates of the protective coating on magnesium disk immersed in saline solution. Morphological and cell proliferation test conducted by Wang et al.[15] showed that monoclinic ZrO_2 coating improved cell proliferation, and Webster et al.[23] demonstrated that nanophase Al_2O_3 was biocompatible.

2. Experimental

2.1. Material fabrication

The oxide coatings were prepared by reactive sputtering from pure metallic targets (Al and Zr) using an AJA International, Inc. Model ATC 1800 F magnetron sputtering system. Argon and oxygen were used as the sputtering and reactive gas, respectively. The flow rates of the gases were controlled using programmable gas flow controllers. The O_2/Ar flow ratio optimization study was done by varying the oxygen flow rate from 0.0 to 3.0 sccm. To eliminate the instabilities in the reactive sputtering process, the oxide coatings were sputtered at a frequency of 250 kHz with an Advance Energy Model Pinnacle Plus+ 5 kW pulsed DC power supply. Commercially-acquired amorphous glass slides (dimensions 30 mm × 22 mm × 0.5 mm) and polished high purity 99.97% Mg (Goodfellow, Germany) disks were used as substrates. The amorphous glass substrates were used for optimization processes and specific characterization task that required elimination of the magnesium substrate effect.

The glass substrates were cleaned in acetone and ethanol, followed by plasma cleaning for 20 min. The magnesium substrates were polished progressively with SiC paper from grade #400 up to grade #1200 using isopropyl alcohol as the lubrication fluid. The polished samples were etched in nital (methanol:nitric acid in the ratio 2:1). Prior to depositions, the substrates were cleaned *in situ* using Ar^+ ion bombardment for 5 min. The Al and Zr targets were pre-sputtered for 2 min to remove their contaminated surface layers and stabilize the surface conditions.

The ratio of oxygen to argon flow for reactive sputtering of Al_2O_3 and ZrO_2 coating were optimized by varying the oxygen flow rate in the chamber, while maintaining the argon flow at 20 sccm. The thicknesses and optical property of the deposited films were analyzed using a stylus profilometer and an optical microscope (Zeiss AxioImager M2m), respectively. The range of oxygen flow and the power used for depositing the oxide coatings are shown in Table 1.

Table 1
Deposition parameters for oxygen content optimization

Material	Range of oxygen flow (sccm)	Power of deposition (W)	Number of samples
Al_2O_3	0–2.0	150	8
ZrO_2	0–2.5	100	18

2.2. Thin film characterization

The surface morphology and crystalline structure of the films were investigated by scanning electron microscopy (SEM, Hitachi SU8000) and X-ray diffraction (XRD, Bruker D8), respectively. The scanning electron microscope was operated at high magnification with a voltage of 2 kV and probe current of 5 mA. The X-ray diffraction experiments were performed using a locked-coupled scan with a scanning range (diffraction angle, 2θ) set between 20° and 80°.

2.3. Potentiodynamic polarization

The potentiodynamic polarization studies were carried out using a Gamry R600 potentiostat (Gamry Instruments). A Gamry para cell with a standard three-electrode configuration consisting of a standard Ag/AgCl electrode and carbon was used as the reference and counter electrodes, respectively, while the sample acted as the working electrode. All the electrochemical measurements were performed in saline solution (0.9 wt% NaCl) at room temperature. Prior to the corrosion measurements, the open circuit potential (OCP) was performed at a sampling rate of 5 s to understand the degradation of coatings based on the changes in potential during the exposure to the saline solution. The scan rate for the potentiodynamic polarization measurements was set at 5 mV/s spanning a scan range of ±0.3 V vs open circuit potential (E_{oc}). The samples were immersed in the test solution for 15, 30 and 180 min before commencing the experiments. Fresh solution was used for each experiment.

2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed at room temperature in the frequency range of 0.1 to 10^5 Hz using a Gamry R600 potentiostat at the open circuit potential with a sinusoidal voltage of amplitude 10 mV. The resulting sinusoidal current was measured at the counter electrode. The samples were immersed in the test solution and time-lapse measurements were taken at internals of 10 min for 1 h and 30 min for the next 2 h. The data analyses were performed using Echem Analyst commercial software developed by Gamry.

3. Results and Discussion

3.1. Material fabrication

The Al_2O_3 and ZrO_2 coatings were developed by optimizing the oxygen flow parameter to achieve a high quality coating while avoiding target poisoning and lower deposition rate associated with reactive sputtering. In order to evaluate the absorbance and/or transmission properties of the oxide coatings, 200 nm thick Al_2O_3 and ZrO_2 coatings were developed on glass substrate, while varying the range of oxygen flow rate. Al and Zr metallic coatings with thickness of 200 nm are opaque, completely reflecting and absorbing light without any transmission. More importantly, at this thickness most crystalline materials can be detected by XRD. The results of the oxygen optimization conditions for Al_2O_3 and ZrO_2 are shown in