Original

Electrochemical Corrosion Behaviour of WE54 Magnesium Alloy

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Abstract. The electrochemical corrosion behaviour of WE54 magnesium alloy in 0.5 wt.% NaCl solution was studied using electrochemical techniques. Polarization results suggested that the rare-earths in WE54 alloy enhanced the passivation tendency of the alloy and decreased the corrosion current by ~30% compared to pure magnesium. Pitting corrosion resistance was also higher in WE54 alloy than that in pure magnesium. Long-term electrochemical impedance results showed that the polarization resistance of WE54 alloy was more than two times higher than that of pure magnesium even after initial passivity breakdown.

Introduction

Magnesium alloys are used in engineering applications due to their attractive mechanical properties and weight saving potential. However, the widespread use of magnesium alloys is still limited by their poor corrosion and creep properties. In recent years, various rare-earths have been added to magnesium and its alloys to improve their creep resistance [1-3]. The studies have shown that WE54 alloy exhibits better creep resistance than the commercially popular AZ91 alloy and also ZE41 alloy which contains rare-earths [1].

Interestingly, some of the rare-earths such as yttrium (Y) and neodymium (Nd) have improved the corrosion resistance of magnesium and its alloys in chloride-containing environments. Luo et al. [4] reported that addition of yttrium (above 0.3wt.%) enhances the corrosion resistance of magnesium. A detailed study by Yao et al. [5] on the passivation behaviour of magnesium-yttrium alloy suggests that yttrium (Y) enhances the passivation behaviour of the alloy and the passive film consists of MgO and Y_2O_3. Krishnamurthy et al. [6] reported the pseudopassivation behaviour of another rare-earth, neodymium (Nd), in magnesium-neodymium alloys, which they attributed to neodymium enrichment on the surface. Also, Chang et al. [7] found that a neodymium-containing magnesium alloy (Mg-3Nd-0.2Zn-0.4Zr) possesses higher corrosion resistance than even the commercially popular AZ91D magnesium alloy. However, the electrochemical corrosion behaviour of WE54 alloy which contains both yttrium and neodymium has not been studied. In this work the electrochemical corrosion behaviour of WE54 alloy in chloride-containing solution was examined using electrochemical techniques.

Experimental Procedure

WE54 alloy having the composition Y (4.85), Nd (1.58), Zr (0.28), Gd (0.13), Er (0.16) Yb (0.13), Ce (0.08), Mg (balance) (all in wt.%) was used in this study. The alloy was heat treated to the peak aged condition i.e. solutionised at 525 °C for 8 h and then peak aged for 16 h at 250 °C. Electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were used to understand the passivation behaviour of WE54 alloy. For comparison, pure magnesium (99% purity) was also investigated. A typical three-electrode system was used in this study, i.e. the sample as a working electrode, silver/silver-chloride (Ag/AgCl) as a reference electrode and graphite as a counter electrode. The electrolyte used in the study was 0.5 wt % NaCl solution. The test samples were ground with SiC paper up to 2500 grit

and later polished with 6 μm alumina paste and then washed with distilled water and ultrasonically cleaned in acetone and rinsed with ethanol prior to the electrochemical experiments. EIS experiments were performed at open circuit potential with AC amplitude of 5 mV over the frequency range 10^{5} Hz to 10^{-2} Hz. In order to understand the long-term passivation behaviour of the alloy, EIS experiments were carried out after different exposure times i.e. 2, 6, 9, 15, 30, 75 and 100 hours. Potentiodynamic polarisation experiments were carried out at a scan rate of 0.5 mV/s. Prior the EIS and polarization experiments the samples were kept immersed in the electrolyte for 2 h to establish the free corrosion potential. Scanning electron microscope (SEM) analysis of the polarized samples was done to identify the mode of corrosion attack.

