



The influence of zirconium additions on the corrosion of magnesium



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ABSTRACT

Sixteen custom binary Mg–Zr alloys and four commercial Zr-containing Mg-alloys were used to investigate the role of Zr on the corrosion of Mg. Mg–Zr alloys were manufactured with a range of different Zr concentrations. It was observed that the Mg–Zr alloys with a smaller mean Zr particle size had more Zr dissolved in solid solution. Both the Zr in solid solution and in metallic particle form were observed to have a deleterious effect on the corrosion rate of Mg. However, this deleterious effect is less pronounced to effect in alloys with multiple alloying additions.

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1. Introduction

Zirconium (Zr) is a common alloying element in magnesium (Mg) alloys. It has a low solid solubility of 0.73 at.% in Mg and does not form any intermetallic phases with Mg [1]. Zr is added to Mg alloys because of its unique and potent ability to refine the grain size of Mg alloys [2–4]. The subsequent reduction in grain size significantly improves both the casting quality and mechanical properties of Mg alloys [5–7], traits that are desired and modified for specific industrial applications. For this reason, Zr is incorporated into several commercially available alloys such as WE54, ZE41, ZK60 and AM-SC1 [8–11]. More recent developments have seen Mg alloys that contain Zr being tested for use in biomedical applications [12]. Thus, there is a substantial and growing interest in Mg alloys, necessitating a fundamental understanding of the influence of Zr additions on the corrosion of Mg.

Some previous studies have reported that the addition of Zr to Mg is beneficial for improving the corrosion resistance [13,14]. However, such studies have usually focused on singular commercial Mg-alloys, where Zr is a minor addition and which include other elements or impurities in the Mg matrix; as opposed to the Mg–Zr binary system. Furthermore, in these studies the Zr content was not altered. Other common alloying additions, such as aluminium (Al) and manganese (Mn), are known to form intermetallic

phases with Zr in Mg alloys. Impurities, such as iron (Fe), are known to cause detrimental micro-galvanic couples with the Mg matrix. Zr additions can however scavenge Fe in the melt [4,13–16], combining to form insoluble particles with the nominal composition of Fe₂Zr [17]. Owing to a large difference in density with Mg, Fe₂Zr particles settle to the bottom of the melt prior to casting. This generally renders Mg alloys containing Zr to be of higher purity [18], as they usually contain <50 ppm Fe [14], which is below any tolerance limit for Fe in Mg to cause a rapid acceleration of corrosion rate [19,20]. However, the influence of Zr when added in isolation, for a series of binary alloys has not been previously reported. In addition, studies to date have not reported results of the fundamental influence of Zr upon Mg alone.

A review of the reports regarding the effect of Zr on corrosion of Mg have also indicated there are negative effects of Zr particles in Mg, and that the distribution of Zr in the Mg matrix may also affect the corrosion kinetics [21–23]. Ben-Hamu observed that when Zr particles are not homogeneously dispersed throughout the Mg matrix, the corrosion rate increases compared to a more even distribution of smaller Zr particles [21]. In another study, Neil observed deep corrosion attack around Zr-rich regions in the Mg alloys ZE41 [22]. Moreover, Neil reported that accelerated corrosion rates appeared to be associated with the variance in size of the Zr-rich particles, with a greater number of both larger and smaller particles found within the grain interiors in ZE41. Both Neil and Song proposed that these elemental Zr particles are detrimental when embedded in the matrix [22,24], acting as micro-galvanic sites with the Mg-alloy matrix under open circuit exposure conditions. However, further mechanistic aspects were not described.

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Whilst such studies have commented on the effect of Zr particles on the corrosion of Mg-alloys, they have not detailed the electrochemical impact or kinetic changes that occur, nor have they studied variations of Zr content in Mg. In regard to this latter point, another variable of interest is the relative proportion of Zr dissolved in solid solution. As such, there exists a paucity of information contrasting the effect of Zr dissolved in solid solution to elemental Zr particles embedded in the Mg matrix, and relating such interactions to changes in the electrochemical kinetics of Mg.

