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Corrosion response of annealed oxide film of pure Mg via plasma electrolytic oxidation in an electrolyte containing $KMnO_4$

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ABSTRACT

The purpose of this study was to investigate the corrosion resistance of the annealed oxide film of pure Mg coated by a plasma electrolytic oxidation (PEO) in an electrolyte containing $KMnO_4$. The effect of the annealing treatments subsequent to PEO coating on the structural development and corrosion characteristics of the PEO-treated pure Mg was studied. The addition of $KMnO_4$ to the electrolyte significantly affected the thickness, surface morphology, and chemical compound of the oxide films. From the results of potentio-dynamic polarization and salt spray tests in a 3.5 wt.% NaCl solution, a superior corrosion resistance of pure Mg could be achieved via the PEO process in a $KMnO_4$ containing electrolyte followed by an annealing treatment at 423 K.

1. Introduction

Mg is one of the lightest structural metallic materials, possessing good physical and mechanical properties such as high specific strength, good electromagnetic shielding, etc. These properties have made possible various applications in electronic devices including computer and mobile frames, where weight reduction is sought [1–4]. Nevertheless, the use of Mg has been strongly limited due to its high electrochemical reactivity under atmospheric corrosion conditions, because Mg hydroxide films formed on Mg become less stable than the passive films of other valve metals [5–7]. To date, a variety of surface treatments, such as anodizing, chemical conversion coating, and plasma electrolytic oxidation (PEO), have been suggested to enhance the corrosion resistance of Mg and its alloys. Among them, PEO was regarded as an eco-friendly coating method of forming an oxide film on metals under the plasma state generated by applying an extremely high anodic potential in an aqueous electrolyte. The surface structures of the PEO-coated oxide films were known to depend on processing factors such as electrolyte composition and annealing treatment. Thus, several strategies have been developed to address the corrosion problems of Mg [8,9]. For instances, the corrosion resistance of AZ91 Mg alloys was markedly enhanced by surface treatment in a bath with potassium permanganate ($KMnO_4$), resulting in pores filled with manganese oxides [10,11]. Recently, Hwang et al. [10] reported that the polarization resistance would be improved by subsequent annealing where the amount of passive MgO increased, whereas the amount of quasi-passive $Mg(OH)_2$ decreased relatively due to the dehydration reaction. However, little research has explored how the corrosion resistance of Mg would change if two beneficial effects coming from the addition of $KMnO_4$ to the electrolyte and annealing were combined in a subsequential manner. Therefore, the main purpose of this study was to investigate the influences of $KMnO_4$ incorporation in the electrolyte and the additional annealing treatment subsequent to the PEO coating on the surface micro morphology, chemical composition, and resultant corrosion resistance of the oxide film formed during electrochemical coating.

2. Experimental procedures

Pure Mg plates (99.9 wt.%) with a thickness of 2 mm were cut into 30 mm × 50 mm samples. Prior to PEO coating, the samples were polished with 1000 grit silicon carbide paper, rinsed with deionized water, and ultrasonically cleaned in ethanol. The samples were dried in warm air after cleaning. PEO treatments were carried out using a 20 kW power supply, a glass-vessel container with a sample holder and a cathode composed of stainless steel in the electrolyte. During the PEO coating, the temperature and current density of 293 K and 100 mA/cm^2 were maintained in order to stabilize the electrochemical reactions. To verify the effects of adding $KMnO_4$ to the aqueous electrolyte and the subsequent annealing on the corrosion responses of the PEO-treated samples, the three different conditions listed in Table 1 were deployed, which were referred to as 'condition A', 'condition B', and 'condition C', respectively. The surface and cross-sectional images of the oxide film formed were observed under a scanning electron microscope (SEM). For

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Table 1
Electrolyte compositions and process parameters used for the present PEO coating of pure Mg.

