

# Corrosion behavior of PEO-treated AZ31 Mg alloy in chloride solution

Sungmo Moon

Received: 1 July 2013 / Revised: 21 August 2013 / Accepted: 30 August 2013 / Published online: 8 September 2013  
© Springer-Verlag Berlin Heidelberg 2013

**Abstract** Corrosion behavior and resistance of plasma electrolyte oxidation (PEO)-treated AZ31 Mg alloy were investigated by immersion and potentiodynamic polarization tests in 0.5 M NaCl solution in view of the PEO film thickness and sealing treatment of the PEO films in boiling water. The PEO films were formed using pulse current for various durations in 1 M NaOH+0.5 M NaF solution. Filiform corrosion was observed during the immersion test while pitting corrosion occurred during the potentiodynamic polarization test, irrespective of sealing treatment of the PEO films. Corrosion resistance of AZ31 Mg alloy was improved remarkably by the formation of thicker PEO films and their sealing treatments.

**Keywords** Corrosion · Mg alloy · Plasma electrolytic oxidation · Sealing

## Introduction

Mg and its alloys have been of great interest because of their low density. However, since their wide applications have been limited by their poor corrosion resistances, many researchers have tried to develop corrosion protection methods of Mg alloys. One of the corrosion protection methods for Mg alloys is anodizing method by which thick anodic films with good chemical stability and corrosion resistance are rendered. Plasma electrolytic oxidation (PEO) is one of the anodic oxidation methods of Mg alloys in which microdischarges are generated repeatedly during the formation of anodic films

by local breakdown and healing of the anodic films under high electric field [1–8].

Corrosion protective properties of PEO films formed on Mg alloys are dependent largely on the substrate composition and solution composition. Many works have been conducted to form corrosion-resistive PEO films on various Mg alloys such as AM50 Mg alloy [9], AM30 Mg alloy [10], ACM522 Mg die-casting alloy [7], AZ31 Mg alloy [11], AZ91D alloy [12], and AM60 Mg alloy [13]. However, at present, as-formed PEO films formed on AZ31 Mg alloy are still not satisfying the requirement of its corrosion protection for practical use because of the presence of pores and cracks in the films. If the pores and cracks in the PEO films are healed by a sealing process, their corrosion resistances are expected to be increased significantly.

In this study, corrosion behavior and corrosion resistance of PEO-treated AZ31 Mg alloy were tested in 0.5 M NaCl solution by immersion and potentiodynamic polarization methods and by observation of corroded specimen surfaces in order to elucidate the effects of PEO film thickness and subsequent sealing treatment on their corrosion protective property. The PEO films were prepared using pulse current for 1, 2, 3, and 5 min in 1 M NaOH+0.5 M NaF solution, and their thickness and morphologies were observed by scanning electron microscopy (SEM).

## Experimental

AZ31 Mg alloy plates (in weight percent; Al, 2.94; Zn, 0.8; Mn, 0.3; Si, <0.1; Fe, <0.005; Cu, <0.05; Ni, <0.005; and Mg, balance) were employed for this study. The alloy plates of 1 mm thickness were cut into 12.5×70 mm size and masked, leaving 10 cm<sup>2</sup> of exposed area, with a masking tape after abrading the specimen surface successively up to #4000 SiC paper with ethanol. The masked specimen was etched for 10 s in 0.5 M H<sub>2</sub>SO<sub>4</sub>+0.5 M HNO<sub>3</sub> solution to remove surface

S. Moon (✉)  
Korea Institute of Materials Science, 797 Changwondaero,  
Sungsan-Gu, Changwon-Si, Kyungnam 642-831, South Korea  
e-mail: sungmo@kims.re.kr

scales and contaminants, washed with deionized (DI) water, and then scrubbed with tissue to remove surface residuals.

The PEO films were formed in 1 M NaOH+0.5 M KF solution at  $15\pm 3$  °C by the application of pulse current with about 0.3 ms width and 65 Hz of frequency. The solution of 4,000 ml volume was contained in a plastic cell within which Teflon tubes are coiled for cooling by pumping cold water/glycol mixture through them. A platinum plate was used as the counter electrode and anodic film formation voltage was monitored by an oscilloscope between the specimen and the counter electrode. The sealing treatment of PEO films were conducted for 40 min in boiling DI water.

