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Electrochemical corrosion behaviour of ZE41 and QE22 magnesium alloys

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Abstract. The study suggests that the rare-earths containing magnesium alloys ZE41 and QE22 exhibit a poorer corrosion resistance than the AZ80 magnesium alloy. Electrochemical experiments showed that the two rare-earths containing alloys are highly susceptible to localized corrosion. Post corrosion analysis revealed intergranular and pitting corrosion in ZE41, whereas QE22 alloy underwent only pitting corrosion.

Introduction

In recent years, magnesium based alloys have attracted great attention in automotive applications due to their favourable high strength to weight ratio. However, it is well known that magnesium alloys are susceptible to various forms of corrosion such as general and localized corrosion which hinders their widespread applications [1–3]. Alloying and surface coating methods have been researched in the past few years.

Rare-earth elements are added to magnesium and its alloys especially to enhance their creep resistance [7]. Interestingly, it is reported in the literature that rare-earth addition also enhances the corrosion resistance of magnesium and its alloys in chloride-containing environments [8-12]. A few authors have reported that the rare-earths enhance the passivation tendency of magnesium and its alloys [9, 12]. Chang et al. [11] reported that Nd containing Mg alloy (Mg-3Nd-0.2Zr) exhibited higher corrosion resistance than even AZ91D Mg alloy. However, corrosion studies on the rare-earths containing magnesium alloys, ZE41 and QE22, which also contain elements like zinc (in ZE41) and silver (in QE22) that are potential corrosion accelerators, are limited. Hence, in this study the electrochemical corrosion behaviour of ZE41 and QE22 were studied using electrochemical methods such as potentiodyanamic polarisation and electrochemical impedance spectroscopy. For comparison, the well-known aluminium-containing AZ80 alloy was also studied.

Experimental Procedure

Rare-earth containing magnesium alloys ZE41 (4.13% Zn, 0.7Zr, 0.003% Fe, 1.18 TRE and Bal. Mg, all wt.%) and QE22 (2.23% Ag, 2.03% Nd, 0.64% Zn, 2.09% TRE and Bal. Mg), and AZ80 (8.59%Al, 0.45%Zn 0.16% Mn, 0.003.% Fe and Bal. Mg) magnesium alloy were studied in this work. The thermo-mechanical treatments given to these alloys are listed in Table 1. The electrochemical corrosion behaviour of the alloys were studied using techniques such as potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS). A potentiostat and a frequency response analyser were used for electrochemical experiments. A typical three electrode system consisting of graphite as a counter electrode, saturated calomel electrode as a reference electrode and sample as a working electrode were used. The samples were grinded with SiC paper up to 2400 grit followed by washing the samples with distilled water and ultrasonically cleaning in acetone. The test electrolyte was a 0.5 wt. % NaCl solution. Prior to testing, the samples were allowed for 2 h to reach a relatively stable open circuit potential. EIS experiments were performed over the frequency range of 10^5 Hz to 10^{-2} Hz at an AC amplitude of 10 mV. Potentiodynamic polarisation experiments were carried out at a scan rate of 0.5 mV/s. After the corrosion tests the samples were examined using scanning electron microscopy (SEM) to identify the mode of corrosion attack.

Table 1: Thermo-mechanical treatments of the magnesium alloys.

Alloy	Thermo-mechanical treatment
AZ80	T4 – Stress relieved for 8 h at 385°C and then aged for 16 h at 420°C.
ZE41	T5 – Stress relieved for 2 h at 330°C and then aged for 16 h at 180°C.
QE22	T6 – Solution treated for 8 h at 520°C followed by hot water quenching and then aged for 16 h at 200°C.

Results and Discussion

The Nyquist plots of the alloys are shown in Fig. 1a. The rare-earths containing alloys showed a lower polarization resistance (R_p) than that of AZ80 alloy, i.e., ZE41 and QE22 exhibited R_p-values of 1.2 x 10^3 Ω.cm^2 and 1.5 x 10^3 Ω.cm^2, respectively, whereas AZ80 exhibited an R_p of 2x10^4 Ω.cm^2. AZ80 alloy revealed two capacitive loops over the frequency range, which is due to the film effect [13, 14]. However, ZE41 and QE22 alloy exhibited only one capacitive loop. This indicates a scarce/no protective film formation on the rare-earths containing alloys after the 2 h exposure period. Interestingly, an inductive loop was observed at low frequency for the rare-earths containing alloys. This behaviour is widely related to pitting corrosion [15,16]. Thus, it can be suggested that the rare-earths containing alloys are more susceptible to pitting corrosion than the AZ80 alloy.

