



# Praseodymium-surface-modified magnesium alloy: Retardation of corrosion in artificial hand sweat



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## ABSTRACT

Surface oxides can retard the onset of corrosion on metals in an aggressive environments. In this work, praseodymium is selected to modify the surface oxides on magnesium alloys based on the reactive element effect and added into pure magnesium and aluminum-containing magnesium alloys by ion implantation. A thicker praseodymium-rich oxide layer is obtained on the magnesium substrate after ion implantation compared to the original oxide film. The corrosion resistance in artificial hand sweat is improved as demonstrated by polarization and immersion tests. The improvement observed from the aluminum-containing magnesium alloy is more significant than that from pure magnesium.

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## 1. Introduction

In addition to being structural materials in automobiles, electronics, and aerospace components, Mg and Mg alloys have attracted much attention as biomaterials due to their natural degradation in the physiological environment [1,2], but rapid corrosion has hampered actual applications [3]. Surface oxides play an important role in controlling the corrosion of metals and the reactive element effect has been exploited in the design of corrosion resistant alloys [4]. In Fe–Cr and Fe–Al alloys, addition of chromium or aluminum facilitates the formation of stable Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> on the surface to resist corrosion attack from the external environment [5,6]. Therefore, this strategy may improve the corrosion resistance of magnesium alloys.

Ion implantation is a versatile technique to modify the surface of metals by providing the possibility to energetically inject different elements into a pre-designed depth of the host materials independent of thermodynamic factors [7]. However, in practice, the high affinity of magnesium to oxygen makes it difficult to select the appropriate reactive elements to passivate the surface. For example, chromium implanted into Mg causes severe galvanic corrosion because most of the Cr atoms exist in the metallic state in the implanted layer. In order to achieve good corrosion

protection, subsequent oxygen ion implantation has been conducted to form a thicker oxidized layer composed of chromium oxide on the surface [8]. Based on these previous studies, it will be better to use an element that can spontaneously form an oxide on magnesium to construct a barrier to retard corrosion. Rare-earth elements such as Ce and Nd are potential candidates in this respect due to their high affinity to oxygen [9,10]. Magnesium–praseodymium alloys have already attracted the concern of metallurgists [11], but there are few reports on Pr-surface-modified Magnesium. In this study, Pr is implanted into pure magnesium and AZ80 magnesium alloy and the corrosion resistance in artificial hand sweat is evaluated.

## 2. Experimental details

The pure magnesium and AZ80 (Mg–7.5 wt% Al–0.8 wt% Zn–0.2 wt% Mn) magnesium alloy samples were mechanically polished by alumina paste up to 1 μm, ultrasonically cleaned in pure ethanol, and dried prior to ion implantation. Ion implantation was carried out on the HEMII-80 ion implanter equipped with a praseodymium cathodic arc source in the Plasma Laboratory in City University of Hong Kong. The important experimental parameters were as follows: base pressure=1 × 10<sup>−3</sup> Pa, arc trigger voltage=10 kV, arc trigger frequency=8 Hz, arc voltage=75 V, acceleration voltage=35 kV, deceleration voltage=1.3 kV, and implantation time=45 min.

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X-ray photoelectron spectroscopy (XPS) was performed using Al K $\alpha$  irradiation to obtain elemental depth profiles and the sputtering rate was about 8 nm/min. The binding energies were referenced to the Au 4f line at 84.0 eV. Electrochemical polarization tests were conducted on a Zahner Zennium electrochemical workstation to evaluate the corrosion resistance. The three-electrode technique was adopted with the potential referenced to a saturated calomel electrode (SCE) and the counter electrode being a platinum sheet. The artificial hand sweat was prepared with 0.5% NaCl, 0.1% lactic acid, and 0.1% urea with a pH adjusted to 6.5 using ammonia [12]. In the test, the specimens with a surface area of 49.12 mm<sup>2</sup> were exposed to the solution and the test was carried out at 1 mV/s at room temperature after immersion for about 10 min. In addition, immersion tests were performed to evaluate the corrosion behavior in the artificial hand sweat and scanning electron microscopy (SEM) was performed to examine the specimens after immersion for 60 min.