Corrosion behavior and resistance were investigated by immersion and potentiodynamic polarization methods in 0.5 M NaCl solution at  $25\pm 1$  °C. Open-circuit potentials of nontreated and PEO-treated specimens were monitored for 5 min and then the polarization experiments were conducted at a scan rate of 1 mV/s using a potentiostat/galvanostat (Solatron SI1287).

The surface and cross-sectional morphologies of unsealed and sealed PEO films were observed by a conventional SEM (Model JSM-6610LV, JEOL). Photographs of the specimens were taken using a digital camera with time up to 15 days during the immersion test in 0.5 M NaCl solution, and photographs of the specimens were also taken after the potentiodynamic polarization test.

## Results and discussion

Anodic films formed on AZ31 Mg alloy by PEO method in 1 M NaOH+0.5 M NaF solution, are presented with PEO treatment time in Fig. 1. Many pores of about 0.2–0.5  $\mu\text{m}$  in diameter were observed for the PEO-treated surface, and the number of pores decreased with PEO treatment time. Cracks were also observed from the relatively thick PEO film-covered surfaces. The cross-sectional images of the PEO films in Fig. 2 showed imperfections of empty spaces and sharp vertical lines within the PEO films, which seem to be pores and cracks, respectively. The thickness of PEO films were obtained to increase with PEO treatment time at a rate of about 1  $\mu\text{m}$  per minute.

Figure 3 shows typical surface images of PEO film before and after sealing treatment in boiling DI water. The sealed PEO film surface showed needle-like structure and no pores and cracks. The needle-like structure seems to result from the hydration of PEO films. It is important to note that imperfections in the PEO films like pore and cracks are removed after the sealing treatment.

Corrosion behavior of PEO-treated AZ31 Mg alloys were observed during the immersion in 0.5 M NaCl solution, as demonstrated in Fig. 4. Corrosion of PEO-treated AZ31 Mg alloys begins after more than 1 day of immersion. The corrosion

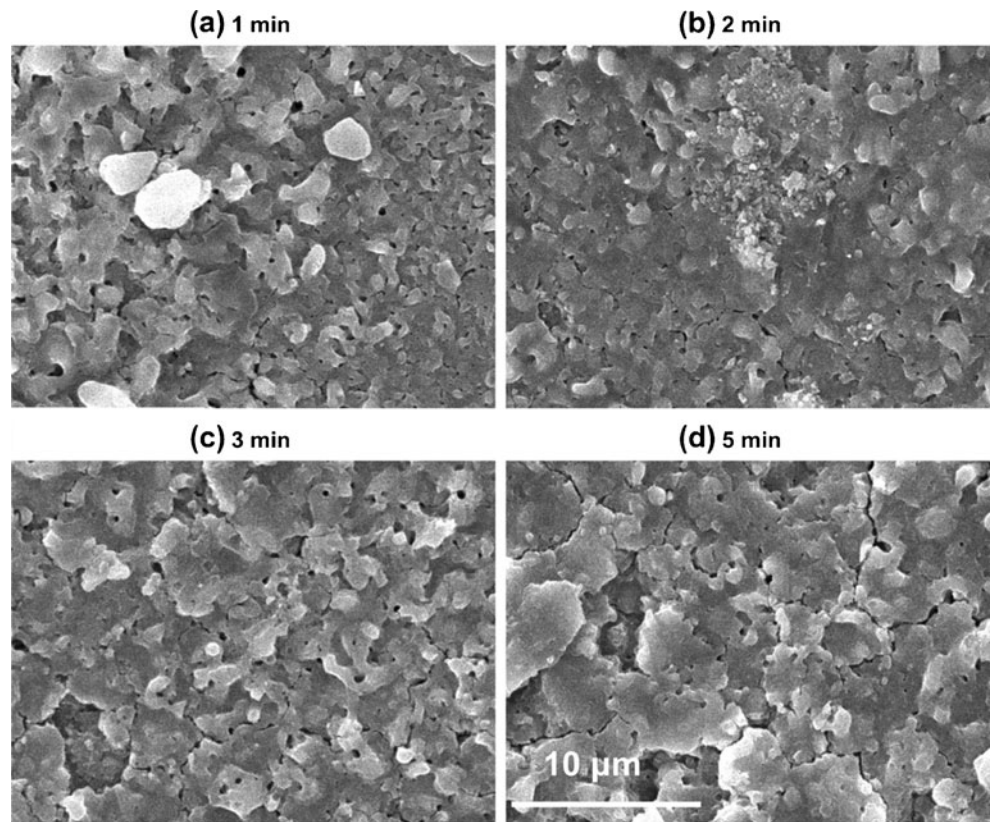
initiation time increased with increasing PEO treatment time and growth rate of corrosion is lowered noticeably with increasing PEO treatment time for both the unsealed and sealed PEO film-covered specimens. These represent that the presence of thicker PEO films is essential for retarding the initiation and growth of corrosion which would be related with lowered supply and accumulation rates of chloride ions at the PEO film/alloy interface. It is also worth commenting that corroded area of PEO-treated AZ31 Mg alloys expands from the original initiation site towards surrounding region like a filiform corrosion.

