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Corrosion Behaviour of as Cast β-$Mg_{17}Al_{12}$ Phase in 3.5 wt% NaCl Solution

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In this study, corrosion behaviour of β-$Mg_{17}Al_{12}$ phase was studied as comparing pure magnesium. The corrosion tests were carried out by potentiodynamic polarisation measurements and immersion tests in 3.5 wt% NaCl solution. Compared to pure Mg, β-$Mg_{17}Al_{12}$ phase has 2.7 times and 2.1 times lower corrosion resistance according the potentiodynamic polarization and immersion test results, respectively. Deep corrosion pits were formed on the surface of the β phase.

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PACS/topics: $Mg_{17}Al_{12}$, pure magnesium, corrosion, intermetallic

1. Introduction

In recent years significant amounts of research have been studied on the corrosion behavior of AZ series magnesium (Mg) alloys such as AZ31 and AZ91 in chloride solutions [1–4]. Aluminum-containing magnesium alloys (AZ, AM, AS series) have become particularly attractive for aviation and automotive industries due to their low density. In fact, the AZ series Mg alloys contain intermetallic particles $Mg_{17}Al_{12}$, known as β-phase [2, 5]. Mg is chemically active and its corrosion resistance in aqueous media is not good, despite its excellent properties such as high specific strength, suitable for high pressure die-casting, good castability [1, 2].

The fact that Mg alloys have poor corrosion resistance has been one of the biggest obstacles to widespread their use as structural materials. The majority of Mg alloys have secondary phases, intermetallic phases, precipitate and can play an important role by exhibiting various behaviors in the corrosion process [3]. For this reason, comprehension of the mechanism of the corrosion process which is effected by the secondary phases such as $Mg_{17}Al_{12}$ and MgZn in Mg–Al–Zn alloys, is of great importance in the field of alloy development, microstructure, mechanical properties and corrosion studies. According to the literature, particularly AZ91 Mg alloy corrosion studies, the amount and distribution of $Mg_{17}Al_{12}$ secondary phases have a significant effect on the corrosion behavior of AZ91 Mg alloy [3–6] They have shown that the secondary phase ($Mg_{17}Al_{12}$ phase in AZ91) causes both micro-galvanic acceleration of the corrosion of the matrix α-phase and also acts as a barrier on the corrosion process and prevents the progression of the matrix α-phase corrosion. The purpose of this study is to investigate the corrosion behavior of β-$Mg_{17}Al_{12}$ intermetallic phase compared with pure Mg.

2. Experimental procedure

Pure Mg and pure Al were used to prepare β-$Mg_{17}Al_{12}$ (β-phase) alloy in a graphite crucible under argon gas atmosphere at 750 °C for this study. The molten alloy was then cast into a cast-iron mould (preheated to 250 °C) having 20 mm diameter and 200 mm length under protective CO_2 + 0.8% SF_6 mixed gas. Pure Mg was also used for comparison. The chemical composition of the samples measured using X-Ray fluorescence (XRF) is presented in Table I. The samples were etched in 5 ml acetic acid, 6 g picric acid, 10 ml distilled water and 100 ml ethanol. Microstructural evaluations were carried out by scanning electron microscopy (SEM).

TABLE I

Chemical composition [wt%] of pure Mg and β-$Mg_{17}Al_{12}$ phase.

Sample	Al	Zn	Mn	Si	Fe	Mg
pure Mg	0.03	0.002	0.004	0.007	0.002	bal.
$\beta-Mg_{17}Al_{12}$	41.10	0.003	0.004	0.009	0.004	bal.

