



# Controllable degradation of biomedical magnesium by chromium and oxygen dual ion implantation

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## ABSTRACT

The surface stability of biodegradable magnesium is crucial to tissue growth on implants in the initial healing stage. Inspired by the design principle of biomedical stainless steels, we implant chromium as a passive element into pure magnesium to alter the surface biodegradation behavior. However, because Cr exists in the metallic state in the implanted layer to induce the galvanic effect, excessively fast degradation is observed. Ensuing implantation of oxygen produces a thicker surface oxidized layer composed of chromium oxide, which successfully retards the surface degradation of pure magnesium. The dual implantation process offers a promising means to improve the initial surface stability of Mg in the physiological environment.

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## 1. Introduction

Magnesium-based materials are considered by many people as revolutionary metallic biomaterials due to their unique biodegradation in the human body [1–4]. Their proper use in securing bone fracture can obviate the need for a second surgery to remove the implant after the tissues have healed sufficiently [5]. However, different from more passive metals such as Ti alloys, CoCr alloys, and stainless steels, the interface between the affected tissues and magnesium implants in the physiological environment is dynamic and uncontrolled degradation can occur. In fact, the degradation rate of magnesium and magnesium alloys is normally too high in the initial stage after implantation [6]. Because tissue healing takes time, it is crucial to control the surface degradation of Mg implants after introduction into the human body.

Stainless steels are one of widely used biomedical implants in clinical applications. Their excellent corrosion resistance in the physiological environment mainly comes from chromium. When the Cr content in the stainless steel exceeds 12%, a layer of chromium-rich oxide is formed on the surface acting as a protective layer from the outside environment [7]. Inspired by this design principle of stainless steels, it is expected addition of a passive element can retard the degradation rate of pure magnesium in the physiological environment. Chromium as one of essential elements in the human body [8] and ion implantation can modify the surface properties of magnesium [9–11]. In ion implantation, the amount and depth of chromium can be independently adjusted by varying the ion fluence and accelerating

voltage. In this study, we investigate the influence of chromium ion implantation on the surface degradation of magnesium and the synergistic effects offered by oxygen co-implantation using electrochemical and immersion tests.

## 2. Experimental details

A commercially available pure magnesium plate was cut into specimens with dimensions of 10 mm × 10 mm × 5 mm, mechanically polished using up to 1 μm diamond paste, and ultrasonically cleaned in ethanol. Chromium ion implantation was carried out by a HEMII-80 ion implanter equipped with a chromium cathodic arc source. The samples were implanted for 1 h at an accelerated voltage of 20 kV and base pressure of  $1.5 \times 10^{-3}$  Pa. The Cr implanted samples were randomly selected for subsequent oxygen ion implantation using a GPI-100 ion implanter. An oxygen plasma was formed in the chamber using an oxygen flow rate of 20 sccm. The pulsed voltage was 30 kV, pulse width was 30 μs, and pulsing frequency was 100 Hz. 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 a Kratos AXIS Ultra X-ray Photoelectron Spectrometer. Al K<sub>α</sub> irradiation was employed to determine the chemical states and the estimated sputtering rate was 0.1 nm/s.

The electrochemical corrosion characteristics were determined by a conventional three-electrode technique using a Zahner Zennium electrochemical workstation. The saturated calomel electrode (SCE) was the reference electrode and platinum sheet served as the counter electrode. The working electrode was connected to the sample by a copper wire and embedded in silicone to expose an area of 10 mm × 10 mm. Simulated body fluids (SBF) [12] were prepared to

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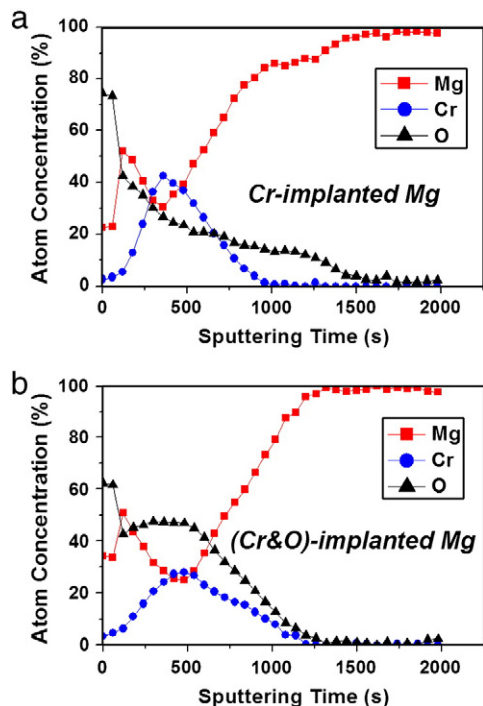


Fig. 1. XPS depth profiles of (a) Cr implanted magnesium and (b) Cr and O implanted magnesium.

evaluate the electrochemical corrosion properties at 37 °C. The polarization tests were conducted at a scanning rate 1 mVs<sup>-1</sup>. Immersion tests were performed to further evaluate the degradation behavior. After the samples were soaked in the SBF at 37 °C for 90 min,

rinsed in ethanol, and dried, scanning electron microscopy (SEM) was performed on the FEI/Philips XL30 Esem-FEG.

