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Water plasma implantation/oxidation of magnesium alloys for corrosion resistance

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Abstract

In order to improve the corrosion resistance of magnesium alloys, plasma immersion ion implantation and oxidation has been employed using water plasma sustained by an inductively coupled radio-frequency plasma source. After the treatment, the corrosion behavior of the samples is evaluated using potentiodynamic polarization tests. The film structure and depth profile of oxygen are characterized using XRD and RBS. The results demonstrate that water plasma implantation can effectively facilitate oxidation and improve the corrosion resistance of magnesium alloys. Our results also indicate that lower temperature processing is preferred to achieve better corrosion resistance.

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Keywords: Water plasma ion implantation; Magnesium alloy; Corrosion resistance

1. Introduction

Lightweight magnesium alloys are used in the automobile, aerospace and electronics industries, but its poor corrosion resistance limits wider applications. Consequently, proper surface modification is needed and a review on surface modification of magnesium alloys has been presented by Gray and Luan [1]. Plasma immersion ion implantation (PIII) has been proven to be an effective surface modification tool [2,3]. The advantages of plasma implantation stem from the capability of treating irregularly shaped components, high efficiency and batch processing. It has been suggested in the literature and our previous research work that ion implantation can improve the corrosion resistance of magnesium [4,5] and a surface magnesium oxide is especially helpful in this respect [6,7]. In this work, we performed plasma immersion ion implantation/oxidation using water plasmas sustained by an external RF plasma source. The aim is to achieve a thick, compact oxide layer to resist surface.

2. Experimental

The samples were AZ31B magnesium alloy (Al: 3.0–4.0 wt.%, Mn: 0.15–0.50 wt.%, Zn: 0.20–0.80 wt.%, Cu: 0.05 wt.%, Si: 0.1 wt.%, Fe: 0.05 wt.%, Be: 0.01 wt.%, Ni: 0.05 wt.%, impurity: 0.30 wt.%, Mg: balance) and the specimen size was 12 mm × 12 mm × 5 mm. One side of each sample was ground with 800-grit diamond paper. The samples were then chemically polished with 10% nitric acid in methanol before loading into the plasma immersion ion implanter [3]. Before PIII, the samples were sputter-cleaned with argon plasma bombardment. The pretreatment instrumental parameters were RF power = 1000 W, DC bias voltage = −500 V, gas flow = 10 sccm and cleaning time = 20 min. Afterwards, water vapor was bled into the vacuum chamber. The purified water was put in a glass

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Table 1
Instrumental parameters during water plasma ion implantation

Sample no.	Pulse voltage (kV)	Pulse frequency (Hz)	Pulse duration (μs)	Implantation time (h)
Untreated	0	0	0	0
H_2O-22	20	200	30	2
H_2O-32	30	200	30	2
H_2O-42	40	200	30	2
H_2O-24	20	200	30	4
H_2O-34	30	200	30	4
H_2O-44	40	200	30	4

vessel connected to the chamber through a tube. A valve was used to control the vapor flow and keep the working pressure at around 6.0×10^{-4} Torr. The water plasma was sustained by 1000 W RF and the instrumental parameters are summarized in Table 1.

To evaluate the corrosion behavior, potentiodynamic polarization tests were conducted using a model 342 softcorrv™ corrosion measurement system. The tests were carried out in a 3 wt.% NaCl solution and the scanning rate was 0.5 mV/s. Rutherford backscattering spectrometry (RBS) was used to measure the elemental depth profiles. Structural identification of the various phases was performed by grazing incidence X-ray diffractometry (GXRD) with the incident beam angle (α) of 2°.