	Electrolyte (mol/L)				Annealing
	KOH	KF	Na_2SiO_3	$KMnO_4$	
Condition A	0.18	0.09	0.08	–	–
Condition B	0.18	0.09	0.08	0.07	–
Condition C	0.18	0.09	0.08	0.07	423 K, 1 h

surface chemical analysis, X-ray photoelectron spectroscopy (XPS) was performed. Potentio-dynamic polarization was tested to evaluate the corrosion properties of the PEO-treated samples in a 3.5 wt.% NaCl solution via a Reference 600 potentio stat (Gamry Instruments), which was composed of a conventional three-electrode cell: a sample as a working electrode, a carbon plate as a counter electrode, and an Ag/AgCl electrode as a reference electrode. The corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic and cathodic Tafel slopes (b_a and b_c) were measured to evaluate the corrosion properties of the coatings. These were derived from the potentio-dynamic polarization curves after Tafel extrapolation. Fitting method to obtain these parameters was found elsewhere [12]. The corrosion resistance of the samples was subjected to salt spray tests for 200 h. In compliance with ASTM standard B117, the chamber temperature was held at 308 K and a salt solution with 3.5 wt.% NaCl was used.

3. Results

3.1. Microstructure

Fig. 1 displays the surface morphologies of the oxide films on pure Mg samples coated with PEO. As shown in Fig. 1(a), the surface of the Mg sample via PEO coating using condition A had a dense, dimple-like structure together with micro-pores, which is a general features of the PEO process accompanying significant dielectric discharge [13,14]. In contrast, the samples treated by PEO under condition B and C exhibited many micro-pores filled with oxide compounds, shown in Fig. 1(b) and (c). To verify the chemical composition of the oxide compounds, the EDX line scanning is performed and its result is shown in Fig. 1(d). The amount of Mn element became higher within the oxide compounds. This finding indicated that some oxide compounds located near/within micro-pores was found to be Mn oxides.

The cross-sectional images of the oxide films of the PEO-treated pure Mg samples under conditions A, B and C are shown in Fig. 2. The film thickness should be same in order to consider the effects of $KMnO_4$ and annealing on corrosion behavior. The thickness values of samples coated in each condition was measured at ~10 μm. As seen in Fig. 2(a), the coarse pores with a size of ~5 μm were locally observed in the oxide film formed under condition A. The oxide films of conditions B and C, however, were comparably dense due to the beneficial effect of Mn oxides uniformly distributed in the

