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Comparative study on corrosion behaviors of Mg−Al−Zn alloys

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Abstract: A comparative study on corrosion behaviors of various Mg−Al−Zn alloys (AZ21, AZ41, AZ61 and AZ91 series, cast under same cooling conditions and controlled alloying composition) was carried out. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used for microstructural examinations. The corrosion behaviors were evaluated by immersion tests and potentiodynamic polarization measurements in 3.5% NaCl solution. The results showed that the influence of Al addition on corrosion resistance was more pronounced up to 4% (i.e. AZ41) above which its influence was at less extent. The deterioration of the corrosion resistance of the alloys, at higher Al contents, was attributed to the amount and morphology of β-$Mg_{17}Al_{12}$ intermetallics and the interruption of continuity of the oxide film on the surface of the alloys owing to coarsened β intermetallics.

Key words: Mg alloy; AZ series alloys; casting; corrosion

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1 Introduction

Aluminum-containing magnesium alloys (AZ, AM, AS series) are particularly attractive for aerospace and automotive industries due to their low densities [1−4]. Among the magnesium alloys, AZ series magnesium alloys are the most successfully used commercial alloys in the manufacturing industry, which contain Al, Zn and a small quantity of Mn [4]. However, the application of the AZ series magnesium alloys is still limited owing to its limited strength and lower corrosion resistance as compared with the aluminium alloys [5].

It is well known that formation of β-intermetallic ($Mg_{17}Al_{12}$) precipitates at the grain boundaries takes place in Mg alloys above 2% Al content [3,6]. The morphology of β intermetallic is mainly depended upon the volume fraction of Al [7−9], solidification rate of the melt [10,11] and minor alloying additions [12−16].

A number of studies have been published on AZ series Mg alloys to understand their corrosion mechanisms [6−8,17−24]. However, the controversial views on the role of Al for the corrosion of AZ series magnesium alloy still exist. According to some researchers [17,18], the corrosion resistance of magnesium alloy improves in a noticeable level when aluminum content reaches 8%−9% due to protective barier effect of β-intermetallic promoted by Al content, while, some other researchers [6,7,23,24] reported that the β-intermetallics may not act as a protective barrier but may act as a micro-galvanic cells with the alloy matrix leading to an increased corrosion. In Refs [8,20,21], the corrosion resistance of AZ91 alloy, which contains 9% Al, is better than that of AZ21 or AZ31 alloys. PARDO et al [8] examined the influence of aluminium content of AZ31, AZ80 and AZ91D alloys and concluded the barier effect of β-intermetallic due to increased Al content in AZ91 alloy. WANG et al [22] reported that corrosion resistance of AZ61 alloy is better comapred with that of AZ31 alloy. Some researchers [8,20−22] observed two key factors for the lowest corrosion rates for AZ91 alloy, the aluminium enrichment on the corroded surfaces and the β-intermetallic which acted as a barrier for the corrosion progress. Unlike the studies above, some other researchers [6,7,23,24] reported that the β-intermetallic may not act as a protective barrier but may act as a micro-galvanic cells with the alloy matrix. They concluded that intensity of the galvanic corrosion appears to be quite higher for AZ91 alloy compared with that of AZ21 or AZ31 alloys owing to increased amount of the β-intermetallic in AZ91 alloy which acted as micro-galvanic cells.

Although, aforementioned studies [7,8,20−24] dealt with corrosion behaviors of AZ series Mg alloys, these studies were carried out in a non-systematic manner.

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For example, AZ31 and/or AZ61 alloys were compared with AZ91 alloy [8,22] and discussed in the frame of their Al content ignoring their production method. In the studies [8,22], AZ91 alloy was obtained in the form of billet and AZ31 alloy was in the form of rolled plate. It is well known that alloying elements [12−16], cooling conditions [10,11] and production methods (i.e cast, rolled, etc.) overwhelmingly affect the microstructure and, therefore, the corrosion resistance of the alloys. The controversial views above on the role of Al on the corrosion of AZ series magnesium alloy still exist. Therefore, the purpose of the present work is to better understand the influence of Al on the corrosion behaviors of various AZ series Mg alloys (AZ21, AZ41, AZ61 and AZ91) cast under similar cooling conditions and controlled alloying compositions.