The 1 min PEO-treated specimen showed relatively fast corrosion initiation time of about 2 days and fast growth of corroded area, irrespective of the sealing treatment, suggesting that healing of pores by the sealing treatment does not retard the diffusion of chloride ions through the PEO film. On the other hand, the PEO-treated specimens more than 2 min showed remarkably increased corrosion initiation time and slowed growth of corroded area by the sealing treatment of PEO films. These suggest that formation of sufficiently thick PEO films and healing of film imperfections are necessary to improve corrosion resistance of Mg alloys. It is noted that the sealed 5 min PEO film-covered AZ31 Mg alloy shows no corrosion up to 300 h of immersion time in 0.5 M NaCl solution.

Electrochemical behavior of nontreated, unsealed, and sealed PEO film-covered AZ31 Mg alloys was investigated by open-circuit potential (OCP) measurement with immersion time in 0.5 M NaCl solution (Fig. 5). The nontreated specimen showed a decrease initially and then an increase, followed by reaching a steady value of about  $-1.58 V_{\text{Ag}/\text{AgCl}}$  after a small decrease with immersion time. The unsealed PEO film-covered specimen showed irregular OCP changes in the initial stage of immersion but reached a constant value of about  $-1.56 V_{\text{Ag}/\text{AgCl}}$  after about 4 min of immersion time. The slightly higher OCP value of unsealed PEO film-covered specimen than nontreated specimen is attributed to the presence of PEO films which may retard anodic dissolution reaction of the alloy.

Sealed PEO film-covered AZ31 Mg alloys showed very low OCP values between  $-1.7$  and  $-1.82 V_{\text{Ag}/\text{AgCl}}$  in the initial stage and then increased to higher values around  $-1.6 V_{\text{Ag}/\text{AgCl}}$ , followed by a sudden large decrease after several minutes which could be related with the local breakdown of the PEO films. The time to the sudden decrease of OCP increased with increasing PEO treatment time. Considering that the PEO film thickness is proportional to the PEO treatment time, it is readily inferred that thicker PEO films need longer immersion time in a chloride solution for their local breakdowns. It should be pointed out that corrosion is visible after more than 1 day of immersion although local breakdown of the sealed PEO films occurs within several minutes of immersion in 0.5 M NaCl solution. Much longer time for the visible corrosion than the corrosion initiation is attributed to easy repassivation of the PEO film-covered surface, as can be seen by a continuous increase of OCP at about 220 s of