The polarisation curves of the alloys are shown in Fig. 1b, and the corresponding electrochemical data are given in Table 1. ZE41 and QE22 alloys showed slightly noble potentials as compared to that of AZ80 alloy. This could be due to the direct effect of alloying elements (i.e., Ag and Zn) which are generally noble to magnesium, i.e., according to the mixed-potential theory the sample potential

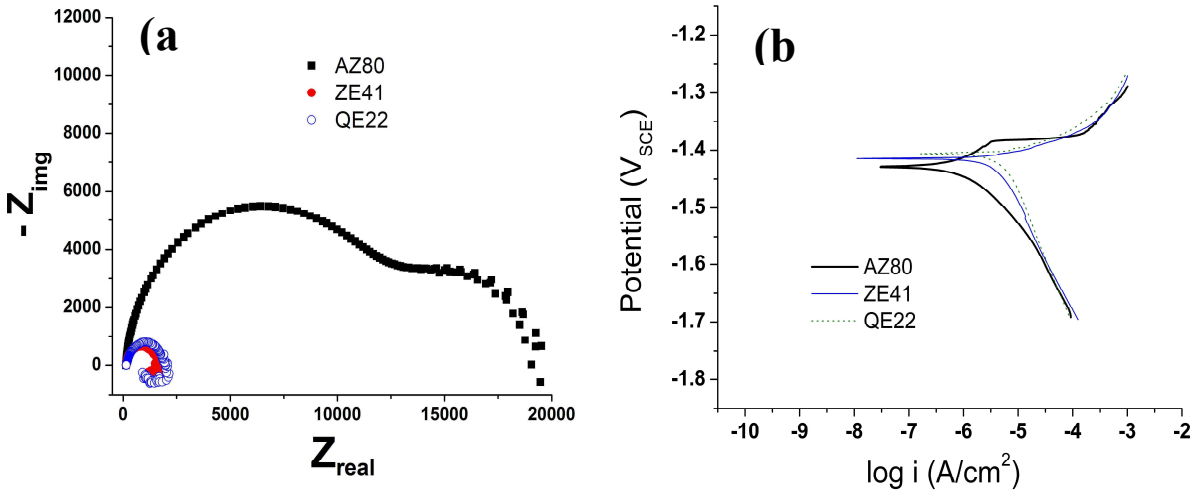

Fig. 1 Electrochemical results of magnesium alloys in 0.5wt.% NaCl solution: (a) EIS, and (b) potentiodynamic polarization.

Table 2: Electrochemical data from the potentiodynamic polarization curves of magnesium alloys.

Alloy	E_{corr} (V_{SCE})	i_{corr} (x 10^{-6} A/cm^2)	E_{bd} (V_{SCE})
AZ80	-1.420	1.237	-1.385
ZE41	-1.414	4.377	-1.414
QE22	-1.406	5.542	-1.406

shifts towards noble direction by adding elements having relatively nobler potentials than the base metal. The cathodic curves of the alloys showed a higher cathodic current for ZE41 and QE21 alloy as compared to AZ80 alloy for at least 100 mV below E_{corr}. As a result, the rare-earths containing alloys showed higher corrosion currents than the AZ80 alloy. Noticably, the anodic polarisation curve of AZ80 showed a passive-like region of about 50 mV above E_{corr} prior to a sharp increase in the current. The breakdown potential in the anodic region is due to the pitting corrosion of the alloy. Intrestingly, ZE41 and QE22 alloys showed a sharp increase in the anodic current just above the E_{corr}. This indicates that pitting corrosion in the rare-earths containing alloys occurs even at their open circuit potential. So, in the case of ZE41 and QE22 alloys the breakdown potential/pitting potential is pinned with their corrosion potential.

Post-corrosion micrographs of the alloys are shown in Fig. 2. AZ80 alloy showed fine pits throughout the sample. It can be noticed that the localized attack is along one direction, which could be due to the extrusion (mechanical treatment) of the alloy. However, ZE41 alloy showed extensive corrosion of the grains. Pitting and intergranular corrosion were also observed in ZE41 alloy. The corrosion attack of the QE22 alloy was slightly different from that of the ZE41 alloy. QE22 showed large pits in both the grains and grain boundaries.