2 Experimental

Mg (99.99%), Al (99.99%) and Zn (99,98) ingots were used as starting materials. Master alloys were prepared by melting pure Mg together with pure Al in an electrical furnace under Ar gas atmosphere at 750 °C and cast as ingot form. Zn addition was carried out for 1 min before the casting to avoid loss of Zn due to vaporization. The master alloy was then remelted and cast into a preheated cast iron mold (250 °C) under protective SF_6 gas with a cooling rate of 5 °C/s. The alloy specimens were used in as-cast form. AZ01 alloy, which contained no Al, was also prepared as control sample. The chemical compositions of the alloys, determined by using Spectrolab M8 optical emission spectrometry (OES), are given in Table 1. Microstructural evaluations were carried out by scanning electron microscopy (SEM). Samples having 15 mm in diameter and 10 mm in length were machined and subsequently ground from 220 to 1200 grit emery papers followed by polishing with 1 μm diamond paste for the immersion tests and microstructural evaluations. For SEM investigations of AZ01, AZ21 and AZ41, polished samples were etched in acetic-picral for a few seconds and for AZ61 and AZ91 alloys, 2% nital was used. X-ray diffraction (XRD) analysis (Philips RV 3710 X-ray diffractometer) was carried out under Cu K_α radiation with the incidence beam angle of 2°.

Table 1 Chemical composition of AZ series magnesium alloys used (mass fraction, %)

Alloy	Al	Mn	Zn	Fe	Mg
AZ01	0.4	0.28	1.22	0.002	Bal.
AZ21	1.9	0.22	1.30	0.002	Bal.
AZ41	4.3	0.26	1.11	0.002	Bal.
AZ61	6.3	0.25	0.93	0.002	Bal.
AZ91	9.5	0.21	0.84	0.002	Bal.

Two different immersion tests were employed: one was for mass loss measurements and the other was for observation of initial stage of the oxide film on the surface of the samples. For the mass loss measurements, the polished samples were weighed and then immersed in 3.5% NaCl solution for 72 h. After the immersion tests, the samples were cleaned with a solution containing 200 g/L CrO_3 for 15 min to remove the corrosion products. Finally, they were cleaned with distilled water, dried and weighed. The mass losses of the samples were then normalized in the unit of mg/(cm^2·d) by considering the total surface area of the samples. For the observation of the initial stage of the oxide film, the polished samples were immersed in 3.5% NaCl solution for 0.25 h then ultrasonically cleaned in distilled water and left to dry at room temperature.

For the potentiodynamic polarization measurements, machined samples of 9 mm × 9 mm × 9 mm were connected to copper wire and embedded in an epoxy resin holder. The surfaces were then abraded up to 1200 mesh emery paper, mechanically polished down to 1 μm diamond paste and washed and ultrasonically rinsed in distilled water. The potentiodynamic curves were performed by means of a Gamry model PC4/300mA potentiostat/galvanostat controlled by a computer with DC105 mass analysis software. The embedded specimens in epoxy resin were utilized as working electrodes. A carbon rod (6 mm in diameter) and a saturated calomel electrode (SCE) were used as a counter electrode and reference electrode, respectively. Experiments were performed at room temperature in a glass cell containing 3.5% NaCl solution. Each polarization experiment was carried out holding the electrode for 45 min at open circuit potential (φ_o) to allow steady-state is to be achieved. Potentiodynamic polarization curves were generated by sweeping the potential from cathodic to anodic direction at a scan rate of 1 mV/s, starting from −2.00 up to 0.20 V. Each data point for both immersion and potentiodynamic polarization tests represents at least average of three different measurements.

3 Results and discussion

3.1 Microstructure

The microstructures of the examined AZ series Mg alloys are shown in Fig. 1. The microstructure consisted of primarily Mg-rich solid solution and secondary intermetallics both at the grain boundaries and occasionally within the α-Mg grains. The XRD analysis indicated that AZ21, AZ41, AZ61 and AZ91 alloys mainly consisted of α-Mg solid solution and the