Electrochemical measurements were performed in a standard three-electrode glass cell system consisting of a sample, embedded in epoxy resin, with exposed surface area of 3 cm^2 as a working electrode, a saturated calomel (SCE) as a reference electrode and a graphite rod with a diameter of 6 mm as a counter electrode by using a computer-controlled VersaStudio corrosion analysis software. Experiments were performed also at room temperature in a glass cell containing 3.5 wt% NaCl solution. Polarization curves were gathered in a scan rate of 0.5 mV s^{-1}. Cylindrical samples 8 mm in length and 17 mm in diameter were machined and subsequently ground with SiC paper up to 2000 grit followed by polishing with 1 μm alumina paste and washed with distilled water and cleaned by ultrasonic cleaner in ethanol prior to the immersion tests and microstructural evaluations. Then, the samples were weighed and immersed in 3.5 wt% NaCl solution for 24 h immersion tests. After the immersion tests, the samples were cleaned with

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a solution containing 180 g/l chromic acid for 15 min to remove the corrosion products. Corrosion loss of the sample was expressed in $\frac{\text{mg}}{\text{cm}^2\text{d}}$ for unitary surface area. The corrosion rate (CR) was calculated using

$$CR = K_1 I_{\text{corr}} E_w/\rho, \tag{1}$$

where CR is given in mm/yr, I_{corr} in μA/cm^2, $K_1 = 3.27 \times 10^{-3}$, ρ is density [g/cm^3], E_w is equivalent weight [7].

3. Results and discussion

SEM image and EDS analysis points of the β-phase are shown in Fig. 1a and b, respectively. It was observed that the microstructure of the matrix β-phase had continuous network and partially and fully divorced structure. EDS analysis at the points indicated in Fig. 1 shows that the Al content of the fully divorced β-phase is about 18%–19% (marks 1, 2 and 6) whereas the Al content of the partially divorced β-phase is about 32% (see Table II). According to the literature [6, 8, 9], partially divorced β-morphologies are formed in the AZ91 Mg alloy at low cooling rates and in higher Al content, while β-morphology is completely divorced in die-casting or lower Al contents.

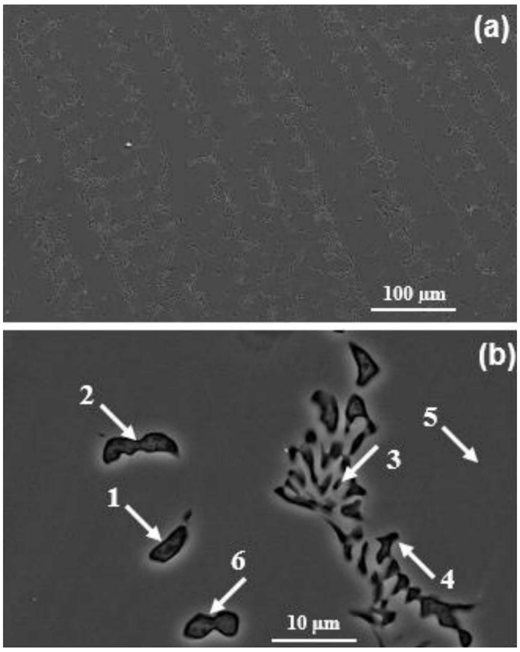

Fig. 1. SEM images (a) and EDS analysis points (b) showing microstructure of β-phase.

TABLE II

Mg and Al ratio [wt%] obtained by EDS analysis for the β-phase microstructures marked 1–6 in Fig. 1b.

Area	1	2	3	4	5	6
Mg	81.78	80.62	67.71	78.42	59.86	82.03
Al	18.22	19.38	32.29	21.58	40.14	17.97

Figure 2 shows the potentiodynamic polarization curves with the electrochemical data (shown in Table III) supplied by electrochemical corrosion tests and corrosion losses resulting after 24 h immersion tests in 3.5 wt% NaCl solution for β-phase and pure Mg. The corrosion potential of β-phase is 220 mV higher than pure Mg. Both β-phase and pure Mg exhibit a breakdown potential above E_{corr} indicating the presence of a passive film. The corrosion current density indicates that β-phase dissolves faster than pure Mg in chloride solution. β-phase and pure Mg exhibited an I_{corr} of 106 μA/cm^2 and 30 μA/cm^2, respectively. The calculated corrosion rate for β phase was 1.90 mm/yr, while for pure Mg it was considerably lower, i.e. 0.70 mm/yr. After immersion test, the corrosion loss values of pure Mg and β-phase are 8.5 and 18.04 $\frac{\text{mg}}{\text{cm}^2\text{d}}$, respectively.