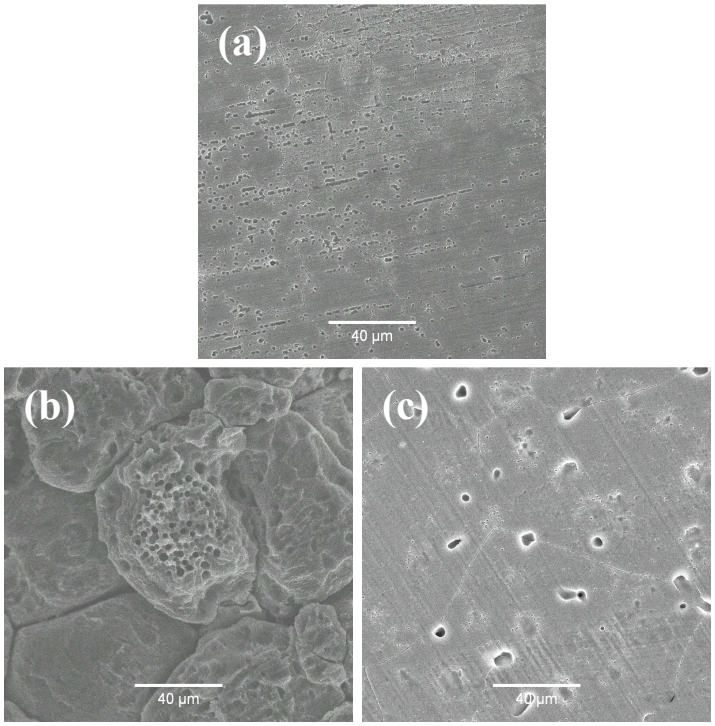

Fig. 2 SEM micrographs of magnesium alloys after potentiodyanamic polarization in 0.5wt.% NaCl solution: (a) AZ80, (b) ZE41, and (c) QE22.

Both the potentiodynamic polarization and EIS experiments showed that rare-earths containing alloys ZE41 and QE22 posses lower corrosion resistance than the AZ80 alloy. Although it is reported in the literature that rare-earth addition to magnesium enhances the passivation tendency of the alloy, it appears from this study that in the presence of other corrosion inducing elements such as zinc (in ZE41) and silver (in QE22) the influence of rare-earth is not significant.

Conclusion

Electrochemical experiments showed that the corrosion resistance of rare-earths containing alloys ZE41 and QE22 is inferior to that of AZ80 alloy in 0.5 wt.% NaCl solution.

References

[1] E. Ghali, W. Dietzel, K.U. Kainer: J. Mater. Eng. Perform 13 (2004), p.7.

[2] M. Bobby Kannan, W. Dietzel, R.K. Singh Raman, P. Lyon: Scripta Mater.

57 (2007), p. 579.

[3] M. Bobby Kannan, W. Dietzel, C. Blawert, A. Atrens, P. Lyon: Mater Sci Eng A 480 (2008), p.529.

[4] G.L. Song, A. Atrens: Adv. Eng. Mater. 5 (2003), p.837.

[5] C. Blawert, V. Heitmann, W. Dietzel, H.M. Nykyforchyn, M.D. Klapkiv: Surface and Coating Technology 201 (2007), p. 8709.

[6] M. Bobby Kannan, D. Gomes, W. Dietzel, V. Abetz: Surface and Coating Technology 202 (2008), p. 4598.

[7] L.L. Rokhlin, in: Taylor and Francis (Eds.), Magnesium Alloys Containing Rare Earth Metals, London, 2003.

[8] I. Nakatsugawa, S. Kamado, Y. Kojima, R. Ninomiya, K. Kubota: Corros. Rev. 16 (1998), p.139.

[9] J. H. Nordlien, K. Nisancioglu, S. Ono, N. Masuko: J. Electrochem. Soc. 144 (1997), p.461.

[10] M. Kiryuu, H. Okumura, S. Kamado, Y. Kojima, R. Ninomiya, I. Nakatsugawa: J. Jpn. Inst. Light Met. 46 (1996), p.39.

[11] J. Chang, X. Guo, P. Fu, L. Peng, W. Ding: Electrochim Acta 52 (2007),p. 3160.

[12] S. Krishnamurthy, M. Khobaib, E. Robertson, F.H. Froes: Mater. Sci. Eng. 99 (1988), p.507.

[13] L.F. Guo, T.M. Yue, H.C. Man: J. Mater. Sci. Lett. 40 (2005), p.3531.

[14] R. Walter, M. Bobby Kannan: Materials Letters 65 (2011), p.748.

[15] S. Jin, S. Amira, E. Ghali: Adv. Eng. Mater. 9 (2007), p.75.

[16] R. Walter, M. Bobby Kannan: Materials and Design 32(2011), p.2350.