

Microstructure modification and corrosion resistance enhancement of die-cast Mg-Al-Re alloy by Sr alloying

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Abstract

The effects of Sr additions on the microstructure and corrosion performance of a Mg-Al-RE alloy in 3.5 wt.% NaCl saturated with Mg(OH)₂ have been investigated. Microstructure examination reveals that the Sr addition introduces additional intermetallic phases, refines intermetallic networks and dendritic grains, and improves the network continuity. More Al and rare earth elements can be identified in the intermetallics and grain boundaries or inter-dendrite regions under a transmission electron microscope and secondary electron microscope, respectively. On the Sr-containing intermetallic phases and the refined microstructure, the oxide films become more protective, resulting in more corrosion resistant boundary areas and thus dendrite grain grooves. Hence, the presence of large amounts of intermetallics and boundaries can enhance the corrosion performance of the Mg-Al-RE alloy containing Sr.

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1. Introduction

Magnesium (Mg) is the lightest engineering metal. Thus, Mg alloys are particularly attractive for the automotive and aerospace industries, as the light materials can enhance the fuel efficiency and reduce carbon emissions due to the weight reduction of structural components [1,2]. The greatest benefits have been achieved with cast Mg alloys, particularly high-pressure die castings (HPDC), which make use of the excellent castability of these Mg alloys [3–5]. These Mg alloys contain alloying elements that improve castability and mechanical properties [3,4,6–8]. However, Mg alloys in general have not found widespread application, because of their

poor corrosion performance [9–15]. Thus it is important to develop cast Mg alloys with improved corrosion performance, and most importantly, understand the role of manufacturing processes on microstructure and corrosion performance.

One mechanism for the improved corrosion performance, as a result of the combination of alloy composition modification and processing conditions, was proposed by Song et al. [16]. According to that model, the surface of a diecast AZ91D has a lower corrosion rate than high-purity Mg, because (i) the essentially continuous second phase network at the surface formed a barrier to corrosion, and (ii) the second phase itself had a corrosion rate less than that of high-purity Mg.

The most common cast Mg alloys are Mg-Al series, for example AZ91 (Mg-9Al-1 Zn, compositions in wt.% and AM60 (Mg-6Al-0.3Mn). These Mg-Al alloys have good mechanical properties at room temperature and excellent die-castability.

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The excellent castability is attributed to the Al content. These alloys have adequate corrosion resistance for many applications. However, they are not suitable for use at temperatures above 130 °C [17–19] because they undergo excessive creep deformation at moderate stress levels, caused by the poor thermal stability of the $Mg_{17}Al_{12}$ phase [20,21]. Mg–Al alloys with better creep resistance [18,22–26] have additional alloying elements (i) that form high-melting-point intermetallic compounds with Al (such as RE, Cs and Sr) (RE=rare earth) and thereby suppress the formation of $Mg_{17}Al_{12}$, or (ii) that form high-melting-point intermetallic compounds with Mg (such as RE, Si, and Sn [27]), or (iii) that form strengthening precipitates to enhance the strength of the Mg alloy (such as Ca and Nd). Corrosion of Al-free Mg alloys has been studied for alloys such as WE43 [28–30], ZE41 [31] and EV31 [32,33]. These alloys are not typically high-pressure die cast.

Typical creep-resistant die-cast Mg alloys include AE42 (Mg–4Al–2RE) [34], AJ52 (Mg–5Al–2Sr) [35], AX53 (Mg–5Al–3Ca) [36], MRI153 (Mg–9Al–0.7Zn–1Ca–0.1Sr) [37] and AE44 (Mg–4Al–4RE) [38,39]. These common commercial Mg alloys have good strength, ductility and creep resistance. For example, AE42 has been used as a benchmark creep-resistant die-cast Mg alloy. AE42 exhibits creep resistance superior to AZ91 at temperatures up to 423 K (150 °C) [40]. Furthermore, the addition of Sr further can improve the elevated temperature strength and the creep resistance of die-cast AE42 [41,42], and improve the grain refining efficiency of Mg–3%Al alloy and inhibit the poisoning effect caused by Fe [43]. However, it is unknown (i) how microstructural factors influence the corrosion performance of the die-cast AE42 containing Sr, and (ii) if the diecast alloys could have a corrosion rate less than that of HP Mg as suggested by Song et al. [15,16].

