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Corrosion behavior of chromium and oxygen plasma-modified magnesium in sulfate solution and simulated body fluid

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ABSTRACT

Because of the unique mechanical properties and biocompatibility, magnesium and its alloys have large potential as lightweight structural materials in the industry in addition to being naturally degradable and resorbable biomaterials. However, their corrosion resistance is usually inadequate especially in an aqueous environment. In this work, pure magnesium is implanted with chromium and oxygen by plasma immersion ion implantation (PIII) and the corrosion behavior is systematically investigated in simulated body fluid and sodium sulfate solution by polarization tests and electrochemical impedance spectroscopy. Our results reveal that chromium and oxygen ion-implanted magnesium have a lower corrosion rate and exhibit less pitting corrosion in the two solutions.

1. Introduction

As lightweight structural materials, magnesium and its alloys have large potential in the aerospace, automotive, and mobile electronics industry [1,2]. Concurrently, magnesium and its alloys have attracted much attention due to their superior specific strength and natural biodegradable properties which are attractive for stents and orthopedic implants. These biomedical implants can degrade naturally and do not require a second surgery to remove them after tissues have healed sufficiently [3]. However, the poor corrosion resistance, especially in an aqueous environment, restricts their application and protection from corrosion remains a critical issue hindering practical applications.

Plasma immersion ion implantation (PIII) is an effective and efficient 3-dimensional surface modification technique [4,5] via ion implanting and formation of graded near-surface structures. Recent studies on implantation of metal ions such as Al [6,7], Ti [7–9], Ta [10], Y [11], Ce [12], and Zr [7] reveal that the implanted Mg alloys exhibit certain degrees of corrosion resistance enhancement in different test solutions. A more compact surface oxide layers can be formed by N [13] and H_2O [14] ion implantation leading to higher corrosion resistance. The corrosion resistance of Mg alloys can also be improved by implanting O [15], H [16], or hydrocarbons such as methane and acetylene [17]. Owing to galvanic effects, the corrosion rates of Mg alloys are accelerated after Zn [18,19] or Cr [20] ion implantation. In contrast, the corrosion rate can be retarded by first implanting Cr followed by oxygen [20]. However, the corrosion behavior and intrinsic mechanism have not been studied systematically.

In this work, the PIII process is optimized and the corrosion behavior and mechanism are investigated systematically in two different environments. To better understand the corrosion behavior of magnesium before and after chromium and oxygen ion implantation, both simulated body fluid (SBF) and 0.1 mol/l sodium sulfate are used in the electrochemical tests (polarization tests and electrochemical impedance spectroscopy). After the immersion tests for different durations, the corrosion products are analyzed by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy. The associated corrosion mechanism is also discussed.

2. Experimental details

The materials were as-cast pure magnesium blocks (99.95% pure; 10 mm × 10 mm × 5 mm) mechanically polished using up to 1 μm alumina powder and ultrasonically cleaned in ethanol. The samples were implanted with chromium ions and then oxygen ion implantation was conducted afterwards. Chromium ion implantation was carried out on the HEMII-80 ion implanter equipped with a chromium cathodic arc source. The samples were implanted for 0.5 h at an accelerating voltage of 15 kV and base pressure of 10^{-4} Pa. Oxygen ion implantation was performed on the GPI-100

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ion implanter. An oxygen plasma was first formed in the chamber at an oxygen flow rate of 20 sccm. A pulsed voltage of 30 kV with a pulse width of 50 μs and pulsing frequency of 100 Hz was applied to the samples and oxygen plasma immersion ion implantation (PIII) was conducted for 3 h.

The Mg, Cr, and O depth profiles were acquired by X-ray photoelectron spectroscopy (XPS) on the Physical Electronics PHI 5802. Al K_α irradiation was employed to determine the chemical states and the estimated sputtering rate was 6.9 nm/min.

The simulated body fluid (SBF) was prepared with deionized water. The concentrations (mmol/l) of the various ions in the SBF were: 142.0 Na^+, 5.0 K^+, 1.5 Mg^{2+}, 2.5 Ca^{2+}, 147.8 Cl^-, 4.2 HCO_3^-, 1.0 HPO_4^{2-}, 0.5 SO_4^{2-}. A 1 mol/l HCl solution was pipetted to adjust the pH to 7.25 at 37 °C. The other electrolyte was 0.1 M Na_2SO_4.