### 3. Results and discussion

The XPS depth profiles obtained from the Cr implanted and Cr-O co-implanted magnesium samples are depicted in Fig. 1a and b. The implanted Cr shows a Gaussian-like distribution and Mg has a sharper distribution in the implanted layer. The oxygen content decreases gradually with depth in the near surface region. As shown in Fig. 1b, introduction of O after Cr implantation does not produce special changes in the distribution of Mg and Cr, except that the oxygen content increases in the near surface. Fig. 2a and b depict the high-resolution XPS spectra of Mg 1s, O 1s, and Cr 2p acquired from the Cr implanted and Cr and O co-implanted Mg samples. As the sputtering time increases, Fig. 2a reveals that the Mg 1s peak shifts from the oxidized state (Mg<sup>2+</sup>) to the metallic state (Mg<sup>0</sup>) while the Cr 2p mainly exists in the metallic state (Cr<sup>0</sup>). According to the Mg, Cr, and O results in Fig. 2b, a thicker oxide layer is formed on the Cr and O co-implanted Mg. The shift in the Cr 2p peak indicates that chromium in the near surface is oxidized.

Fig. 3 shows the polarization curves of the implanted and un-implanted samples. After ion implantation, the corrosion potential of magnesium increases from -1.98 to -1.55 V (Cr implanted Mg) and -1.63 V (Cr and O implanted Mg). According to the deduction from the cathodic region of the curves, the corrosion current densities of Mg, Cr implanted Mg, and Cr-O implanted Mg are  $1.68 \times 10^{-4}$  A/cm<sup>2</sup>,  $1.67 \times 10^{-3}$  A/cm<sup>2</sup>, and  $5.89 \times 10^{-5}$  A/cm<sup>2</sup>, respectively. The lower the corrosion current density, the higher is the corrosion resistance. Therefore, the degradation rate of Mg is increased by Cr implantation but reduced by ensuing oxygen implantation. Fig. 4a–c depict the SEM micrographs of pure magnesium, Cr implanted Mg, and Cr-O co-implanted Mg after the immersion tests, respectively. After 90 min of

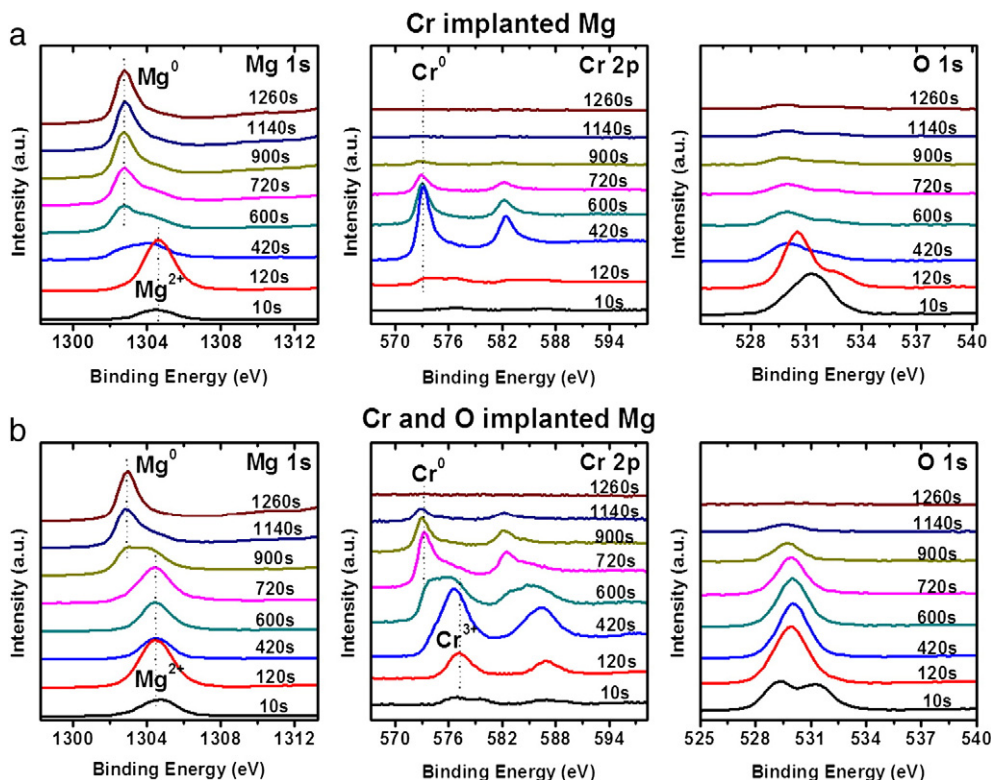


Fig. 2. High-resolution XPS spectra of (a) Cr implanted magnesium and (b) Cr and O implanted magnesium.