The present paper (i) firstly characterized the microstructure of die-cast AE42 with and without 1 wt.% Sr using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), and (ii) then identified the mechanism for the influence of Sr on the corrosion performance and microstructure through immersion test and using electrochemical techniques.

2. Experimental methods

Cylindrical specimens were cut from AE42 and AE42–1%Sr alloys. These two alloys were high pressure die cast in a multicavity die using a 200 ton clamping force Frech cold chamber machine at Norsk Hydro Research Centre, Porsgrunn, Norway as described in our previous work [41]. A protective gas cover of 0.3% SF_6 in dried air was used. The metal was hand-ladled into the casting machine, requiring a melt temperature 20 °C higher than normally used with an automated metering system due larger heat losses in the manual operation; the melt temperature before casting was 700 °C. The die was equipped with an oil heating/cooling system. The small shot weight of the castings (250 g), combined with the low specific heat of the magnesium alloys necessitated a

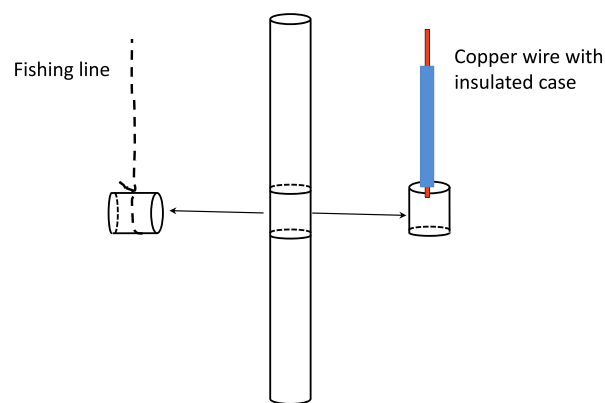


Fig. 1. Schematic diagram of samples cut from die-cast AE42 or AE42Sr1 bars for the immersion test and the electrochemical test.

Table 1

Chemical composition (wt.%) analysed by ICP-AES of AE42 and AE42Sr1 alloys.

Alloy	Al	Zn	Mn	RE	Fe	Sr	Mg
AE42	3.6	0.05	0.1	1.9	<0.01	–	Bal.
AE42Sr1	3.7	0.02	0.1	1.9	<0.01	1.0	Bal.

net heat input from the oil heating system. The temperature of the oil heater was set to 240 °C. The phase one piston speed was 0.2 m s^{−1}, phase two 2.7 m s^{−1} and the phase three piston pressure was 0.75 MPa.

The samples for immersion tests and electrochemical tests were cut from diecast AE42 and AE42–1 wt.%Sr (AE42Sr1) bars as shown in Fig. 1. The sample for electrochemical measurement were electrically connected with plug-in copper wire, as detailed by Shi and Atrons [44]. Table 1 presents the chemical composition of the diecast AE42 and AE42Sr1 analysed by ICP-AES. Each surface of each sample was ground from 400 to 1200 grit SiC paper step by step with anhydrous ethanol as coolant during grinding, rinsed using an ultrasonic cleaner with anhydrous ethanol, and dried with compressed air flow.

Immersion tests were carried out using triplicate samples for each Mg alloy in 3.5 wt.% NaCl solution saturated with $Mg(OH)_2$ at 24 ± 2 °C, using weight loss and evolved hydrogen collection. The hydrogen evolution rates were converted into average daily corrosion rates. The weight decrease was measured on the 7th day of the immersion test after the corrosion products were removed in 200 g/L chromic acid + 2 g/L $AgNO_3$ solution.

Polarisation curves and electrochemical impedance spectra (EIS) were measured in the 3.5 wt.% NaCl solution saturated with $Mg(OH)_2$ at 24 ± 2 °C. EIS spectra were measured before the polarisation curve in the frequency range from 100 kHz to 10 mHz with the amplitude of the potential of 8 mV. The polarisation curves were measured in the potential range of ±300 mV vs the corrosion potential. Both EIS and polarisation measurements were carried out by a PARSTAT 2273 potentiostat/galvanostat controlled by PARC Powersuite software. The reference electrode was Ag/AgCl saturated with