3. Results

Fig. 1 depicts the RBS spectra acquired from the water implanted and control samples. A clear surface oxide can be observed due to the high affinity of oxygen to magnesium. The initial oxide film has an estimated thickness of 2.5 nm [8]. When the implantation voltage and treatment time are increased, the incident dose increases and the total thickness of the oxide layer also increases. The incident dose including native oxygen is calculated to be about 1.9×10^{17} cm^{-2}, 2.84×10^{17} cm^{-2}, respectively, for samples H_2O-32 and H_2O-42. Meanwhile, the oxygen content is 2.0×10^{17} cm^{-2} and 2.28×10^{17} cm^{-2} for samples H_2O-24 and H_2O-34, respectively. It should be noted that using an implantation voltage of 40 kV and treatment time of 4 h, the oxide layer gets substantially thicker and the oxygen concentration is about 6.0×10^{17} cm^{-2}. Traces of aluminum and zinc are also detected by RBS perhaps due to contamination from the vacuum chamber.

The glancing incidence X-ray diffraction patterns are shown in Fig. 2. The intensity of the magnesium oxide is smaller than that of the magnesium matrix indicating a thin oxide layer. Near 43°, a MgO peak exists on the implanted and untreated samples. The intensity of the MgO peak increases with higher implantation voltage indicating more oxygen inclusion. The results are consistent with RBS data.

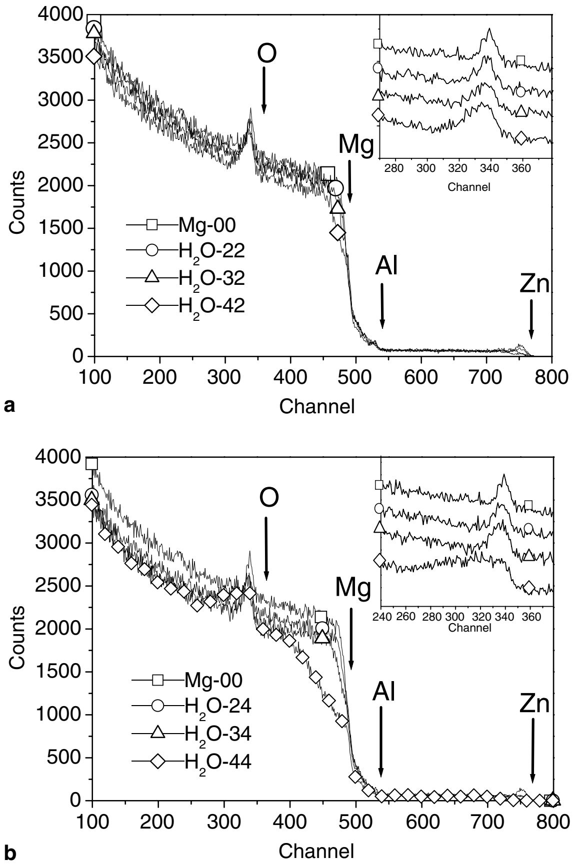

Fig. 1. RBS spectra of samples treated under different parameters. Treatment time (a) 2 h and (b) 4 h.

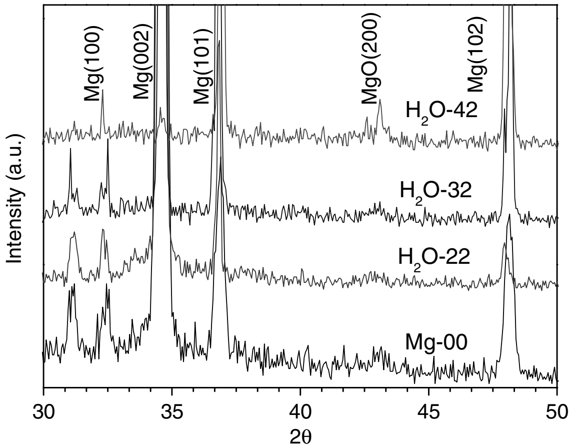

Fig. 2. Glancing incident XRD patterns acquired from unimplanted and plasma-implanted samples for 2 h (Mg-00 is the control sample).

