Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 516 (2007) 422–427
www.elsevier.com/locate/tsf

Corrosion behavior of AZ91 magnesium alloy treated by plasma immersion ion implantation and deposition in artificial physiological fluids

Chenglong Liu [a], Yunchang Xin [a,b], Xiubo Tian [a,c], Paul K. Chu [a,*]

[a] Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
[b] Tsinghua University, Shenzhen Graduate School, Shenzhen 518055, China
[c] State Key Laboratory of Welding Production Technology, School of Materials Science and Engineering, Harbin Institute of Technology, 15001, China

Available online 2 June 2007

Abstract

Due to the good biocompatibility and tensile yield strength, magnesium alloys are promising in degradable prosthetic implants. The objective of this study is to investigate the corrosion behavior of surgical AZ91 magnesium alloy treated by aluminum, zirconium, and titanium plasma immersion ion implantation and deposition (PIII&D) at 10 kV in artificial physiological fluids. The surface layers show a characteristic intermixed layer and the outer surface are mainly composed of aluminum, zirconium or titanium oxide with a lesser amount of magnesium oxide. Comparing the three sets of samples, aluminum PIII&D significantly shifts the open circuit potential (OCP) to a more positive potential and improves the corrosion resistance at OCP.

PACS: 87.68.+z Biomaterials; 52.77.Dq Plasma-based ion implantation and deposition; 81.65.Kn Corrosion protection
Keywords: Magnesium alloy; Plasma immersion ion implantation and deposition; Corrosion; Physiological fluid

1. Introduction

Magnesium alloys were first introduced into orthopedic and trauma surgery in the first half of the last century [1]. Compared to current implant materials such as Ti and titanium alloy, stainless steel and CoCr alloy, AZ91 magnesium alloys provide a lower elastic modulus (45 GPa) and higher tensile yield strength (200 MPa) [2]. However, the poor corrosion in physiological fluids has hampered widespread use in prosthetic devices. Although the development of casting technique has improved the corrosion resistance of magnesium alloys, the associated process is quite complex and costly. Plasma immersion ion implantation and deposition (PIII&D) is one of the effective ways to synthesize an intermixed structure in the near-surface of materials for improved surface properties [3–5]. Some studies on metal or non-metal ion implantation with magnesium or magnesium alloy have recently been performed. Ion implantation of metal ions such as Cr [5], Al [6], Ta [7] can form a new oxidized film on the surface as well as an intermixed layer composed of the metallic compound resulting in enhanced corrosion resistance in different media. The effects of N^+, H^+, and H_2O implantation on the corrosion behavior of magnesium alloy have been studied. The more compactness surface oxide layer in conjunction with N^+ or H_2O implantation gives rise to higher corrosion resistance [8,9]. At the same time, formation of MgH_2 enhances the corrosion resistance of H-implanted high purity magnesium or AZ91 magnesium alloys [10]. These studies were conducted for industrial applications and the biological effects have not been extensively investigates. There have been few reports on the corrosion behavior of AZ91 Mg alloy after surface modification by metal plasma immersion ion implantation and deposition (PIII&D) in simulated body fluids. In this work, we investigate the effects of different PIII&D on the corrosion behavior of AZ91 magnesium in simulated body fluids.

2. Experimental details

Commercially available extruded AZ91 alloys with dimensions of 10 mm × 10 mm × 2 mm were prepared. The specimens were ground with water-proof SiC paper No. 400, 1200 and

* Corresponding author. Tel.: +852 27887724; fax: +852 27889549.
E-mail address: paul.chu@cityu.edu.hk (P.K. Chu).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.05.048

2400 grits sequentially and then ultrasonically washed in ethanol for 10 min. In the aluminum, zirconium and titanium PIII&D experiments, a metal vapor vacuum arc source was used and a pulsed high voltage of −10 kV was applied to the specimens. During the high-voltage off-cycles, deposition of metal particles occurred and ion implantation was conducted during the on-cycles. Implantation and deposition thus proceeded alternately and the PIII&D time was 4 h.

The surface composition and depth profiles were obtained by X-ray photoelectron spectroscopy (XPS, PHI 5802) by means of argon sputtering using a monochromatic Al K_α radiation. High-resolution XPS spectra were taken at different sputtered depths to investigate the chemical states of the implanted species. The corrosion and electrochemical behavior of the as-received and PIII&D specimens were studied in Hank's simulated body fluid (SBF) at 37±1 °C. The open circuit potential (OCP) tests were conducted on an EG&G 263A potentiostat/galvanostat. Changes in the OCP were recorded as a function of time during an exposure time of about 4000 s. The electrochemical impedance spectroscopy (EIS) measurements were carried out on the GAMRY PCI4/300 at a stable OCP. The perturbing signal had an AC amplitude of 10 mV and frequency range from 100 kHz to 10 mHz. The data were analyzed through the software Gamry Echem Analyst.

