Corrosion Rate of EZ33-xPr Magnesium Alloy

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Abstract— Unalloyed magnesium is widely utilized in structural applications. therefore, the corrosion resistance of magnesium alloys is of major focus, hence, studies on the corrosion principles are highly significant. Though single-rare earth element (REE) modification has been confirmed to develop the properties of Mg alloys, the action mechanisms of multi-REE modification are still uncertain. Multiple REEs has many ways to enhance material properties. Thus, in this study, the effects of single addition of praseodymium (Pr) on the corrosion resistance of EZ33 Mg alloy was investigated. Weight loss corrosion test and optical microstructure examination were used to measure corrosion rate of EZ33-xPr magnesium alloys with different addition of Pr. Corrosion rate amounts of EZ-33, EZ-33-0.5 Pr, EZ-33-0.75 Pr and EZ-33-1.25 Pr were 0.0087, 0.011, 0.0123, and 0.0096 mm/year respectively. Furthermore, the last addition of Pr (1.75 wt/%) led to increase corrosion rate of base alloy with about 0.03 mm/year. The microstructure images showed that the corrosion attacks the grain boundaries more than the grains per se, where the intermetallic phases were formed, also pitting spots was observed at particular zones inside the grains, thus, the present results would offer some useful information for a better understanding of the corrosion behavior of Mg-RE alloys concerning the RE alloying addition to develop a new generation of Mg-based alloys with excellent corrosion resistance and therefore extend their use in a variety of applications.

Keywords— weight loss, magnesium, corrosion, intermetallic

I. INTRODUCTION

Magnesium (Mg) alloys are utilized in many nonstructural and structural applications, because they have lightweight, better stiffness and strength at high temperatures than many other structural alloys. Mg alloys have increasing interest as light alloys for automobile and aerospace projects as well as power tools [1, 2]. Keeping in mind, the common disadvantages such as the low strength and corrosion resistance because of their poor formability [3, 4]. Some Mg alloys have remarkable stiffness-to-weight specifications. However, since magnesium alloys are chemically more reactive than other structural metals, emphasis must be placed on the efficacy and care of protective systems applied to these alloys. Unquestionably, because of the mentioned features they are preferred in aircraft manufacturing, as they are facing numerous environmental changes, such as salts, high humidity, moisture, liquid fuels, and oils. On the protective film of helicopters, a damage can occur to exposed magnesium result from impact of grit or small stones lifted by rotor-caused air turbulence. Further usages of magnesium alloys would be accomplished if protection methods from corrosion is improved [5]. Required properties of Mg alloys such as high specific strength, low density, , good castability, excellent machinability and weldability [6] cause high efficiency and reduced carbon emissions by the weight reduction of active components [7]. Alloying rare-earth (RE) elements is an effective method to improve the strength and ductility of magnesium alloys, such as Gd, Nd, Pr, and Y [8]. However, their lack of stability to corrosion can affect their uses. Some alloying element can enhance corrosion resistance of Mg alloys. Two groups of RE elements considered for Mg alloys are yttrium (Y), gadolinium (Gd), and dysprosium (Dy), which are significantly soluble, and neodymium (Nd), cerium (Ce), and lanthanum (La), which are less soluble; both groups are used to improve the properties of Mg alloys [9, 10]. The strength of an Mg–RE alloy is enhanced by the addition of zirconium (Zr) to refine the grain size, and the strength is more increased if zinc (Zn) is added as well. EZ33 is a magnesium base alloy containing zinc, rare earth (as mish metal) and zirconium. The alloy has very good casting properties [11, 12]. Previous studies reported that the as-cast microstructure of EZ33 magnesium alloy consists of α-Mg matrix and a $(Mg, Zn)_{12}RE$ intermetallic phase crystallized along the grain boundaries [13]. Praseodymium (Pr) is a RE metal used as an alloying agent for Mg to create high-strength metals used in aircraft engines. Pr has low solid solubility in Mg (1.7wt%) at the eutectic temperature of 575°C [14]. Addition of Pr into EZ33 alloy led to form Mg-Zn-Ce-Pr phase, where Pr combined with the original second phase. The solubility of zinc and Pr in magnesium formed Zn-rich particles around grain boundaries, furthermore, the hardness and ultimate tensile strength of the EZ33 magnesium alloy improved, due to that Pr altered the grain size of the alloy [14, 15]. The mechanical properties of Mg alloys have been reported to be improved by the addition of Pr [16]**.** However, bad corrosion resistance restricted magnesium alloy industrialization and commercial magnesium alloy use as industrial components. Thus, the