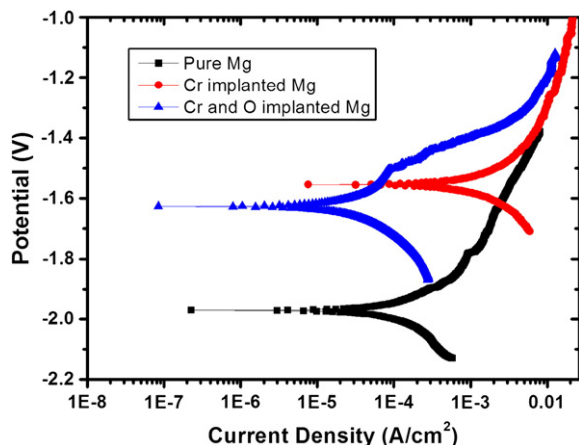


Fig. 3. Polarization curves of the prepared samples in simulated body fluids.

immersion in SBF, different topographies emerge on the surfaces of pure Mg, Cr implanted Mg and Cr and O co-implanted Mg. According to previous studies [13–15], a thin oxide layer exists on the surface of Mg when it is exposed to the natural environment. Based on previous studies, this layer is loose and has no protective ability because the Pilling–Bedworth ratio is less than 1.0 [16]. In fact, the surface of pure magnesium is severely corroded showing block-like products and small cracks. Cr addition is expected to passivate the surface of Mg, but most Cr exists in the metallic state in the implanted layer thus inducing severe galvanic corrosion as shown in Fig. 4b. It is postulated that the Cr rich regions serve as the cathode with the Mg matrix being the anode in the galvanic cell when aggressive media penetrate the loose top oxide layer. Subsequent introduction of O triggers the formation of a thicker oxidized layer composed of chromium oxide on the surface. Our data reveal that surface degradation can be controlled by the modified oxide layer. Localized corrosion happens via some weak regions on the top surface and propagates underneath. Therefore, dual ion implantation is demonstrated to be a promising approach to improve the surface stability of pure magnesium in the physiological environment, especially in the critical initial stage after surgical introduction. It is also expected to promote proper tissue growth on the magnesium implant in the initial healing stage.

#### 4. Conclusion

Chromium and oxygen dual ion implantation is conducted to alter the surface degradation behavior of pure magnesium. Although Cr is the critical passive element in biomedical stainless steels, Cr ion implantation does not reduce the degradation rate of pure magnesium due to the severe galvanic effect. By means of subsequent oxygen ion implantation, the chromium-containing oxide layer on the surface can be optimized to control the degradation rate, especially in the initial stage.

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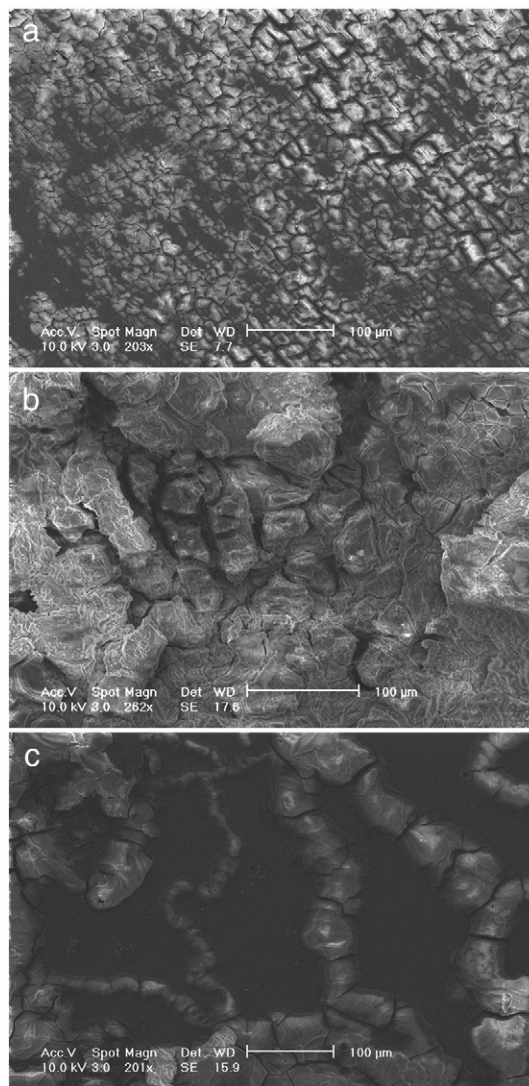


Fig. 4. SEM micrographs of the corroded surface after immersion in SBF: (a) pure magnesium, (b) Cr implanted magnesium, and (c) Cr and O implanted magnesium.

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