**Fig. 1** Surface morphologies of PEO-treated AZ31 Mg alloys in 1 M NaOH+0.5 M NaF solution with PEO treatment time

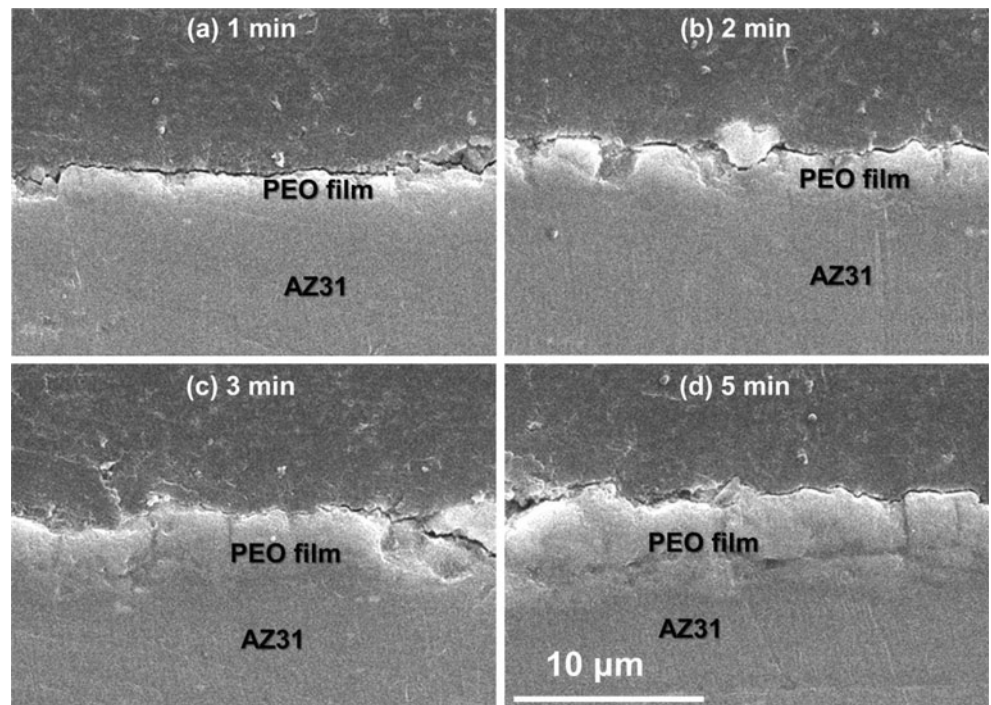


immersion time after a sudden decrease at about 200 s for 2 min of PEO-treated specimen in Fig. 5.

Corrosion resistances of nontreated, unsealed, and sealed PEO film-covered AZ31 Mg alloys were also tested by

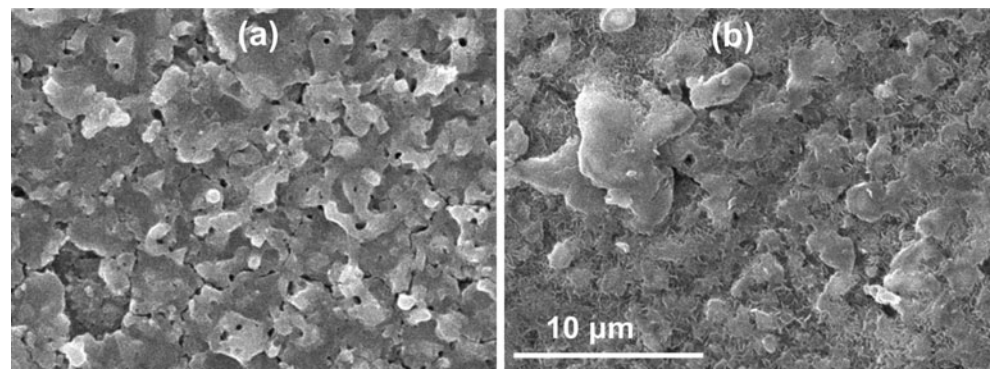
potentiodynamic polarization experiment in 0.5 M NaCl solution, as illustrated in Fig. 6. The unsealed PEO film-covered specimens showed 1 order-reduced cathodic current density and corrosion current density but their corrosion potentials

**Fig. 2** Cross-sectional morphologies of PEO films formed on AZ31 Mg alloy for 1, 2, 3, and 5 min in 1 M NaOH+0.5 M NaF solution