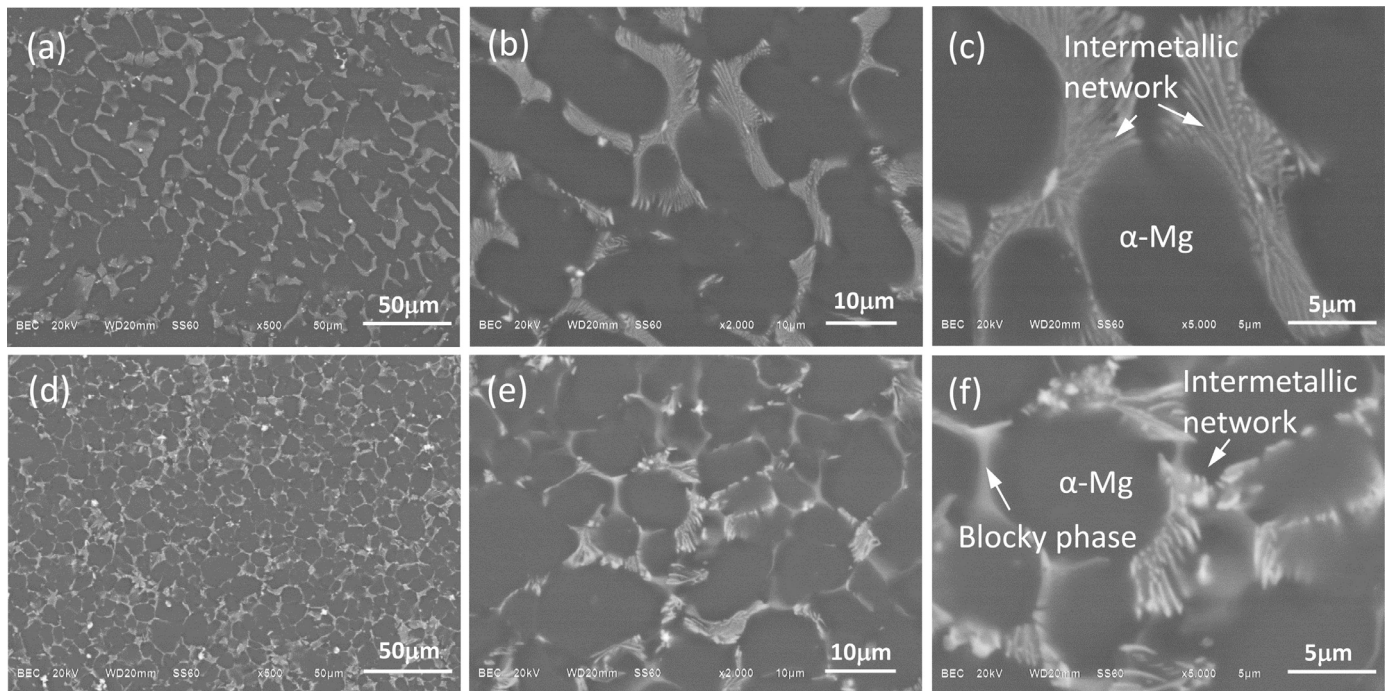


Fig. 2. SEM-BSE micrographs showing die-cast microstructure in (a), (b) and (c) AE42, and (d), (e) and (f) AE42 with 1 wt.% Sr addition (AE42Sr1).

potassium chloride solution. A platinum plate electrode was used as the counter electrode. The EIS data were simulated by Scribner ZPlot 3.5e software to evaluate the polarisation resistance.

The surfaces of the corroded magnesium alloy samples were recorded using a digital camera. Scanning electron microscopy (SEM) examination was conducted using a JOEL 6460LA SEM. Transmission electron microscopy (TEM) samples were prepared using a Zeiss Auriga 60 Focus Ion Beam (FIB) SEM. TEM, high angle annular dark field scanning TEM (HAADF-STEM), and STEM-energy-dispersive X-ray spectroscopy (EDS) analyses were carried out using a JEM 2200FS transmission electron microscope, operated at 200 kV. Cross-sections of the corroded sample with corrosion product were cut along the longitude and transverse direction and moulded with Strueres Polyfast resin for SEM investigation using Hitachi TM3030 SEM.