After water plasma implantation, the corrosion resistance is significantly enhanced as shown in Fig. 3. The corrosion potential becomes noble and corrosion current decreases in all the implanted samples except the one treated with the higher voltage and longer processing time (sample H_2O-44). The corrosion potential is -1500 mV and -1470 mV for samples H_2O-24 and H_2O-34, respectively, while that of the untreated control is -1530 mV. The corrosion current decreases by one to two orders of magnitude depending on the treatment conditions. These findings unequivocally demonstrate the effectiveness of

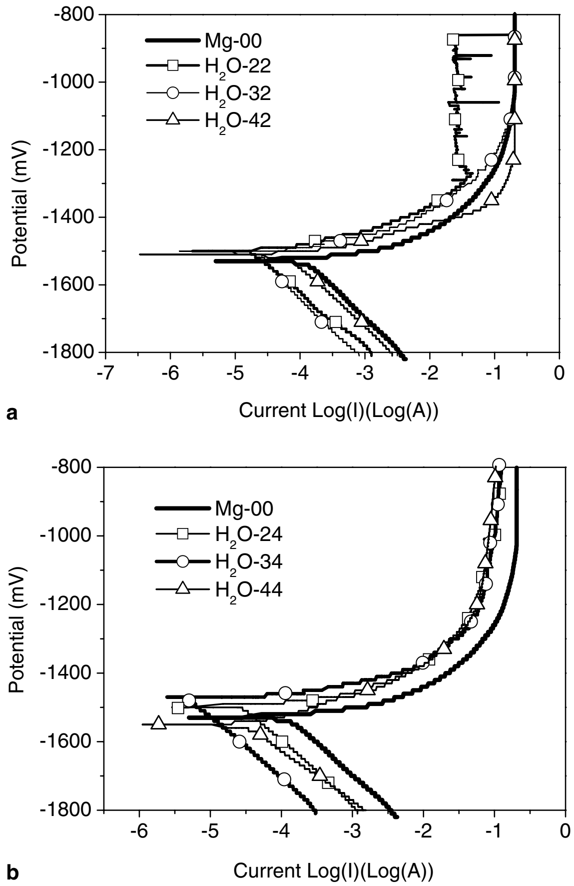

Fig. 3. Potentiodynamic polarization curves obtained in 3% NaCl solution. Samples treated for (a) 2 h and (b) 4 h.

water plasma implantation to improve the corrosion resistance of magnesium alloys.

4. Discussion

Water plasma implantation is preferred here due to its higher efficiency and simpler instrumentation compared to beam-line oxygen ion implantation. The water plasma also facilitates deeper penetration since the net impact energy of O in H_2O is nearly twice that in an oxygen molecule O_2 under the same biasing voltage. Our results show that the enhancement stems from the formation of a compact oxide layer in our process and while a natural native oxide is not compact enough to achieve this purpose [9]. In water plasma implantation, oxygen species are forced into the substrate at high energy thereby resulting in a denser oxide film. With increasing treatment time and implantation voltage, the corrosion resistance is further improved. However, if the voltage is too high or the treatment time is too long, e.g. in the case of sample H_2O-44, the corrosion resistance may be worsened and the corrosion potential decreases to −1550 mV. It may be due to ion heating effects. When the implantation voltage is raised from 30 to 40 kV, the incident dose should increases by 15% [10], but our experiments indicate that the incident dose increases by 160%. The discrepancy can be explained by the oxidation effect at elevated temperature induced by the injected ions [11]. It is accepted that at low temperature, the growth of a compact MgO film is controlled by solid-state diffusion through the adherent oxide areas followed by the reaction with oxygen at the oxide/gas interface [12]. When the temperature is too high, oxygen can more easily penetrate to the metal surface leaving the oxide not as dense [13]. In this way, the oxide layer is not compact although it is thicker. Consequently, the corrosion resistance is not improved and similar phenomena have been observed in annealing after ion implantation [14,15].

5. Conclusion

Oxygen plasma immersion ion implantation/oxidation has been performed using water plasma. The oxide layer consists of a native oxide layer and oxidized layer induced by water implantation. With increasing treatment time and voltage, the oxygen content in the layers increases. The oxidation mechanism changes if the treatment temperature is too high due to ion heating effect. The corrosion resistance can be effectively improved using the proper water implantation/oxidation conditions. Our results indicate that the success can be attributed to the formation of a compact oxide layer.

Acknowledgements

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