corrosion behavior of magnesium alloys became the focus of magnesium research [17]. The effects of microstructure on the corrosion of a model Mg–Zn–RE alloy have studied by Zhao et al. [4]. They found that the intermetallic (Mg_7Zn_3RE) phase which distributed at the grain boundaries acts as a cathode to the neighbouring α-Mg matrix, resulting in a galvanic couple between the grain boundary phase and the Mg-rich matrix, as the dominant the corrosion mechanism. The corrosion rate of EZ33 alloy according to ASTM B117 salt spray test is 3.5 mg/cm²/day [11]. The present work mainly aims to measure corrosion rate of EZ33 magnesium cast alloy with different addition of Pr, by immersion of the alloys into 5 wt.% NaCl solution.

II. EXPERIMENTAL PROCEDURE

EZ33 magnesium alloy with the chemical composition of Mg-2wt%Zn-1wt%Zr-3wt.% RE (rare earth added as mish metal) has been used as a base alloy in this study. The base alloy is melted in an electrical resistance furnace with a steel crucible under a cover-gas mixture of Ar and 2 vol% of SF_6. Pr is added in contents of 0.50 wt%, 0.75wt%, 1.25wt%, and 1.75wt% separately as small pieces after the base alloy melted at approximately 730°C. After the addition, the melt is stirred for few minutes to ensure dissolution of the alloying elements. The molten metal is then poured into a steel mold preheated to 350°C. Three specimens are taken from each alloy for corrosion rate measurements, which are cut into plates (25 mm×15 mm×5 mm) and then grounded and polished. Subsequently, they are immersed into 5 wt.% NaCl aqueous solution for 24, 48, 120, 144, 168, 192, and 216 h at room temperature. After removal from the test solution, the specimens were cleaned with distilled water then dried. The corrosion weight loss is measured using a 1/10000 electronic balance, and the average corrosion rate can be obtained simply from standard relationships based on Faraday's law [18]:

$$CR = \frac{KW}{AT\rho} , \text{mm/year}$$

(1)

Where K is a constant ($8.76*10^4$), T is the time of exposure (hours), A is the surface area (cm²), W is mass loss (grams), and ρ is material density in g/cm³. Furthermore, an optical microscopy with a scale is used to observe corrosion effect at specimens microstructure. Figure 1 shows experimental setup.
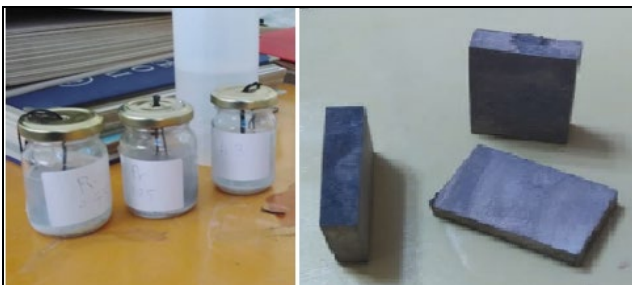