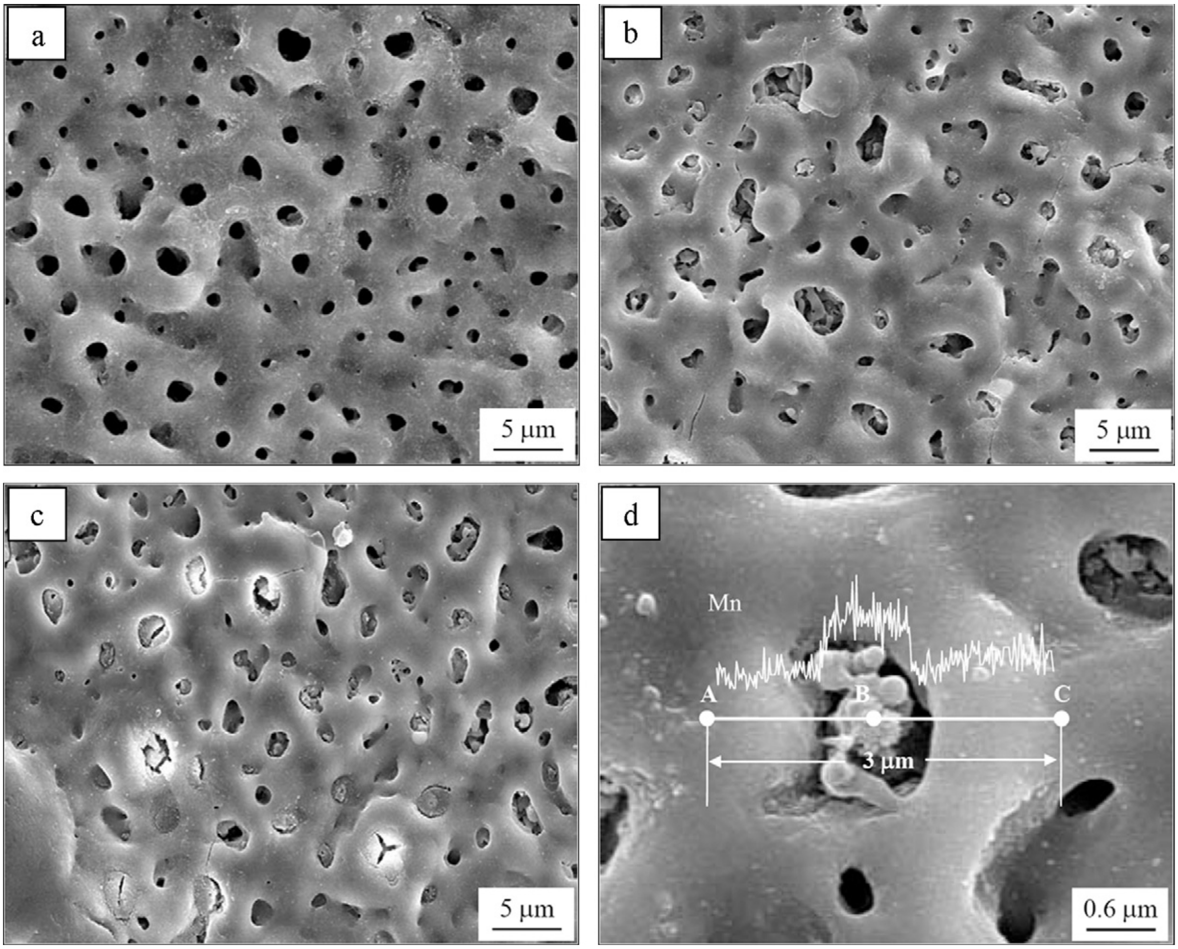

Fig. 1. SEM micrographs showing surface structures of the oxide films on pure Mg subjected to PEO coating under (a) condition A; (b) condition B; (c) condition C; and (d) EDX line scanning result for the sample under condition B.