3. Results and discussion

3.1. Effect of Sr addition on microstructure

3.1.1. Formation of blocky phase and continuity of second phase

The typical SEM-BSE microstructures of die-cast AE42 with and without 1 wt.% Sr are presented in Fig. 2. The microstructures of both alloys contained primary α -Mg dendrites surrounded by intermetallic-containing eutectics in the interdendritic regions, although there were the following differences. Firstly, the primary α -Mg dendrite size in AE42 (Fig. 2(a) and (b)) was larger than that for AE42Sr1

(Fig. 2(d) and (e)). Secondly, the eutectic intermetallics connected each other to form an interconnected network. The network in AE42Sr1 (Fig. 2(e)) was better connected than that in AE42 (Fig. 2(b)). There were smaller discontinuous breaks in the intermetallic networks in the AE42Sr1 visible at low magnification (Fig. 2(d)), and finer intermetallics visible at high magnification (Fig. 2(e)), so that the intermetallics formed a more continuous network than those in AE42 (Fig. 2(a) and (b)). Thirdly, the intermetallic-phase network in AE42 consists of massive fine lamellar and particulate phases (Fig. 2(c)). In contrast, the Sr-containing alloy had small amounts of the massive intermetallic regions consisting of the lamellar and particulate phases, and large amounts of the blocky intermetallic phase (Fig. 2(e) and (f)). This additional blocky phase was bigger than the other two intermetallic phases in the intermetallic networks (Fig. 2(c) and (f)). The presence of the blocky phase between the massive intermetallic regions in AE42Sr1 significantly enhanced the continuity of the intermetallic phase network (Fig. 2(e) and (f)).

Fig. 3 presents the distribution of the chemical elements in AE42 and AE42Sr1. Both the lamellar phase and the particulate phase contained significant amounts of Al, small amounts of the rare earth elements La and Ce, but no Sr. The blocky phase contained a large amount of Sr but no Ce (Fig. 3(b)). This Sr-containing blocky phase has not been detected in any known binary Mg-Sr and Al-Sr phase diagram or ternary Mg-Al-Sr phase diagram. Its composition was close to $\text{Mg}_8\text{Al}_4\text{Sr}$ [42]. The lamellar, particulate and blocky intermetallic phases have been investigated in previous studies [42]. The diffraction patterns of the lamellar phase and the particulate phase can be consistently indexed as Al_{11}Ce (body-centred

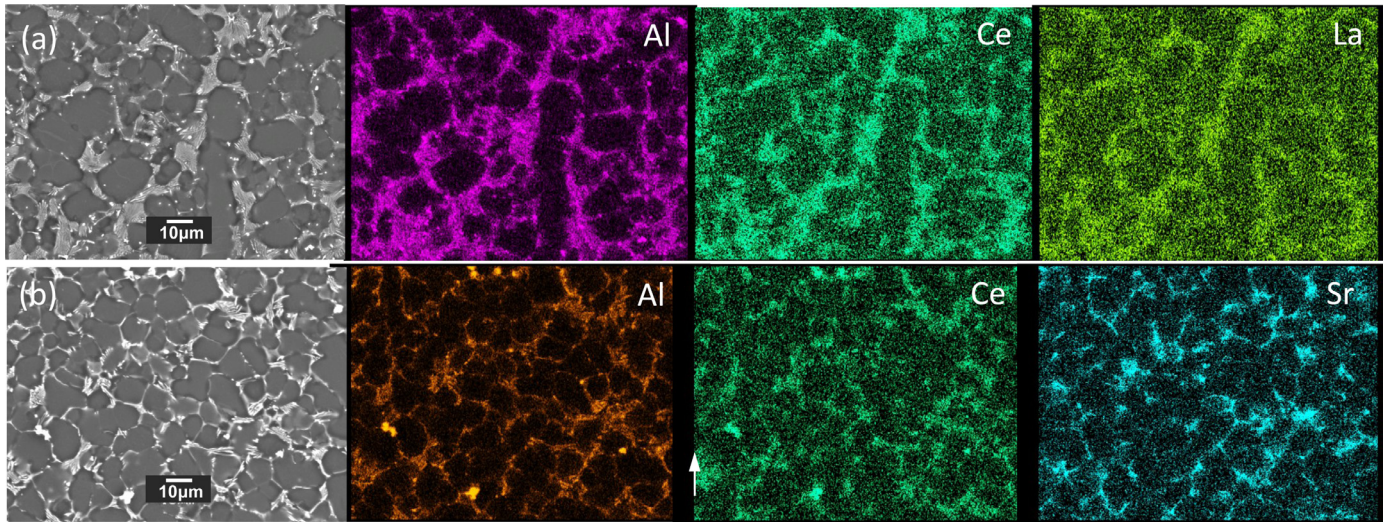


Fig. 3. The distribution of chemical elements in the Mg-Al-RE alloys of (a) AE42 and (b) AE42Sr1.