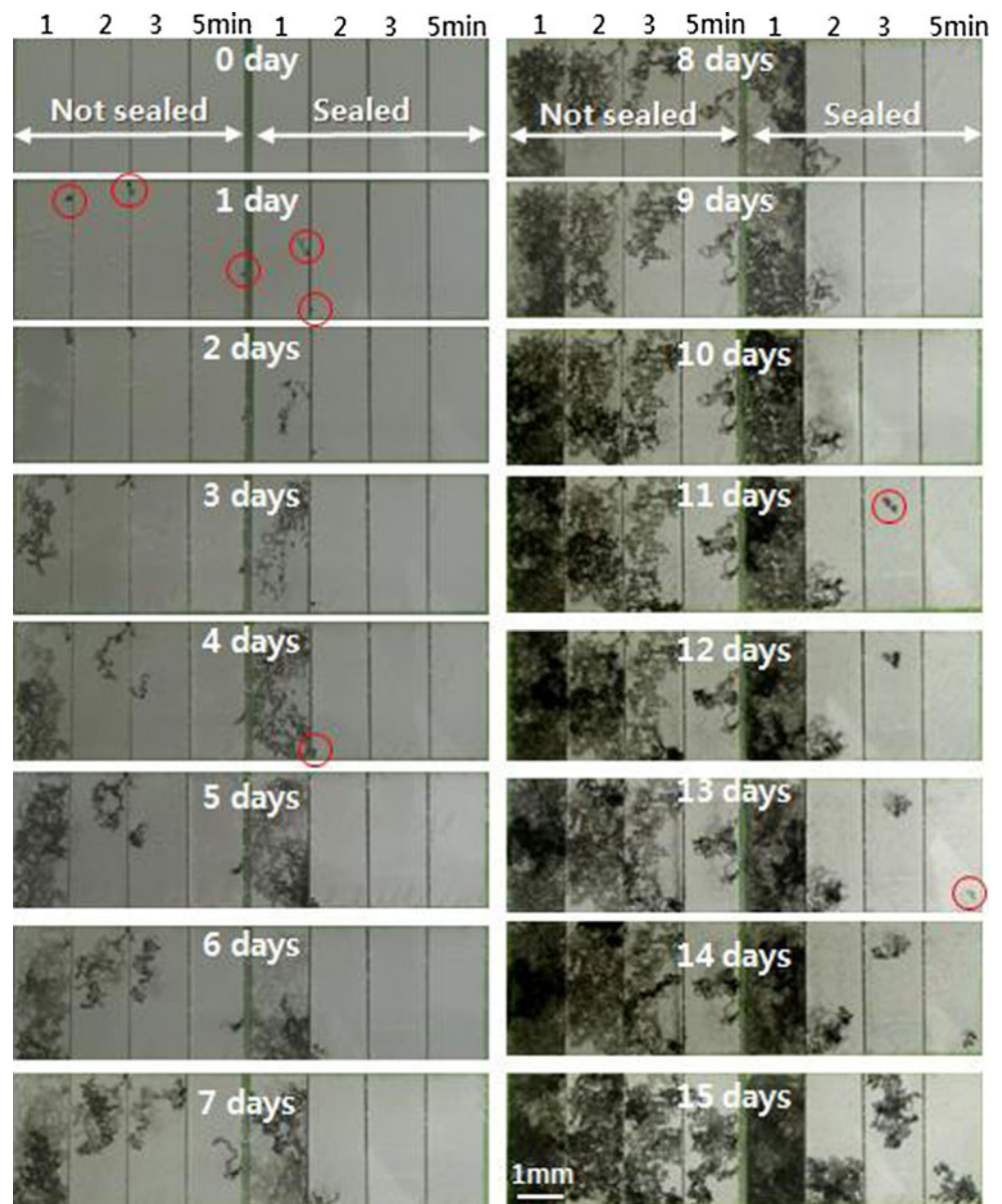
**Fig. 3** Typical surface morphologies of PEO film formed on AZ31 Mg alloy for 3 min in 1 M NaOH+0.5 M NaF solution before (a) and after (b) sealing treatment in boiling water