### 3. Results and discussion

Fig. 1 shows the XPS elemental depth profiles of the Pr-implanted and un-implanted samples. Pr exhibits a Gaussian-like distribution in the ion-implanted layer. In the Pr-implanted Mg (Fig. 2b), the maximum atomic concentration of Pr is about 30% at the depth of about 40 nm. For the Pr-implanted AZ80 alloy (Fig. 2d), the maximum atomic concentration of Pr is at the similar depth. The existence of Al in the implanted layer reduces the Pr concentration to about 25%. In all the samples, the O concentration declines gradually with depth and the surface oxide layers in the

implanted samples are thicker than the native one. Fig. 2 shows the chemical state changes in the Mg 1s, Al 2p, Pr 3d peaks. Theoretically, it is feasible to distinguish metallic Mg (Al, Pr) from oxidized Mg (Al, Pr) from the XPS spectra. In the spectra of the un-implanted Mg (Fig. 2a), Mg gradually changes from the oxidized state to metallic state with sputtering time further providing evidence about the native oxide layer on the surface. After ion implantation, the shift of Pr 3d to the metallic position (Fig. 2b) reveals that praseodymium in the near surface is oxidized. Hence, a composite oxide film is formed on the surface since both praseodymium and magnesium are oxidized. Similarly, Fig. 2c and d indicates that both praseodymium oxide and magnesium oxide exist in the Pr-implanted AZ80 alloy. The Al concentration in the implanted layer is very small according to Fig. 1d and most of the Al exists in the metallic state.

Fig. 3a displays the polarization curves of the implanted and un-implanted samples. Usually, most anodic polarization curves of magnesium alloys do not show a clear Tafel region and therefore, cathodic Tafel fitting is applied to determine the corrosion current density and corrosion potential based on the extrapolation [13]. As shown in Fig. 3a, the curves of the Pr-implanted samples shift toward a smaller current density and nobler potential. The fitted results in Fig. 3b show that the corrosion potential of magnesium increases from  $-1.985$  V to  $-1.881$  V and that of AZ80 alloy increases from  $-1.653$  V to  $-1.488$  V after ion implantation. Meanwhile, the corrosion current density of the Pr-implanted magnesium is reduced from  $1.322 \times 10^{-4}$  to  $7.962 \times 10^{-5}$  A/cm<sup>2</sup> and that of the Pr-implanted AZ80 alloy is reduced from  $3.541 \times 10^{-4}$  to  $1.112 \times 10^{-5}$  A/cm<sup>2</sup>. Moreover, a larger reduction in the corrosion current density is observed from the AZ80 alloy

