

# The corrosion behavior of Ce-implanted magnesium alloys

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## ARTICLE DATA

### Article history:

Received 27 February 2007

Received in revised form

11 May 2007

Accepted 11 May 2007

### Keywords:

Ion implantation

Magnesium alloys

Corrosion resistance

X-ray photoelectron spectroscopy (XPS)

Auger electron spectroscopy (AES)

## ABSTRACT

The aim of this study was to investigate the effect of cerium ion implantation on the corrosion behavior of AZ31 magnesium alloys. Samples were implanted with doses of  $5 \times 10^{16}$ ,  $1 \times 10^{17}$  and  $5 \times 10^{17}$  ion/cm<sup>2</sup>, respectively, using a metal vapor vacuum arc (MEVVA) source at an extraction voltage of 45 kV. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to analyze the depth distribution and the valence states of elements in the implanted layer, respectively. The potentiodynamic polarization technique was applied to evaluate the corrosion resistance of the implanted samples in a 3.5 wt.% NaCl solution saturated with Mg(OH)<sub>2</sub>. The results showed that under an optimal dose the corrosion resistance of the implanted sample was improved compared with that of the bare sample. Finally, the corrosion mechanism of the Ce-implanted samples was discussed.

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## 1. Introduction

As the least noble material ( $E^\circ = -2.34$  V vs normal hydrogen electrode), magnesium has a high tendency to atmospheric and galvanic corrosion [1,2]. The galvanic corrosion can cause severe pitting in the metal, which leads to the decreased mechanical stability and an unattractive appearance. Consequently, this disadvantage has greatly hindered the widespread use of magnesium alloys as light materials in electronic, aerospace and automobile industries [3,4]. Additions of rare earth elements into magnesium alloys have been proved to increase the corrosion resistance, but alloying Mg with RE elements is relatively difficult in practice. Therefore, surface modification seems to be an effective method to overcome this disadvantage. Up to now, many surface techniques such as electrochemical plating [5,6], microarc oxidation [7], physical vapor deposition (PVD) [8,9], laser cladding [10] and ion implantation [11,12], etc. have been utilized to improve the corrosion resistance of magnesium alloys.

Within these surface techniques, ion implantation offers the unique possibility to induce a controlled concentration of an element into a thin surface layer. Nearly all kinds of dopant can be implanted into the substrate. The temperature of the process is relatively low, which prevents from the unwanted modification of bulk properties [13,14]. Thus, ion implantation has been applied and proved to be feasible to increase the corrosion resistance of materials such as stainless steels and zircaloy alloys [15,16], etc. Although several mechanisms have been proposed to understand the effect of ion implantation on the corrosion properties, the corresponding mechanisms are still not very clear. Moreover, in the case of magnesium alloys, only a few works have been reported on the corrosion behavior of the alloys after ion implantation treatment [17,18].

In the present study, an attempt has been made to improve the corrosion resistance of AZ31 magnesium alloys by cerium ion implantation. The characterization of the implanted layer was analyzed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The corrosion resistance of

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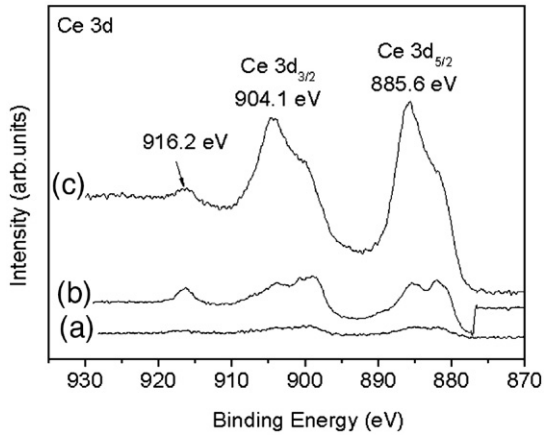


Fig. 1 – Ce 3d spectra for cerium ion implantation: (a)  $5 \times 10^{16}$  ions/cm<sup>2</sup>; (b)  $1 \times 10^{17}$  ions/cm<sup>2</sup>; (c)  $5 \times 10^{17}$  ions/cm<sup>2</sup>.

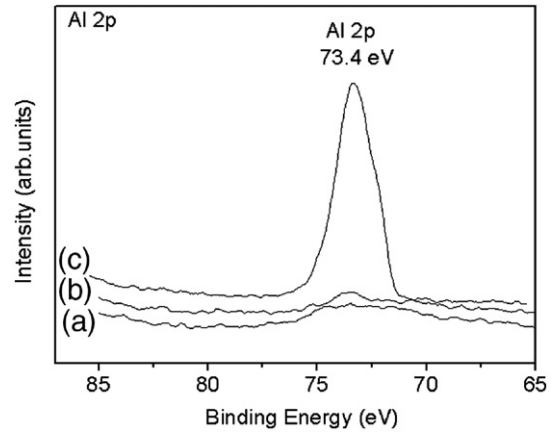


Fig. 3 – Al 2p spectra for cerium ion implantation: (a)  $5 \times 10^{16}$  ions/cm<sup>2</sup>; (b)  $1 \times 10^{17}$  ions/cm<sup>2</sup>; (c)  $5 \times 10^{17}$  ions/cm<sup>2</sup>.

the implanted samples was investigated by potentiodynamic polarization tests.