Results and Discussion

Fig. 1 shows the Nyquist plots of pure magnesium and WE54 alloy in 0.5 wt.% NaCl solution for different exposure times. After 2 h exposure, both pure magnesium and WE54 alloy exhibited two capacitive loops, one at high frequency and another at mid frequency, and the diameter of the loops can be related to the charge transfer resistance and the surface film resistance for mass transfer, respectively [8,9]. The second capacitive loop for pure magnesium disappeared after 6 h of exposure, whereas for WE54 alloy it faded only after 15 h exposure and interestingly reappeared in the final 100 h exposure test. This suggests that the partially protective film on pure magnesium was destroyed heavily after 6 h exposure and in WE54 alloy the film was relatively stable for a longer period of time and also the alloy had the repassivation capacity. There was also evidence of inductive loop for both pure magnesium and WE54 alloy after 2 h exposure. This kind of phenomenon in magnesium and its alloys is generally related to their pitting corrosion susceptibility [10,11]. It is well known that magnesium and its alloys are prone to pitting corrosion in chloride-containing environments [12-15]. As the exposure time increased, the inductive loop continued to exist for pure magnesium, but for WE54 alloy it was absent until 15 h exposure and appeared after 30 h exposure and again faded after 100 h exposure. The appearance and disappearance of the inductive loop can also be correlated to the stability of the passive film i.e. when the surface film is relatively stable then the inductive loop disappears and when the surface film is destroyed heavily then the inductive loop appears.
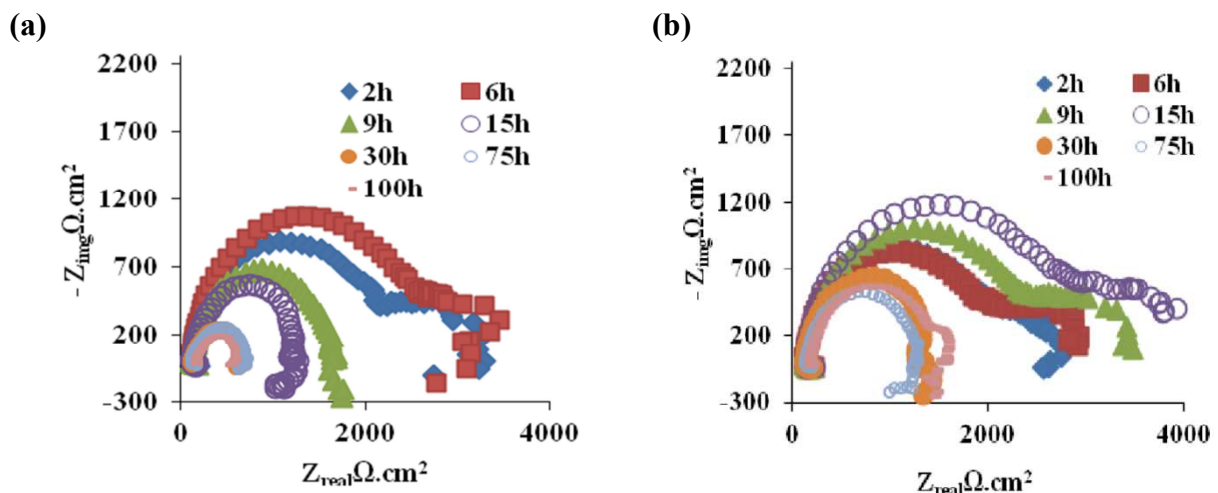
(a) **(b)**

Fig. 1. Nyquist plots for (a) pure magnesium and (b) WE54 alloy in 0.5 wt.% NaCl solution.

The polarization resistance R_p (calculated by adding the charge transfer resistance and the surface film resistance for mass transfer) of pure magnesium and WE54 alloy against the exposure time is plotted in Fig. 2. Pure magnesium exhibited R_p of 2400 $\Omega.cm^2$ after 2h exposure, whereas WE54 alloy showed 2120 $\Omega.cm^2$ of R_p. As the exposure time increased to 6 h, both the samples showed marginal increase in the R_p. However, pure magnesium showed continuous drastic fall in the R_p after 9 h to 30 h exposure. The R_p of pure magnesium at 30 h exposure was 470 $\Omega.cm^2$.

Although the R_p marginally increased after 75 h it dropped again at the final test (after 100 h exposure). Interestingly, WE54 alloy showed increase in R_p value until 15 h, which exposure and then drastically decreased when tested at 30 h exposure. However, the R_p of WE54 alloy (1020 $\Omega.cm^2$) after 30 h exposure was higher than that of pure magnesium (470 $\Omega.cm^2$). Further, WE54 alloy showed increase in R_p as the exposure time increased to 75 h and 100 h. The initial lower R_p for WE54 alloy compared to that of pure magnesium could be due to the microgalvanic effect of rare-earths and magnesium leading to surface film formation, and the sharp fall in the R_p observed in pure magnesium (after 6 h) and WE54 alloy (after 15 h) could be related to the surface film breakdown, which also suggests that the surface film on WE54 alloy is relatively more protective than that on pure magnesium.