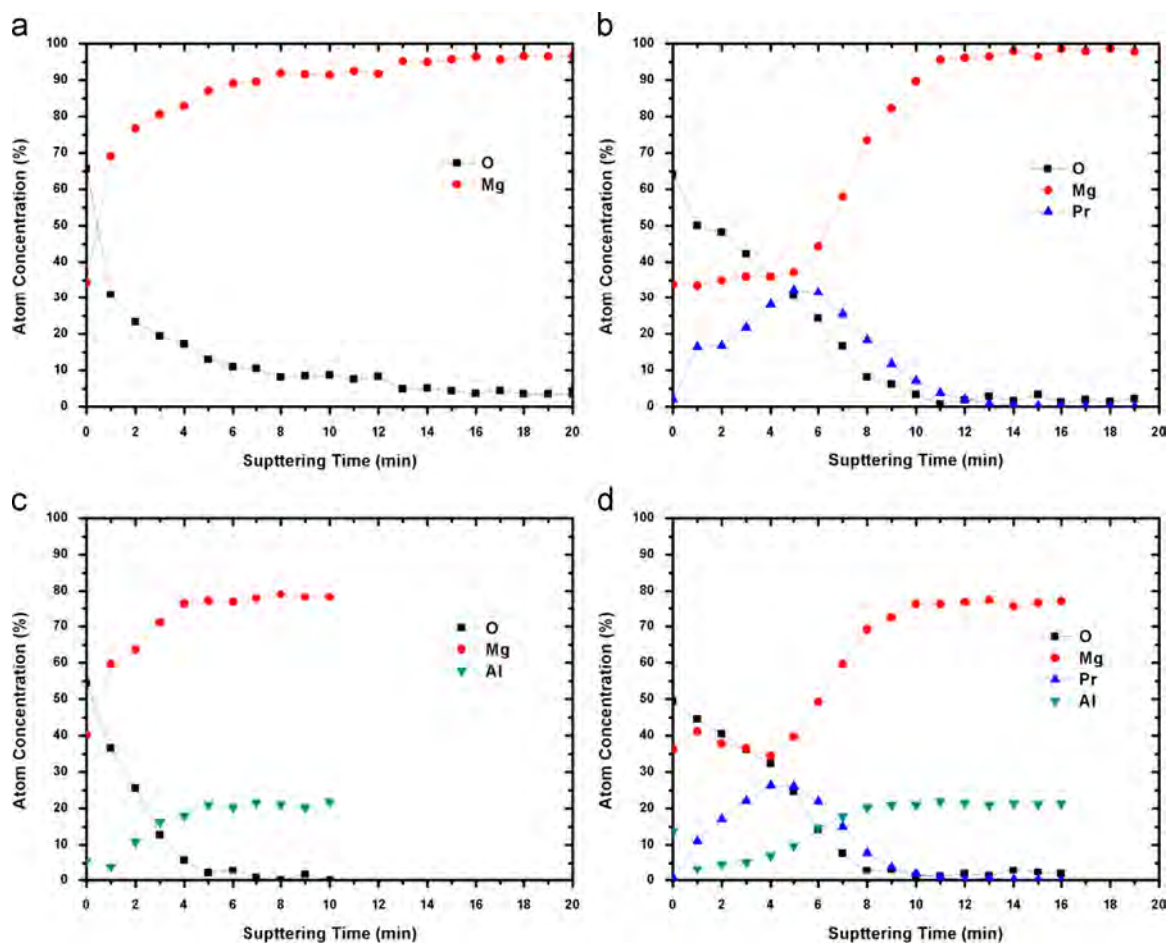


Fig. 1. XPS depth profiles: (a) pure magnesium, (b) Pr-implanted magnesium, (c) AZ80 alloy, and (d) Pr-implanted AZ80 alloy.