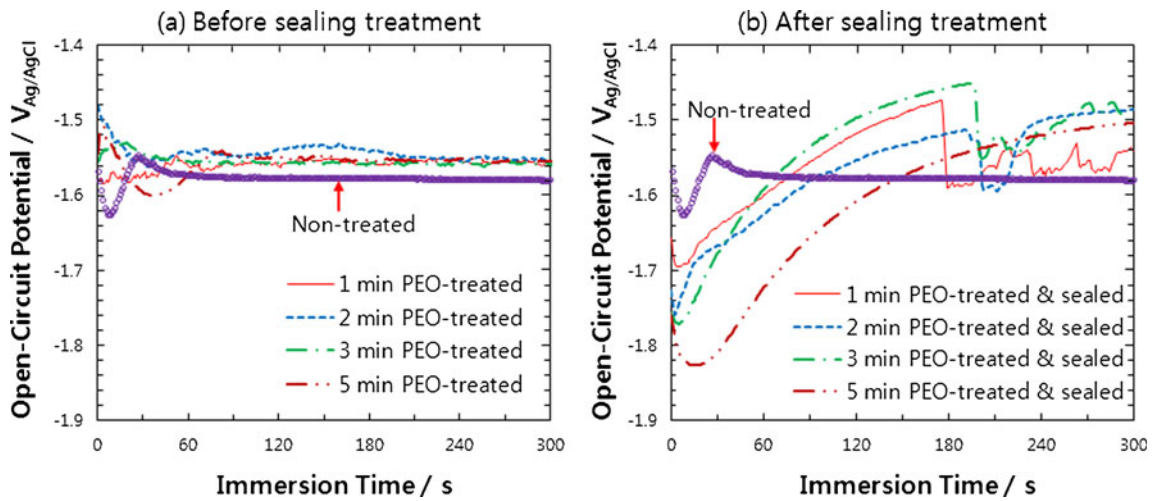


and anodic dissolution current densities were same with those of nontreated specimen. The 1 order lower cathodic current density of unsealed PEO film-covered specimens than that of

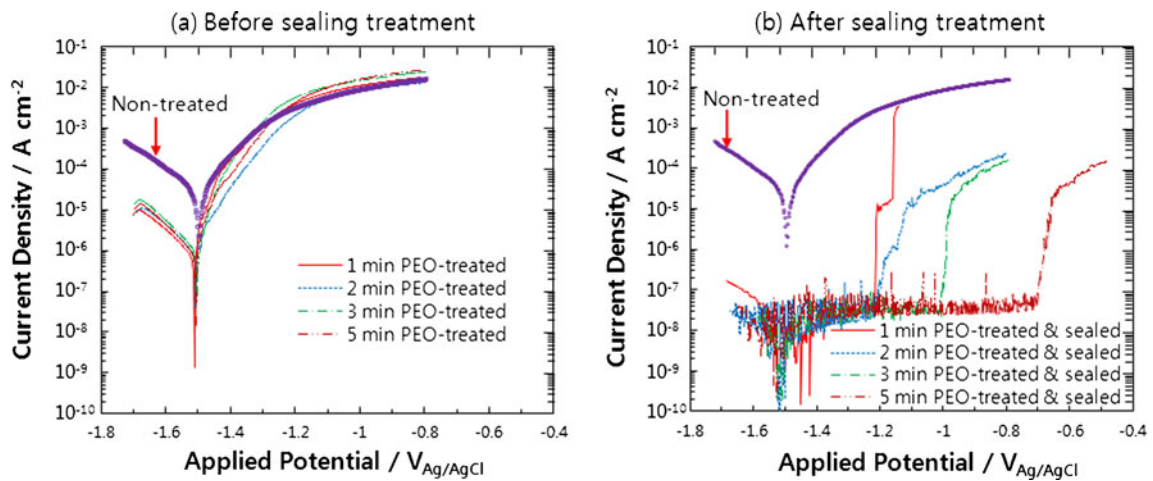
nontreated specimen is attributed to the reduced surface area useful for hydrogen evolution reaction. The same anodic dissolution current density of nontreated specimen with

**Fig. 4** Photographs of PEO-treated AZ31 Mg alloys with immersion time in 0.5 M NaCl solution. The PEO coatings were formed for of 1, 2, 3, and 5 min in 1 M NaOH+0.5 M NaF solution, and sealing treatments of the PEO coatings were conducted for 40 min in boiling water



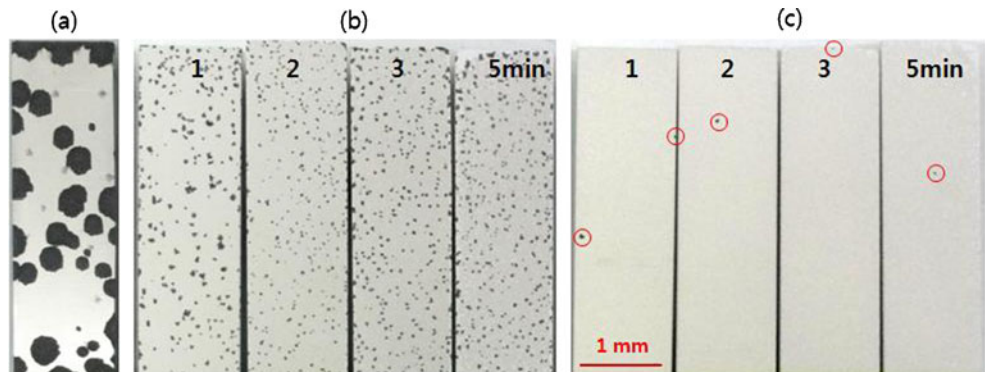


**Fig. 5** Open-circuit potential transients of nontreated and PEO-treated AZ31 Mg alloys in 0.5 M NaCl solution before (a) and after (b) sealing treatment in boiling water