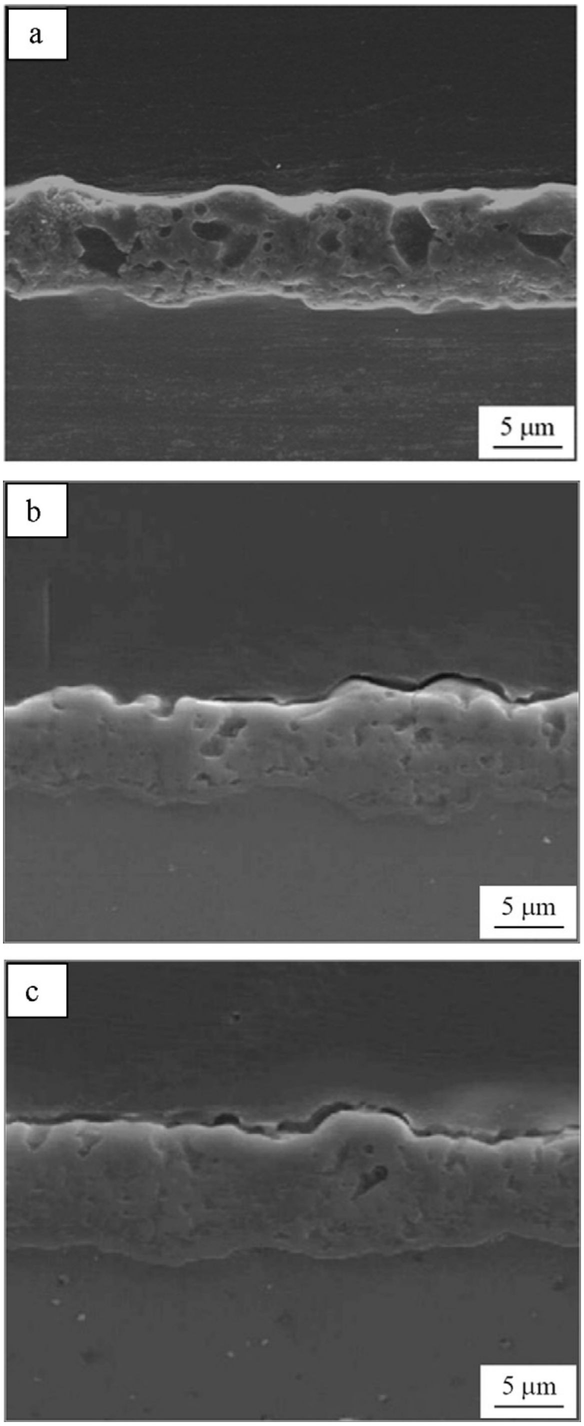

Fig. 2. SEM micrographs showing cross-sections of the oxide films on pure Mg subjected to PEO coating under (a) condition A; (b) condition B; and (c) condition C.

oxide films, causing significant augmentation in corrosion resistance. Furthermore, a comparison of Fig. 2(b) and (c) revealed that annealing treatment at 423 K had only little influence on the density of the oxide films.

3.2. Constituent compound

Fig. 3 presents the XPS spectra (Mg 2p 3/2) of the PEO-treated pure Mg with and without annealing treatment, corresponding to conditions B and C. There were two different compounds such as $Mg(OH)_2$ and MgO present in the Mg oxide film. The binding energy at 49.4 eV indicated the existence of $Mg(OH)_2$, whereas the binding energy at 50.3 eV was related to the formation of MgO [15,16]. The peak intensity of MgO was relatively lower for the sample without annealing treatment than that with annealing. Qualitative difference in peak intensity found between Fig. 3(a) and (b) showed that the amount of MgO compound in the oxide films increased and the amount of $Mg(OH)_2$ decreased when the sample was additionally annealed after PEO coating. An individual spectrum (Mn 2p 3/2) was measured to clarify the reacting products of Mn oxides in the oxide films formed under conditions B having $KMnO_4$ (Fig. 3(c)). The binding energy was found to be 641.7 eV [17], which suggested the formation of Mn_2O_3.