Fig. 1. Experimental setup

III. RESULTS AND DISCUSSION

Figure 2 shows the surface morphologies of base alloy and base alloys treated with Pr after 216 h of immersion in 5% NaCl solution. As can be seen, the surfaces of the alloys extremely affected by the extension of immersion time, and the surface revealed significant pitting corrosion. Magnesium alloys are known for their high susceptibility to general and localized corrosion such as pitting and stress corrosion cracking [19, 20]. In stagnant distilled water at room temperature, magnesium alloys rapidly form a protective film that prevents further corrosion. Small amounts of dissolved salts in water, particularly chlorides or heavy-metal salts, will break down the protective film locally, which usually results in pitting [18]. The presence of Cl ions in the solution accelerates the dissolution of the protective film by penetrating in the micro-pores and transforming the $Mg(OH)_2$ into more soluble $MgCl_2$, which cause accumulation of massive corrosion [21].
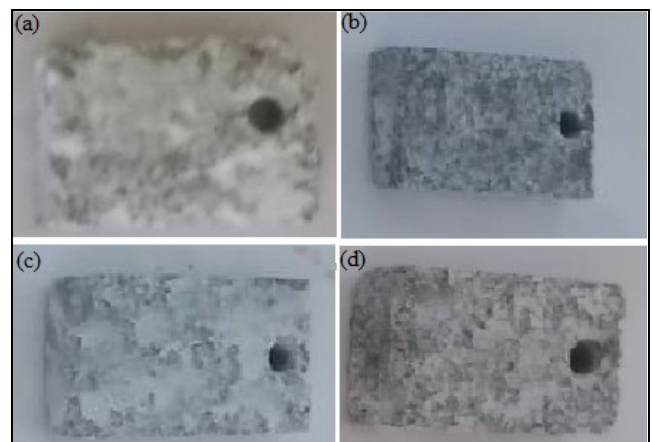

Fig. 2. Photographs of the alloys surface after 216 h immersion in 5% NaCl solution: (a) EZ33, (b) EZ33-0.75 Pr, (c) EZ33-1.25 Pr, and (d) EZ33-1.75 Pr

Table 1 present the weight loss corrosion rates of EZ33 magnesium alloy (base alloy-B A) and EZ33 magnesium alloys treated with different ratios of Pr, and three samples each. The average corrosion rates for three samples of each alloy are presented in Figure 3. The specimen of the EZ33-1.75 Pr exhibited an extremely high average corrosion rate compared with rates for other alloys along the immersion time. That the corrosion rates of the alloys after first 24 h period time were similar as ranged from 0.008 to 0.012 mm/year, except the last addition 1.75 wt.% Pr (EZ33-1.75 Pr), which obtained as a highest value with approximately 0.03 mm/year. Furthermore, along the rest exposure time of test, the alloy with 1.75 wt.% of Pr showed same behavior as the maximum amount of corrosion rate. The corrosion resistance of EZ33-0.5 Pr, EZ33-0.75 Pr, and EZ33-1.25 Pr alloys improved compared with base alloy after 48 h.

The next amounts of corrosion rate were taken after 120 h, which explain the high values, as the samples did not daily cleaned with distilled water to measure loss weight, due to that Mg alloys rapidly form a protective film when immersion into distilled water at room temperature, which lead to prevents further corrosion, meanwhile addition of small amounts of dissolved salts in water, particularly chlorides or heavy-metal salts will break down the protective film locally, which usually results in pitting [18]. As the immersion time reached 192 h and 216 h, the corrosion rates

declined slightly. The erratic corrosion behavior noted can be attributed to a number of possible factors including microstructural and compositional inhomogeneity, grain size, grain morphology and microporosity [22], Figure 4 shows optical microstructure of the alloys after immersion in 5% wt. NaCl.