In this study, the effect of systematic Zr additions (for the unique purposes of investigating the effect of Zr variations) on the corrosion rate of Mg is examined. Electrochemical testing is augmented by mass-loss testing to capture the effect of Zr on corrosion for Mg–Zr alloys made from the two commercially available Mg–Zr master alloys, Microzir (formally known as AM–Cast) and Zirmax. These master alloys contain different Zr particle sizes which result in Mg–Zr alloys with varying contents of Zr dissolved in solid solution. Production of such master alloys is specialised, since Zr has a low solubility in Mg, and Zr-containing Mg-alloys have the Zr introduced via such master alloys as opposed to the addition of pure (high melting point) Zr.

2. Experimental methods

2.1. Alloy production and characterisation

The Mg–Zr master alloys used in this study were Microzir (nominally Mg–27 wt.% Zr), supplied by Magontec, and Zirmax (nominally Mg–33 wt.% Zr) supplied by Magnesium Elektron. Melting was carried out in a resistance furnace using AM–Cover[®] as a cover gas. Pure Mg was initially melted in a steel crucible at 700 °C, to which small amounts of either Mg–Zr master alloy was added to attain specific Zr levels, up to roughly 0.2 wt.%, in the final ingot castings. The Mg melt was poured into a graphite coated cast iron mould and the ingots were allowed to air cool.

During each of the production runs for the Microzir and Zirmax containing Mg–Zr alloys the Zr addition levels were calculated and added to the Mg melt to achieve similar nominal compositions. Stirred and unstirred alloy samples were taken from the same nominal melt charge. Stirred alloys were vigorously stirred immediately prior to casting; whereas the unstirred alloys were held for 20 min prior to casting. The Mg–Zr alloys investigated in this study had Zr additions below the levels required for significant grain refinement to occur [25]. Four commercially available Zr containing Mg alloys with were also selected for examination in this study.

The chosen commercial alloys were ZE41, ZK60, WE54 and AM–SC1 with heat treatment for peak strength conditions. These commercial alloys contain Zr for the purpose of grain refinement and combinations of additional alloying elements such as zinc, yttrium and other rare earth elements for additional improvements to the mechanical properties of the alloys.

The compositions of the alloys (custom and commercial) were analysed independently via inductively coupled plasma – atomic emission spectroscopy, ICP–AES (Spectrometer Services, Coburg, Australia). The specific compositions of the binary Mg–Zr alloys produced in this study are given in Table 1 and the commercial alloys tested are in Table 2. The values for overall Zr content and percentage of Zr dissolved in solid solution were measured via an acid pre-treatment procedure prior to ICP–AES analysis as per Crawley [26]. The soluble Zr content was determined by dissolving the sample in a 10% HCl solution. The total Zr content was determined by dissolving the specimen in a 50% HCl–6% HF solution.

Several alloys were examined via scanning electron microscopy (SEM). Mg–Zr alloy specimens and both Mg–Zr master alloys were polished to a 1 µm diamond paste finish and then imaged using a JEOL 7001F SEM in back scattered electron (BSE) mode. The microscope was equipped with energy dispersive X-ray spectroscopy (EDX) (Oxford Instruments X–Max 80 detector). Post-corrosion SEM and EDX analysis was also performed on selected Microzir and Zirmax specimens. The samples were polished to a 1 µm diamond paste finish and immersed in a 0.1 M NaCl solution for 15 min. They were then cleaned by immersion in ethanol before being examined in the JEOL 7001F SEM.

2.2. Electrochemical and corrosion testing

Specimen surfaces were ground to a 2000 grit surface finish. A 3-electrode flat-cell with an exposed sample area of 1 cm² was used in conjunction with a VMP 3Z potentiostat. All testing was carried out in 0.1 M NaCl, and potentiodynamic polarisation was conducted at 1 mV/s with a saturated calomel electrode (SCE). Prior to polarisation the samples were conditioned for ten minutes at open circuit to ascertain a close to stable potential. The polarisation curves were used to determine i_{corr} (via a Tafel-type fit) using EC–Lab software. Tafel-type fits were executed by selecting a portion of the curve that commenced >50 mV from E_{corr} , and i_{corr} was estimated from the value where the fit intercepted the potential value of the true E_{corr} . It is noted that the Tafel slopes presented herein include some curvature, to which a linear fit was executed for the purposes of analysis. Importantly however,

Table 1
Composition (tested via ICP–AES) and corrosion properties of alloys produced in this study.