3. Results and discussion

AZ91 alloy is mainly composed of Mg, Al, and Zn. XPS measurements were carried out to determine the elemental concentration in the modified layer as a function of depth. Fig. 1 depicts the XPS depth profiles acquired from the Ti-PIII&D AZ91 alloys. Fig. 1(a) shows a roughly Gaussian Ti depth distribution in the Ti-PIII&D sample. The peak concentration is approximately 52 at.% at a depth of ~28 nm. At depths exceeding 40 nm, the Mg and Al concentrations increase gradually. Fig. 1(b) depicts the changes in the Mg, Ti, Al, and O valence states with depths. At the near-surface region, the Mg 1s peak at 1302.7 eV corresponds to $Mg(OH)_2$. At a depth of about 40 nm, the peak at 1304.0 eV indicates the existence of $MgAl_2O_4$ and at 56 nm, the peaks at 1303.1 eV and 1304.0 eV correspond to metallic Mg. Based on the Ti 2p patterns in Fig. 2(a), the surface is composed partially of titanium oxide as indicated by the two

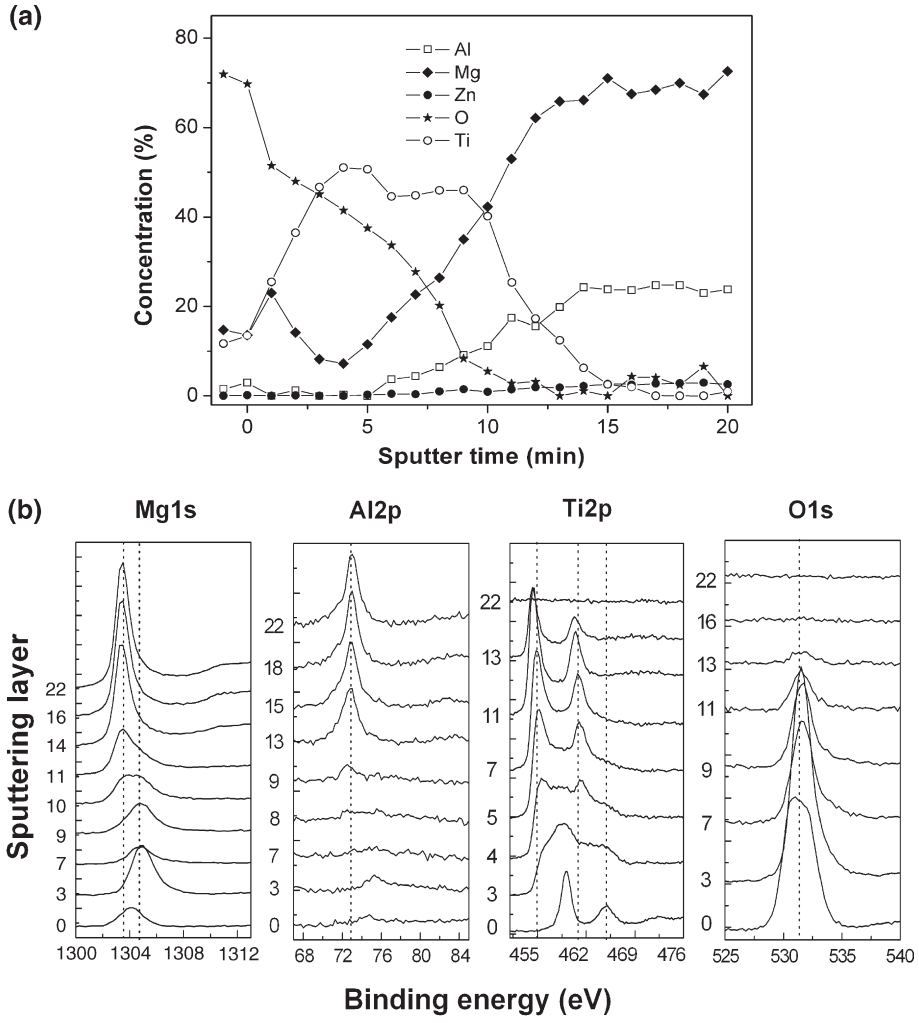

Fig. 1. (a) XPS depth profiles obtained from the magnesium alloy after Ti PIII&D at 10 kV (sputtering rate = 5.6 nm/min). (b) High-resolution XPS spectra of Mg1s, Al2p, Ti2p and O1s obtained from the Ti-PIII&D magnesium alloy.