TABLE I. EFFECT OF PRASEODYMIUM ADDITION ON CORROSION RATE OF EZ33 MAGNESIUM ALLOY

| Alloy	Time (h)	Sample 1		Sample 2		Sample 3		Avg. CR (mm/y)
		Mass loss (g)	CR (mm/y)	Mass loss (g)	CR (mm/y)	Mass loss (g)	CR (mm/y)	
B A	24	0.0694	0.0162	0.0406	0.0071	0.0346	0.0029	0.0087
	48	0.2349	0.0548	0.0282	0.0049	0.0124	0.0047	0.0215
	120	0.1062	0.0248	0.1171	0.0207	0.0198	0.0100	0.0185
	144	0.0387	0.0090	0.0537	0.0095	0.0419	0.0040	0.0075
	168	0.0153	0.0035	0.0106	0.0018	0.017	0.0040	0.0031
	192	0.0204	0.0047	0.0167	0.0029	0.0245	0.0058	0.0045
	216	0.0219	0.0003	0.0213	0.0037	0.0283	0.0066	0.0036
0.5 Pr	24	0.0693	0.0114	0.0752	0.0128	0.0501	0.0089	0.0110
	48	0.0590	0.0097	0.0620	0.0105	0.0527	0.0094	0.0099
	120	0.3078	0.0509	0.2621	0.0446	0.2571	0.0459	0.0471
	144	0.0605	0.0100	0.0586	0.0099	0.0472	0.0132	0.0110
	168	0.0732	0.0121	0.0758	0.0129	0.0623	0.0111	0.0120
	192	0.0316	0.0052	0.0573	0.0097	0.0286	0.0051	0.0066
	216	0.0644	0.0110	0.0587	0.0099	0.0624	0.0115	0.0108
0.75 Pr	24	0.0673	0.0110	0.0736	0.0122	0.0826	0.0138	0.0123
	48	0.0359	0.0059	0.0422	0.0070	0.0370	0.0062	0.0063
	120	0.0521	0.0380	0.2766	0.0459	0.2665	0.0447	0.0429
	144	0.0638	0.0105	0.0527	0.0087	0.0583	0.0097	0.0096
	168	0.0446	0.0073	0.059	0.0097	0.1139	0.0191	0.0120
	192	0.2163	0.0356	0.0869	0.0144	0.0323	0.0211	0.0237
	216	0.0719	0.1217	0.0152	0.0025	0.1259	0.0211	0.0484
1.25 Pr	24	0.1194	0.0020	0.0848	0.0146	0.0684	0.0121	0.0096
	48	0.0150	0.0025	0.059	0.0102	0.0484	0.0085	0.0071
	120	0.2769	0.0475	0.2398	0.0415	0.2547	0.0450	0.0447
	144	0.0732	0.0125	0.0678	0.0117	0.0746	0.0132	0.0125
	168	0.0578	0.0099	0.0471	0.0081	0.0580	0.0102	0.0094
	192	0.0485	0.0083	0.0316	0.0054	0.0345	0.0061	0.0066
	216	0.0418	0.0071	0.0569	0.0098	0.0350	0.0061	0.0077
1.75 Pr	24	0.1734	0.0351	0.1692	0.0365	0.0631	0.0191	0.0302
	48	0.0987	0.0200	0.0599	0.0129	0.0595	0.0180	0.0170
	120	0.3467	0.0707	0.2843	0.0613	0.3259	0.0990	0.0770
	144	0.0620	0.0125	0.0512	0.0110	0.0532	0.0161	0.0132
	168	0.0839	0.0170	0.0704	0.0151	0.0935	0.0284	0.0202
	192	0.05462	0.0110	0.043	0.0092	0.0563	0.0171	0.0124
	216	0.2103	0.0423	0.0452	0.0097	0.0214	0.0065	0.0195
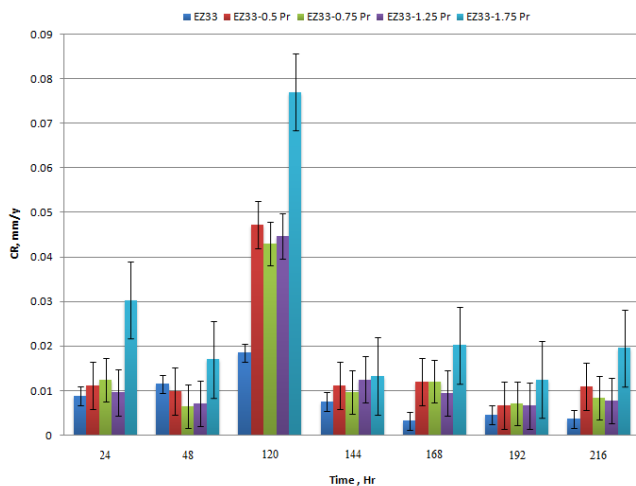
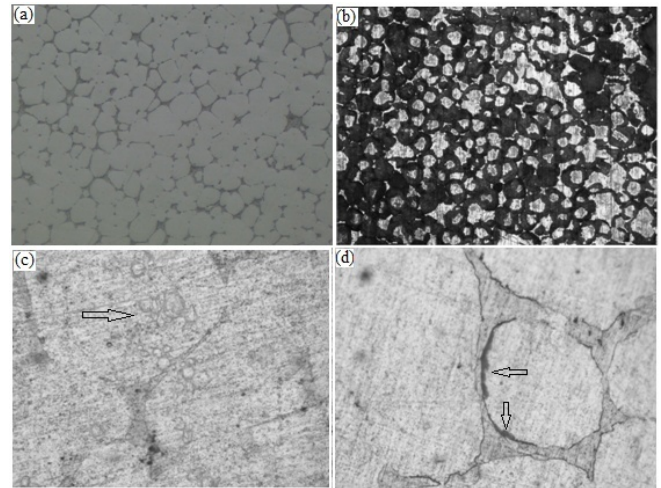Fig. 3. Average corrosion rate of base alloy and base alloy treated with Pr