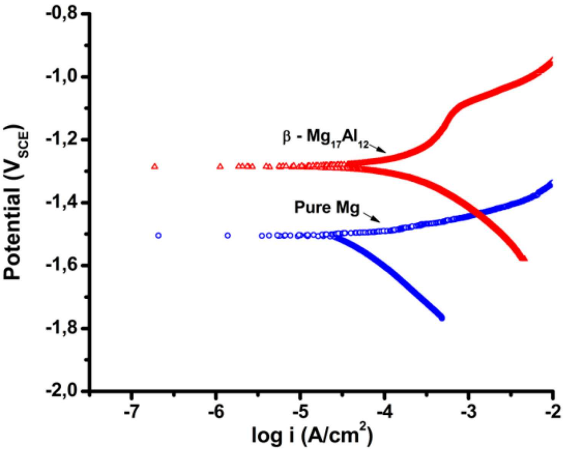

Fig. 2. Potentiodynamic polarization curves of pure Mg and β-phase.

TABLE III

Electrochemical data obtained from potentiodynamic polarization curves and immersion test of pure magnesium and β-phase.

Sample	E_{corr} [V$_{SCE}$]	E_{bd} [V$_{SCE}$]	I_{corr} [μA/cm^2]	Corrosion rate [$\frac{\text{mm}}{\text{yr}}$]	Corrosion loss (after immersion) [$\frac{\text{mg}}{\text{cm}^2\text{d}}$]
pure Mg	−1.506	−1.45	30	0.70	8.5
β-Mg$_{17}$Al$_{12}$	−1.286	−1.10	106	1.90	18.04

TABLE IV

Mg, O, and Al ratio [wt%] obtained by EDS analysis for pure Mg at points marked 1–2 in Fig. 3a and for β-phase microstructures marked 1–2 in Fig. 3b .

Sample	Area	Mg	Al	O
pure Mg	1	89.91	–	10.09
	2	97.23	–	2.77
β-Mg$_{17}$Al$_{12}$	1	33.41	17.93	48.66
	2	58.77	38.65	2.58

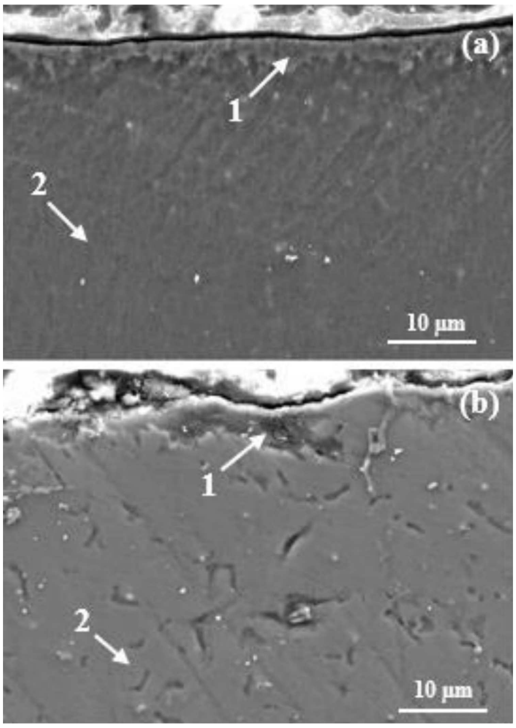

Fig. 3. SEM images showing cross section of (a) pure Mg, (b) β-$Mg_{17}Al_{12}$ exposed to 3.5 wt% NaCl for 24 h.

Figure 3 shows the cross section SEM images and Table IV gives EDS analysis of both pure Mg (Fig. 3a) and β phase (Fig. 3b) samples, immersed in 3.5 wt% NaCl for 24 h. It is observed that the corrosion progression is more in the β-phase, spread from the surface to the inner part, and there is a deep corrosion pit on the surface. However, pure Mg also shows that the corrosion on the surface is slower than the β-phase and no pits are formed.

4. Conclusion

Corrosion behaviour of the β-$Mg_{17}Al_{12}$ was studied and compared with pure Mg in 3.5 wt% NaCl solution. As compared to β-$Mg_{17}Al_{12}$, the corrosion rate of pure Mg was 65% and 55% lower after electrochemical test and immersion test, respectively. Deep corrosion pits were formed on the surface of the β-phase.

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