The polarization curves of pure magnesium and WE54 alloy in 0.5 wt % NaCl solution are shown in Fig. 3. The data obtained from the polarization curves are given in Table 1. The corrosion potential of WE54 alloy (-1.515 V) was ~40 mV nobler than pure magnesium (-1.555 V). The corrosion current (i_{corr}), calculated based on only the cathodic slopes because of the negative difference effect in the anodic curves [15,16], showed that WE54 possess ~30% lower i_{corr} compared to that of pure magnesium, i.e., i_{corr} for pure magnesium was 11.91 $\mu A/cm^2$ and for WE54 was 8.13 $\mu A/cm^2$, which suggests that the corrosion resistance of WE54 alloy is higher than that of pure magnesium. The better passivation behaviour of WE54 alloy compared to pure magnesium was clearly evident when comparing the current in the anodic curves.
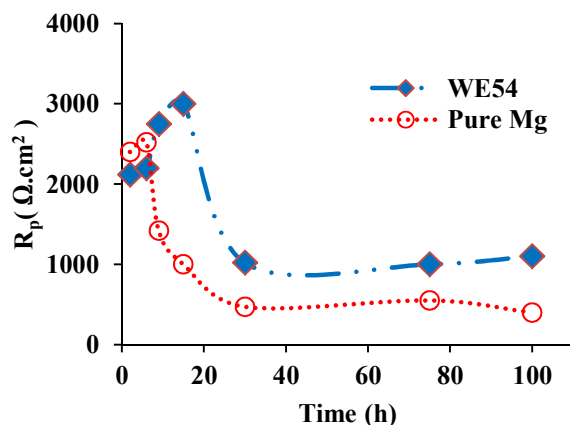

Fig. 2. Change in polarisation resistance with increase in exposure time intervals in 0.5 wt.% NaCl solution.
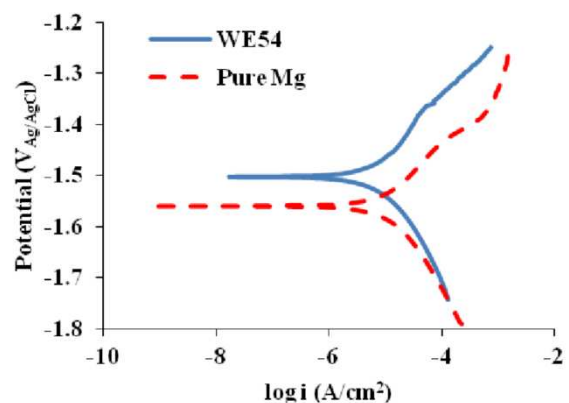
Fig. 3. Polarisation curves for WE54 alloy and pure magnesium in 0.5 wt.% NaCl solution.
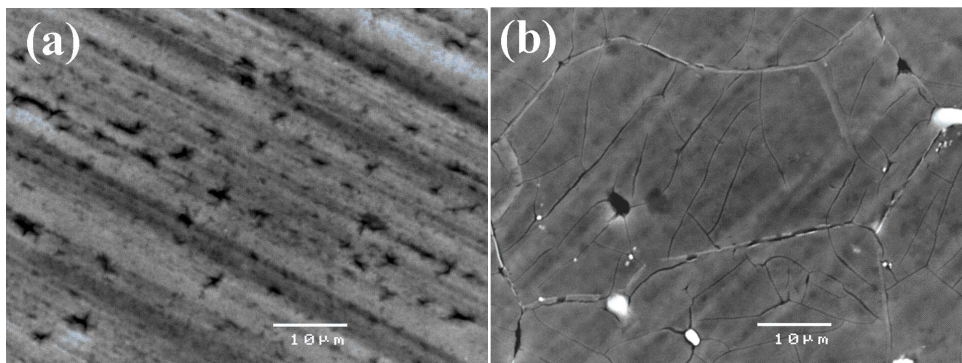

Fig. 4. Post-corrosion SEM micrographs of: (a) pure Mg and (b) WE54 alloy.

Fig. 4 shows post corrosion SEM micrographs for pure magnesium and WE54 alloy. Pure magnesium exhibited a large number of fine pits. In contrast, WE54 alloy did not show high susceptibility to pitting corrosion, only a few small pits were observed which appears to be due to detachment of secondary phase particles. Apparently, the secondary phase precipitates did not show

any sign of dissolution, which means that they are noble with respect to the magnesium matrix. The pit morphology in WE54 alloy suggests that the matrix in the vicinity of the coarse particles has dissolved, consequently allowing the particles to detach from the alloy.

Another observation was that the WE54 alloy after polarization revealed film cracking on the surface which confirms the surface film formation on the alloy, whereas pure magnesium did not show any such morphology. Hence, it can be stated that the rare-earths in WE54 alloy have improved the passivation tendency of the alloy in 0.5 wt.% NaCl solution when compared to pure magnesium.

Conclusions

Electrochemical corrosion experiments showed that the passivation tendency and corrosion resistance of WE54 alloy was higher than that of pure magnesium in 0.5 wt.% NaCl solution. The rare-earths in WE54 alloy lead to enhanced the passivation behaviour of the alloy. As a result of the better passivation behaviour, WE54 alloy exhibited higher pitting corrosion resistance compared to that of pure magnesium.

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