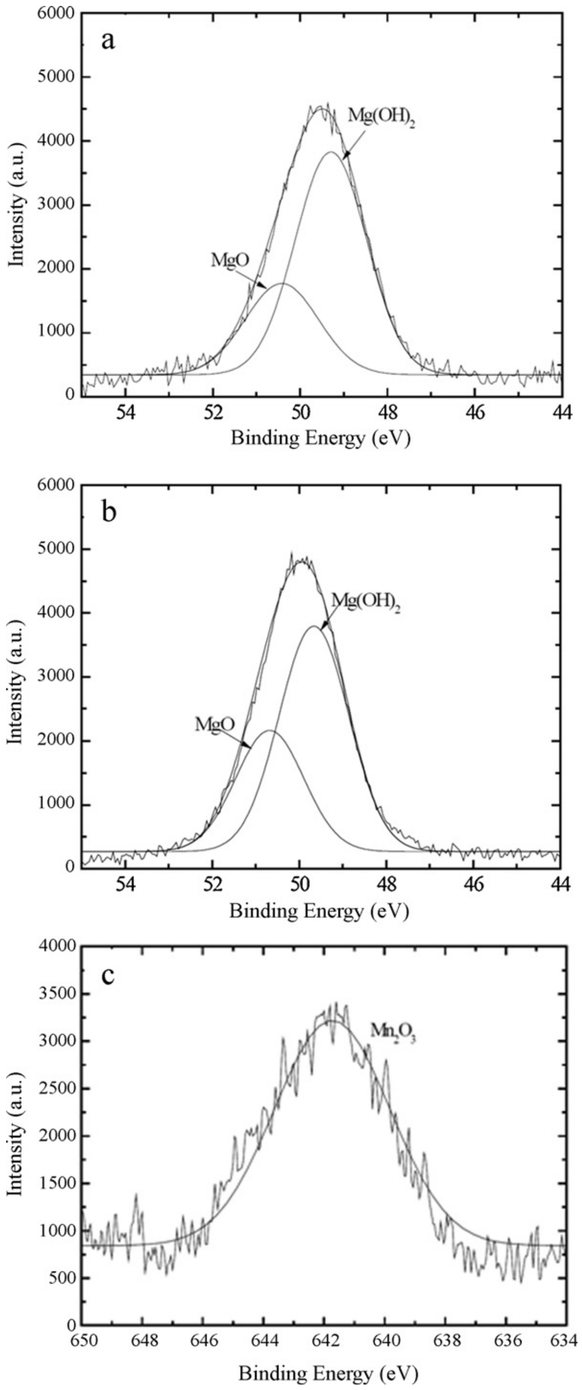

Fig. 3. XPS data (Mg 2p 2/3) of the oxide films on pure Mg subjected to PEO coating under (a) condition B; (b) condition C; and (c) XPS data (Mn 2p 2/3) under condition B.

Table 2
Results of potentio-dynamic corrosion tests on the samples under a seawater condition. The corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic and cathodic Tafel slopes (b_a and b_c) were determined by the potentio-dynamic polarization curves after Tafel extrapolation.

	E_{corr} (V)	i_{corr} (A/cm^2)	IE (%)	b_a (mV)	b_c (mV)
Pure Mg	−1.54	3.51×10^{-5}	–	0.062	0.157
Condition A	−1.35	5.61×10^{-7}	98.4	0.126	0.101
Condition B	−1.24	2.45×10^{-7}	99.3	0.073	0.187
Condition C	−1.15	1.05×10^{-7}	99.7	0.093	0.102

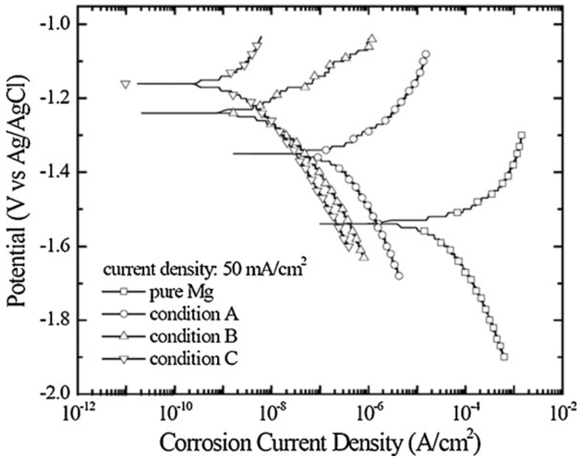

Fig. 4. Potentio-dynamic polarization curves of the samples under three different conditions in comparison to their uncoated counterparts.

3.3. Corrosion behavior

As shown in Fig. 4, the corrosion behavior of the PEO-treated samples prepared under three different conditions was evaluated by potentio-dynamic polarization in a 3.5 wt.% NaCl solution and was compared to that of substrate Mg. In addition, the inhibition efficiency (*IE*) was calculated by the following equation [18]:

$$IE_{(\%)} = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \qquad (1)$$

where i^0_{corr} and i_{corr} are the corrosion current density of the samples with and without coating in 3.5 wt.% NaCl solution, respectively. All electrochemical parameter values are listed in Table 2. In general, corrosion properties were enhanced by increasing the corrosion potential and/or decreasing the corrosion current density. The corrosion potential increased in the order of pure Mg for conditions A, B, and C. Moreover, the value of corrosion current density decreased by two orders of magnitude with respect to the uncoated Mg sample and was the lowest for condition C. This tendency was consistent with the analysis based on Eq. (1). These facts implied that the corrosion resistance obviously improved when PEO coating in the electrolyte containing KMnO4 was followed by static annealing.

To inspect the corrosion behavior under more realistic conditions, salt spray tests were carried out for 200 h on the three different samples. The results are shown in Fig. 5.