Fig. 4. Optical microstructure of (a) base alloy before test, x100, (b) base alloy after immersion in NaCl, x100, (c) EZ33-0.75 Pr, x1000, and (d) EZ33-0.5 Pr x1000.

It can be seen that the centre of the grains and the grain boundaries were dark or heavily stained suggesting preferential attack. The dark, optically opaque areas, are consistent with a thick coating of corrosion product. Between the staining in the centre of the grain and the grain boundaries were areas of isolated staining (Fig. 4b). Same behavior found by W.C. Neil, et al. [23], through investigate the mechanism of corrosion and the interaction between the grain boundary intermetallic phases of ZE41 magnesium-rare earth alloy. Furthermore, Fig. 4 (d) showed that corrosion had occurred in the matrix adjacent to the grain boundaries (dark color ,noted by arrows), where the intermetallic phases are formed, as mentioned in previous studies [14-16]. It was reported that corrosion pitting involved three stages, firstly, the anodic phase dissolved followed by the corrosion of the Mg matrix and then the pitting corrosion appeared along with the depth of the dissolved phases (Mg-Zn-RE intermetallic phases which crystallized along the grain boundaries) [24]. Increase ratio of Pr into base alloy led to form massive morphology of intermetallic phases at grain boundaries [15], as more intermetallic compounds formed, this area is more susceptible to corrosion attack, may caused increase corrosion rate for the alloy, which was founded in this study. In addition, it has been reported that the presence of a high fraction of the some intermetallic phases along the grains boundaries may cause severe pitting corrosion by acting as anodic phase [25]. Moreover, pitting could be formed inside the matrix of grains, as can be seen in Fig. 4 c, these region has been noted in a previous study as Zr-rich zones [23]. Another researchers [4], found that the intermetallic (Mg-Zn-RE) phase which distributed at the grain boundaries acts as a cathode to the neighbouring α-Mg matrix, resulting in a galvanic couple between the grain boundary phase and the Mg-rich matrix, as the dominant the corrosion mechanism, which noted as a common feature of magnesium alloys. Furthermore, RE elements are more active than Mg, it was demonstrated recently that the second phases in Mg-RE based alloys preferentially dissolved at the initial corrosion stage by acting as micro-anodes, which is completely different from the role of second phases in traditional Mg-based alloys such as AZ91 alloy [26]. Solid solubility of alloying element is another factor can impact on corrosion resistance, as it has been reported that the RE elements, which have a high solubility in the Mg matrix (Ex.

Dy and Gd are 25.23% and 23.49%, respectively) are more distributed into the Mg matrix since their solubility in the Mg matrix are much higher than that of RE with low solid solubility in Mg, such as Ce (0.23%), Nd (3.6%), La (0.74%) or Pr (1.7%). Therefore it is expected that the potential difference between the Mg matrix and the second phase will be small which will reduce the corrosion [25]. However, the diversity of the intermetallic phases is the reason of the poor corrosion of the Mg alloys by providing more cathodic phases and causing more dissolution of the Mg matrix.

IV. CONCLUSIONS

Corrosion rate of EZ33 magnesium alloy with addition of Pr was investigated. From the analysis, the following can be summarized:

- During exposure time of test, the corrosion rates were almost stable for base alloy and base alloy treated with 0.5, 0.75 and 1.25 wt.% of Pr, otherwise, the corrosion rates of EZ33-1.75 Pr alloy gradually enlarges.

- With an increased immersion time, for the amounts taken after 3 days (at 120 h), the corrosion rates of the alloys increment sharply about three times.

- Microstructure images showed a corrosion attack concentrated at grain boundaries, also pitting at some zones within the grains was noted,

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