The electrochemical corrosion behavior of the implanted magnesium and pure magnesium were studied on a Zennium electrochemical workstation. The samples were encapsulated by silicone so that only an area of 10 mm × 10 mm was exposed to 80 ml of the test solutions. Potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) were conducted in a standard electrochemical cell using three electrodes. The sample was the working electrode. A saturated calomel electrode (SCE) was used as a reference electrode and a platinum electrode served as the counter electrode. The SBF was placed in a water bath at 37 °C and the test in the Na_2SO_4 solution was performed at about 22 °C. The polarization tests were conducted at a scanning rate of 1 mV s^{-1} and EIS were conducted from 100 mHz to 100 kHz. To evaluate the corrosion behavior systematically, the implanted magnesium and pure magnesium samples were immersed in the two solutions for 3 h and 18 h. The temperature of the SBF was kept at 37 °C in a water bath and the Na_2SO_4 solution was kept at about 22 °C. The morphology and microstructure of the corroded surfaces were examined using the Canon EOS 600D Digital SLR camera (DC) coupled with scanning electron microscopy (SEM, FEI/Philips XL30 Esem-FEG). The chemical state of the corrosion product was identified by XPS and energy-dispersive X-ray spectroscopy (EDS, JEOL SM820).

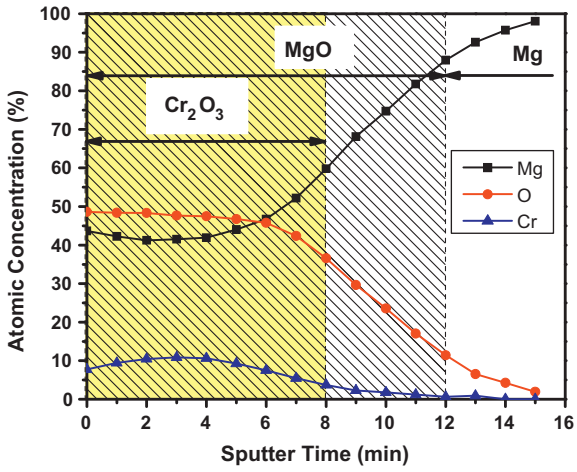

Fig. 1. XPS depth profiles of the implanted sample.

3. Results and discussion

The XPS depth profiles obtained from the implanted sample depicted in Fig. 1 confirm that Cr has a Gaussian-type distribution with a peak concentration of about 10 at%. The O concentration does not change much in the beginning but decreases quickly afterwards whereas the Mg concentration increases gradually as the concentrations of the implanted elements diminish in depth.

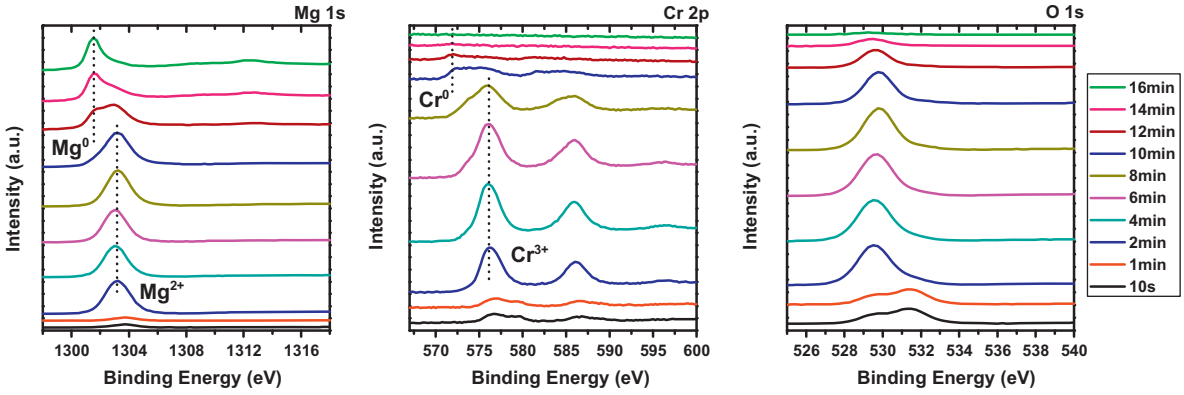

Fig. 2. High-resolution XPS spectra of the implanted sample.

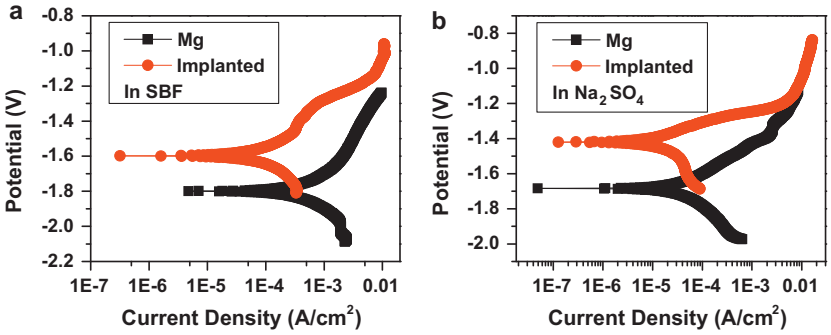

Fig. 3. Polarization curves of Mg and implanted samples in: (a) SBF and (b) Na_2SO_4 solution.