Sample ID	Mg wt.%	Zr wt.% (total)	Overall % of Zr (total) in solid solution	Fe wt.%	i_{corr} (A/cm ²)	E_{corr} (mV _{SCE})	β_a (mV/decade)	β_c (mV/decade)
Microzir-1 Stirred	~Bal	0.028	42.9	0.010	$4.8 (\pm 0.5) \times 10^{-5}$	–1535 (±5)	59 (±4.2)	–228 (±5.7)
Microzir-1 Unstirred	~Bal	0.012	33.3	0.008	$5.2 (\pm 0.5) \times 10^{-5}$	–1529 (±7)	42 (±2.6)	–218 (±6.3)
Microzir-2 Stirred	~Bal	0.061	36.1	0.010	$4.5 (\pm 0.7) \times 10^{-5}$	–1547 (±7)	51 (±2.3)	–214 (±9.5)
Microzir-2 Unstirred	~Bal	0.014	42.9	0.008	$4.6 (\pm 0.6) \times 10^{-5}$	–1504 (±5)	46 (±2.3)	–226 (±5.6)
Microzir-3 Stirred	~Bal	0.120	45.0	0.011	$4.1 (\pm 0.5) \times 10^{-5}$	–1572 (±5)	82 (±1.9)	–188 (±5.1)
Microzir-3 Unstirred	~Bal	0.019	47.4	0.005	$2.7 (\pm 0.4) \times 10^{-5}$	–1549 (±6)	57 (±2.8)	–196 (±8.3)
Microzir-4 Stirred	~Bal	0.220	47.3	0.014	$4.9 (\pm 0.4) \times 10^{-5}$	–1546 (±12)	68 (±5.0)	–225 (±7.5)
Microzir-4 Unstirred	~Bal	0.037	51.4	0.006	$3.6 (\pm 0.5) \times 10^{-5}$	–1569 (±8)	53 (±5.5)	–218 (±7.6)
Zirmax-1 Stirred	~Bal	0.028	25.0	0.006	$3.7 (\pm 0.4) \times 10^{-5}$	–1522 (±10)	45 (±4.4)	–222 (±7.9)
Zirmax-1 Unstirred	~Bal	0.018	22.2	0.006	$4.4 (\pm 0.4) \times 10^{-5}$	–1513 (±2)	56 (±5.1)	–220 (±6.5)
Zirmax-2 stirred	~Bal	0.057	15.8	0.006	$4.3 (\pm 0.3) \times 10^{-5}$	–1576 (±5)	65 (±3.8)	–208 (±3.5)
Zirmax-2 unstirred	~Bal	0.025	16.0	0.005	$4.5 (\pm 0.3) \times 10^{-5}$	–1531 (±5)	63 (±3.9)	–222 (±3.9)
Zirmax-3 stirred	~Bal	0.120	10.0	0.001	$4.7 (\pm 0.5) \times 10^{-5}$	–1564 (±8)	89 (±2.5)	–206 (±12.0)
Zirmax-3 unstirred	~Bal	0.056	8.93	0.005	$3.5 (\pm 0.5) \times 10^{-5}$	–1555 (±5)	51 (±6.3)	–200 (±4.1)
Zirmax-4 stirred	~Bal	0.190	10.5	0.006	$5.5 (\pm 0.5) \times 10^{-5}$	–1572 (±8)	85 (±6.3)	–243 (±6.0)
Zirmax-4 unstirred	~Bal	0.075	8.00	0.013	$4.7 (\pm 0.2) \times 10^{-5}$	–1536 (±10)	67 (±4.7)	–225 (±4.3)
Commercial purity Mg	~Bal	0.002	N/A	0.001	$3.2 (\pm 0.4) \times 10^{-5}$	–1502 (±11)	75 (±8.7)	–239 (±5.2)

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