## 2. Experimental

The samples were die cast AZ31 magnesium alloys (Al: 3 wt.%, Zn: 1 wt.%, Mg: balance), and the corresponding sizes were 10 mm × 10 mm × 3 mm. Before implanting, one side of each sample was mechanically polished with silicon carbide paper up to 1500 grid, and then ultrasonically rinsed in acetone. Then, cerium ion implantations, at nominal doses of  $5 \times 10^{16}$ ,  $1 \times 10^{17}$  and  $5 \times 10^{17}$  ion/cm<sup>2</sup>, were undertaken using an MEVVA source with an extraction voltage of 45 kV. The background pressure of the metal vapor vacuum arc implanter target chamber was  $1.4 \times 10^{-3}$  Pa. Although the implantation system had no magnet analytic capability, the extracted cerium ions were expected to consist of 3% Ce<sup>+</sup>, 83% Ce<sup>2+</sup>, 14% Ce<sup>3+</sup>. During implantation process, the samples were not cooled. Therefore, the implantation temperature depended on the beam current density. To reduce the heating effects, the ion current density

was controlled to be below  $26.6 \mu\text{A}/\text{cm}^2$ . Thus, the maximum implantation temperature was expected to be no more than 523 K.

After argon ion erosion of a 50 nm depth outermost layer, the valence states of elements in the implanted layer were analyzed by X-ray photoelectron spectroscopy (THERMO ESCALAB 250, Al K $\alpha$  1486.6 eV). To compensate for the systematic error in XPS measurement, all the binding energies were first adjusted to the C 1s signal at 285 eV. Auger electron spectrometer (PHI-550 ESCA/SAM) was applied to obtain the composition and depth profiles of elements in the implanted layer. A 2 keV argon ion beam with a current density of  $100 \mu\text{A}/\text{cm}^2$  was used to measure the depth profiles, and the sputter rate was estimated to be approximately 10 nm/min.

To evaluate the corrosion behavior, potentiodynamic polarization tests were performed using a Parstat 2273 potentiostat system. The tests were carried out in a 3.5 wt.% NaCl solution saturated with Mg(OH)<sub>2</sub>, and the scan rate was 1 mV/s. In addition, the micro-morphologies of the samples after immersion test were observed by Scanning electron microscopy (FEI, SIRION-200).

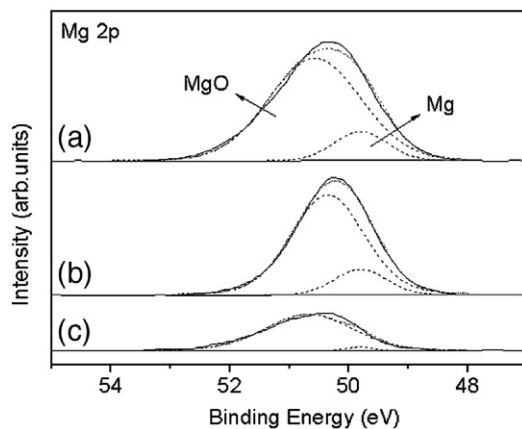


Fig. 2 – Mg 2p spectra for cerium ion implantation: (a)  $5 \times 10^{16}$  ions/cm<sup>2</sup>; (b)  $1 \times 10^{17}$  ions/cm<sup>2</sup>; (c)  $5 \times 10^{17}$  ions/cm<sup>2</sup>.

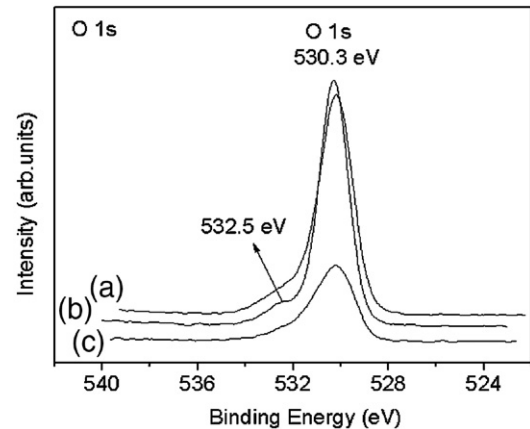


Fig. 4 – O 1s spectra for cerium ion implantation: (a)  $5 \times 10^{16}$  ions/cm<sup>2</sup>; (b)  $1 \times 10^{17}$  ions/cm<sup>2</sup>; (c)  $5 \times 10^{17}$  ions/cm<sup>2</sup>.

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