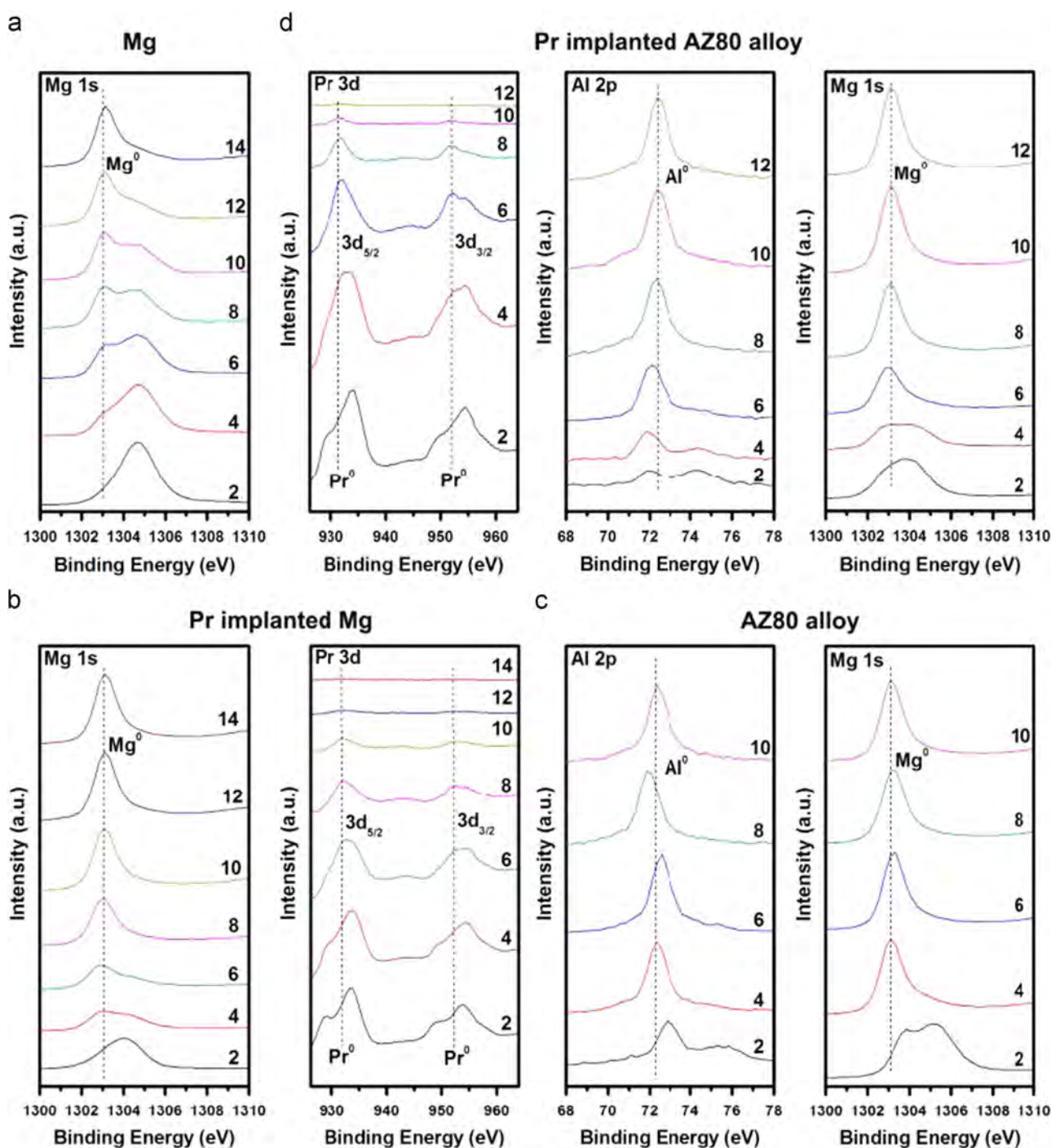


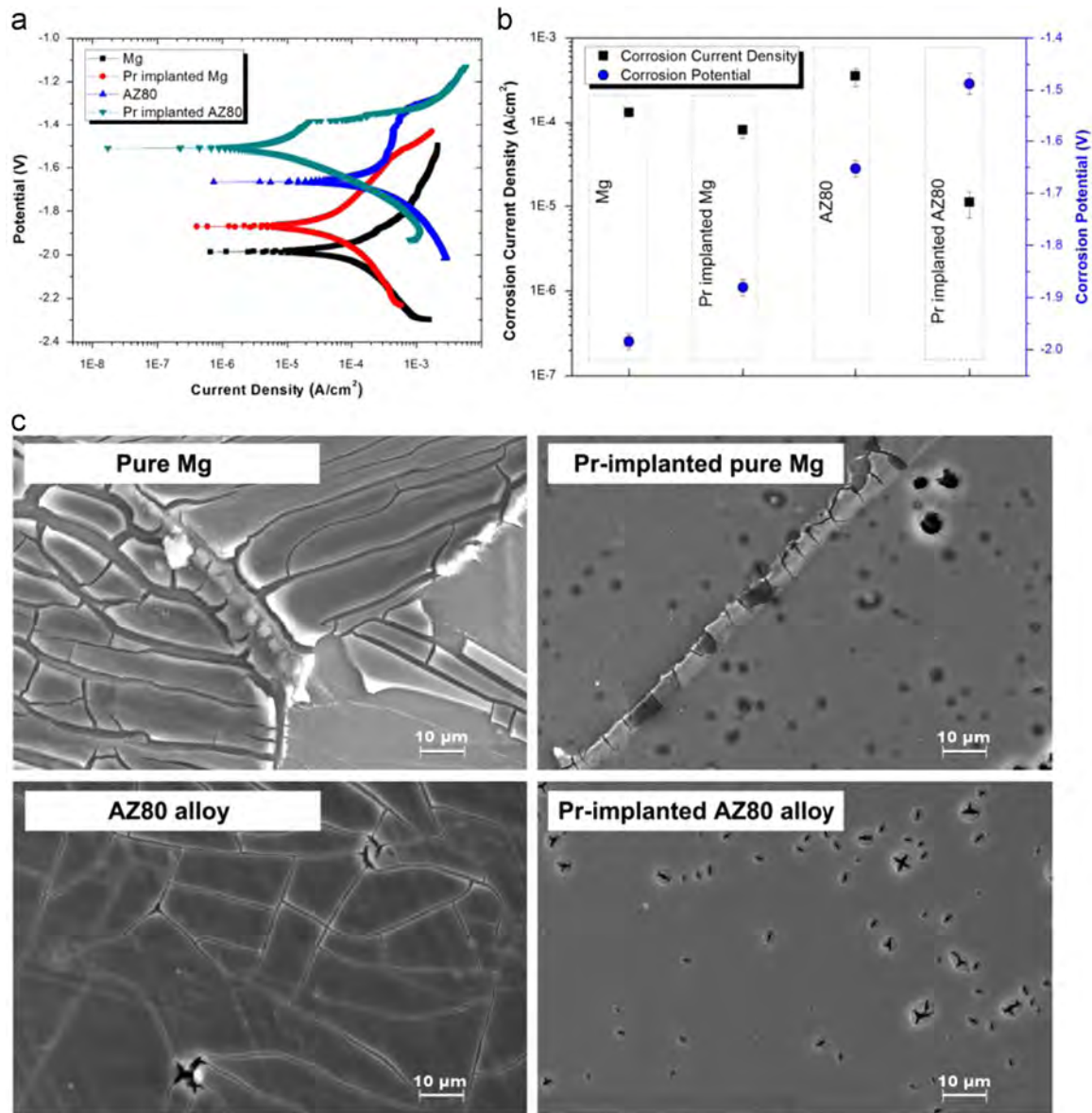
Fig. 2. High-resolution XPS spectra: (a) pure magnesium, (b) Pr-implanted magnesium, (c) AZ80 alloy, and (d) Pr-implanted AZ80 alloy.

compared to pure magnesium. In addition, the polarization resistance can be further calculated based on Stern–Geary equation using corrosion current density. The polarization resistance of the Pr-implanted magnesium increases from 558.047 to 1084.270  $\Omega \text{ cm}^2$  and that of the Pr-implanted AZ80 alloy increases from 196.550 to 3264.460  $\Omega \text{ cm}^2$ . In a word, a smaller corrosion current density (or a higher polarization resistance) indicates a higher corrosion resistance and hence, Pr ion implantation has a retarding effect on corrosion.

Fig. 3c depicts the SEM micrographs of pure magnesium, Pr implanted magnesium, AZ80 alloy, and Pr implanted AZ80 alloy after immersion in the artificial hand sweat for 60 min. Different

surface morphologies are observed from the implanted and un-implanted samples. Block-like products and many cracks indicative of corrosion are observed from the pure magnesium and AZ80 alloy. In contrast, only some pits from weak regions appear on the Pr-implanted samples, which indicates that fewer areas are severely damaged. Theoretically, a layer of corrosion product is formed on magnesium alloys in most aqueous solutions [14]. Cracks are formed possibly due to dehydration of the corrosion products after exposure to air and the possibility of cracks is smaller if there are less corrosion products [15]. This is also an indirect proof that the corrosion resistance in artificial hand sweat is improved by Pr ion implantation. Our experiments provide





**Fig. 3.** (a) Polarization curves of the samples. (b) Corrosion potential and corrosion current density obtained from the polarization curves by cathodic Tafel fitting. (c) Surface morphologies of the samples after immersion in artificial hand sweat for 60 min.

experimental evidence that Pr ion implantation retards surface corrosion on both pure magnesium and AZ80 alloy in artificial hand sweat.

#### 4. Conclusion

Praseodymium ion implantation is conducted to modify the pure magnesium and AZ80 magnesium alloy and the surface corrosion resistance is significantly improved due to the formation of the praseodymium-rich oxide film.

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