**Fig. 6** Potentiodynamic polarization curves of nontreated and PEO-treated AZ31 Mg alloys in 0.5 M NaCl solution before (a) and after (b) sealing treatment in boiling water

**Fig. 7** Photographs of nontreated (a), unsealed PEO film-covered (b), and sealed PEO film-covered AZ31 Mg alloys after potentiodynamic polarization tests in Fig. 6



those of unsealed PEO film-covered specimens could be ascribed to a localized form of corrosion, as can be seen in Fig. 7a,b, in which surface area for anodic dissolution reaction may be the same.

Sealed PEO film-covered AZ31 Mg alloys showed three orders lowered cathodic current densities and more than 3 orders lowered anodic current densities than those of non-treated specimen (Fig. 6b). Pitting potential where abrupt increase of anodic current density occurs was observed for the sealed PEO film-covered specimens. The pitting potentials appear to be generally higher with PEO film thickness but they are also highly scattered because the PEO film thickness and pore size and shape are not uniform. The number of pits observed after the potentiodynamic polarization experiments appeared to be around 3 and 5 for the sealed PEO film-covered specimens, while it was more than 200 for the unsealed PEO film-covered specimens, as can be seen in Fig. 7. This represents that there are a number of corrosion initiation sites in as-formed PEO films but they are healed by sealing treatment in boiling DI water. The healing of corrosion initiation sites which can be pores and cracks seems to occur by volume expansion of the PEO films through hydration process of the anodic oxide films.

## Conclusions

Anodic films were formed on AZ31 Mg alloy by PEO method using pulse current for various durations in 1 M NaOH+0.5 M NaF solution, and their corrosion behavior and resistance were tested by immersion and potentiodynamic polarization methods before and after sealing treatment of the PEO films in boiling water. Corrosion of PEO-treated specimen occurred in the form of filiform corrosion during the immersion while it

showed pitting corrosion during potentiodynamic polarization tests in 0.5 M NaCl solution. Corrosion resistance of PEO-treated specimen appeared to be increased by the formation of thicker PEO films. Sealing treatment of the PEO films in boiling water improved remarkably the corrosion resistance of PEO-treated specimen which seems to be related with healing of the defects like pores and cracks by volume expansion of the PEO films through hydration process. No corrosion was observed for the sealed 5 min PEO film-covered AZ31 Mg alloy up to 300 h in 0.5 M NaCl solution.

**Acknowledgments** This research was financially supported by a research grant from the general research program from Korea Institute of Materials Science.

## References

1. Arrabal R, Matykina Viejo EF, Skeldon P, Thompson GE (2008) *Corros Sci* 50:1744–1752
2. Chai L, Yu X, Yang Z, Wang Y, Okido M (2008) *Corros Sci* 50: 3274–3279
3. Yabuki A, Sakai M (2009) *Corros Sci* 51:793–798
4. Zhang EF, Zhang SF (2009) *Corros Sci* 51:2820–2825
5. Forno AD, Bestetti M (2010) *Surf Coat Tech* 205:1783–1788
6. Zhang RF (2010) *Corros Sci* 52:1285–1290
7. Yagi S, Sengoku A, Kubota K, Matsubara E (2012) *Corros Sci* 57: 74–80
8. Moon S, Nam Y (2012) *Corros Sci* 65:494–501
9. Liang J, Srinivasan PB, Blawert C, Dietzel W (2009) *Corros Sci* 51: 2483–2492
10. Liu F, Shan D, Song Y, Han EH, Ke W (2011) *Corros Sci* 53:3845–3852
11. Lim TS, Ryu HS, Hong SH (2012) *Corros Sci* 62:104–111
12. Barchiche CE, Rocca E, Hazan J (2008) *Surf Coat Tech* 202:4145–4152
13. Verdier S, Boinet M, Maximovitch S, Dalard F (2005) *Corros Sci* 47: 1429–1444