A number of filliform corrosion marks were observable on the surface of the sample via PEO coating using condition A. This tendency decreased in the order of pure Mg for conditions A, B, and C. As we could also expect from the polarization tests, the corrosion resistance of the oxide film formed under condition C seemed to be the highest of all conditions. Accordingly, the electrolyte including $KMnO_4$ as well as the annealing treatment of 423 K will be the optimum condition suitable for the PEO-processed pure Mg, satisfying the requirement of high stability in a corrosive environment.

4. Discussion

Based on the present EDS and XPS analysis, it was confirmed that when $KMnO_4$ was added, Mn oxides were readily formed, because the reaction between Mn ions coming from $KMnO_4$ in the electrolyte and oxygen was favored rather than that between Mn ions and Mg [19]. As for chemical reaction, MnO_2 was first produced by the anodic reaction through the decomposition of the electrolyte containing Mn ions (MnO_4^-) during the PEO coating. The formation of Mn_2O_3 could be generated by successive oxidation of MnO_2, as described below:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \qquad (2)$$

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^- \qquad (3)$$

Despite the addition of $KMnO_4$ and even annealing treatment, however, average pore size and distribution of samples remained constant. This suggested that the influence of $KMnO_4$ addition and annealing treatment on the surface pore structure was less significant.

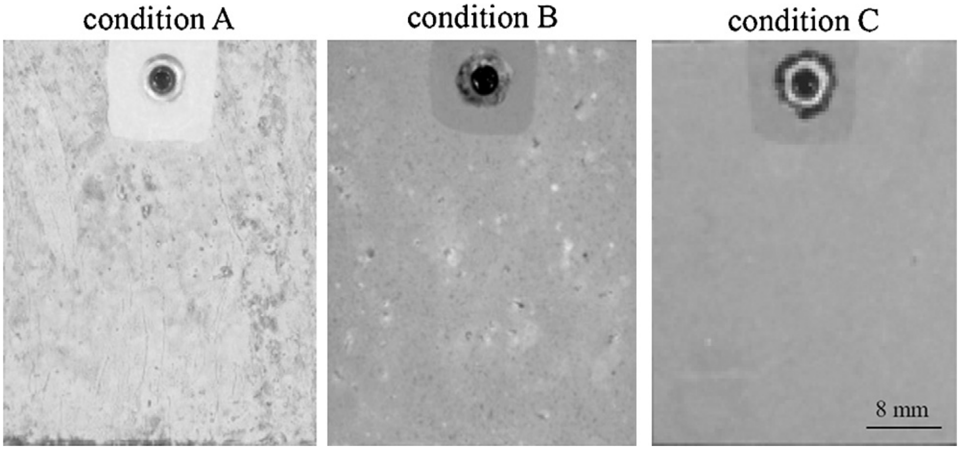

Fig. 5. Surface changes of the PEO-coated Mg samples after salt spray testing for 200 h.

De-convolution analysis based on the present XPS results (Fig. 3) showed that the amount of MgO compound in the oxide films increased while the amount of $Mg(OH)_2$ decreased when the sample was additionally annealed after PEO coating. Sharma et al. [20] reported that the dehydration reaction was thermodynamically endothermic and would take place at ~410 K where $Mg(OH)_2$ in the oxide film decomposed into MgO and H_2O [21]. Thus, the relative ratio of $MgO/Mg(OH)_2$ in the oxide films depended on subsequent annealing. An annealing temperature of 423 K was found to be desirable for increasing the amount of MgO working as a hard phase.

As discussed earlier [9,22], the corrosion resistance was mainly related to the thickness of the oxide film. Irrespective of the $KMnO_4$ addition and additional annealing, the thickness of the oxide films remained constant. Under this situation, corrosion resistance depended upon the micro morphology and chemical compounds being present in the oxide film. First, the presence of Mn ions in the electrolyte rendered the Mn oxides prone to being located in the vicinity of micro-pores as shown in Fig. 1(d). This altered the topography of the oxide film, which could contribute to a better corrosion resistance by decreasing the contact area between the external corrosive ions and Mg substrate. Second, comparing conditions B and C, the corrosion resistance was further improved. During subsequent annealing, the transformation of $Mg(OH)_2$ led to the increase in the relative amount of the MgO compound. Since MgO was more stable than $Mg(OH)_2$, an increment of the MgO content present in the oxide film was important in improving the corrosion resistance. It is thought that the good combinations of the electrolyte including $KMnO_4$ and the annealing treatment will be beneficial for improving corrosion-protection properties of the pure Mg via PEO coating.

5. Summary

The influence of $KMnO_4$ and annealing treatment on morphological changes and corrosion characteristics of PEO-treated pure Mg was studied. Corrosion resistance of the PEO-treated sample in the electrolyte with $KMnO_4$ was superior to that of the sample without $KMnO_4$ because the addition of $KMnO_4$ resulted in the occurrence of Mn_2O_3. The annealing treatment associated with dehydration of $Mg(OH)_2$ was also effective, allowing MgO content in the oxide film to increase. Consequently, we believe that the electrolyte in $KMnO_4$ condition with SA treatment in this study should be selected for its achievement of good electrochemical properties of pure Mg after the PEO technique.

Acknowledgements

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References

[1] A.L. Rudd, C.B. Breslin, F. Mansfeld, Corros. Sci. 42 (2000) 275–288.
[2] E. Aghion, B. Bronfin, D. Elezer, J. Mater. Proc. Technol. 117 (2001) 381–385.
[3] L. Wang, L. Chena, Z. Yana, H. Wanga, J. Penga, J. Alloys Compd. 480 (2009) 469–474.
[4] N.J. Park, J.H. Hwang, J.S. Roh, J. Kor. Inst. Met. Mater. 47 (2009) 1–6.
[5] R. Arrabal, E. Matykina, T. Hashimoto, P. Skeldon, G.E. Thompson, Surf. Coat. Technol. 203 (2009) 2207–2220.
[6] Y. Zhang, C. Yan, Surf. Coat. Technol. 201 (2006) 2381–2386.
[7] J.Y. Lee, G. Han, Y.C. Kim, J.Y. Byun, J. Jang, H.K. Seok, S.J. Yang, Met. Mater. Int. 15 (2009) 955–961.
[8] G.L. Song, A. Atrens, Adv. Eng. Mater. 5 (2003) 837–858.
[9] H.P. Duan, C.W. Yan, F.H. Wang, Electrochim. Acta 52 (2007) 3785–3793.
[10] D.Y. Hwang, Y.M. Kim, D.Y. Park, B. Yoo, D.H. Shin, Electrochim. Acta 54 (2009) 5479–5485.
[11] Y.G. Ko, K.M. Lee, K.R. Shin, D.H. Shin, Kor. J. Met. Mater. 48 (2010) 724–729.
[12] M. Stern, A.L. Geary, J. Electrochem. Soc. 104 (1957) 56–63.
[13] P. Su, X. Wu, Y. Guo, Z. Jiang, J. Alloys Compd. 475 (2009) 773–777.
[14] H. Duan, C. Yan, F. Wang, Electrochim. Acta 52 (2007) 5002–5009.
[15] H. Umehara, M. Takaya, S. Terauchi, Surf. Coat. Technol. 169 (2003) 666–669.
[16] H.Y. Hsiao, P. Chung, W.T. Tsai, Corros. Sci. 49 (2007) 781–793.
[17] J.T. Beng, J.K. Kenneth, M.A.S. Peter, J. Am. Chem. Soc. 113 (1991) 855–861.
[18] S.E. Manahan, Environmental Chemistry, 6th ed., Lewis, Boca Raton, 1994.
[19] A.L. Yerokhin, X. Nie, A. Leyand, A. Mattews, S.J. Dowey, Surf. Coat. Technol. 122 (1999) 73–93.
[20] A.K. Sharma, R. Uma Rani, S.M. Mayanna, Thermochim. Acta 376 (2001) 67–75.
[21] Y. Zhang, C. Yan, F. Wang, W. Li, Corros. Sci. 47 (2005) 2816–2831.
[22] D.Y. Hwang, Y.G. Ko, Y.M. Kim, B. Yoo, D.H. Shin, Mater. Trans. 51 (2010) 408–412.