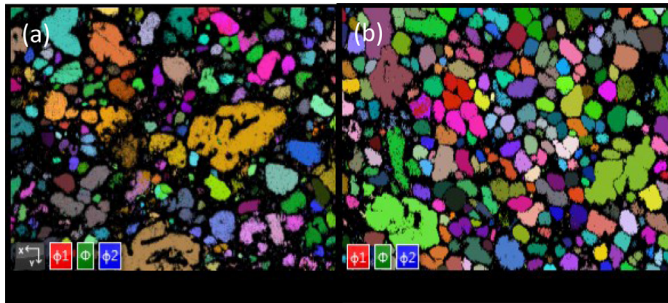


Fig. 4. EBSD micrographs of (a) AE42 and (b) AE42Sr1.

orthorhombic) and Al_2Ce (diamond cubic) structures, respectively. The indexing of the diffraction patterns of the blocky phase indicates that this phase has a hexagonal structure with lattice parameters of $a = 0.597 \text{ nm}$ and $c = 0.514 \text{ nm}$ [42]. Like $\text{Al}_{11}\text{RE}_3$ and Al_2RE , the $\text{Mg}_8\text{Al}_4\text{Sr}$ phase is thermally stable at temperatures up to 200°C [42].

3.1.2. Effect of Sr addition on grain size

Fig. 4 presents EBSD micrographs for the die-cast AE42 and AE42Sr1. There are slightly smaller grains in AE42Sr1 than in AE42 with an average size range from $5.9 \mu\text{m}$ to $10.3 \mu\text{m}$. Hence, the addition of Sr refined the grains, increased the amounts of grain boundaries, and the area of the intermetallic network.

Fig. 5 presents the morphologies of the intermetallic phases in the eutectic regions, examined using TEM in bright field (BF) and HAADF STEM modes. The intermetallic phases in both alloys exhibited dark contrast in the STEM-BF images (Fig. 5(a) and (c)), and bright contrast in the STEM-HAADF images (Fig. 5(b) and (d)). The HAADF contrast increases with atomic number (Z), indicating that the intermetallic phases contained more Al and rare earth elements.

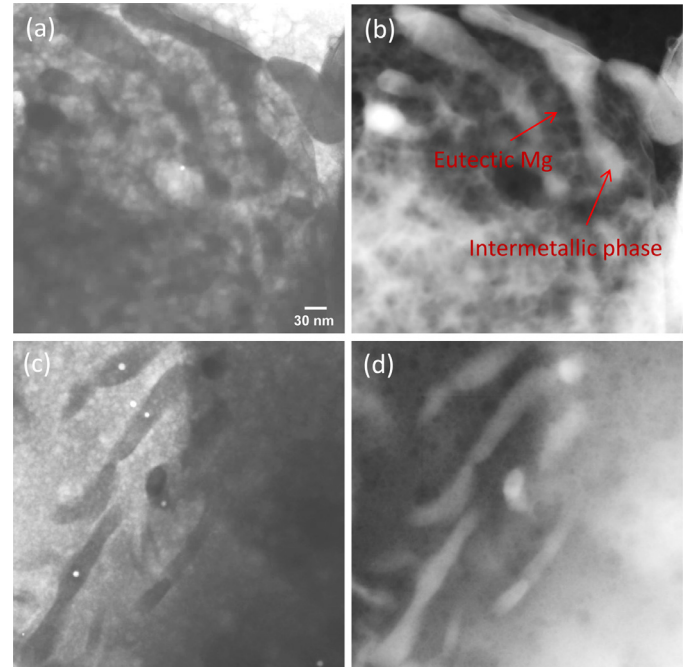


Fig. 5. STEM morphologies of intermetallic phases in Mg-Al-RE alloys. (a) AE42, BF, (b) AE42, HAADF, (c) AE42Sr1, BF, and (d) AE42Sr1, HAADF.

Fig. 6 presents the high magnification STEM images of the grain microstructure in AE42 and AE42Sr1. There were many small phases showing white contrast in the STEM-BF mode (Fig. 6(a) and (c)) and dark contrast in the STEM-HAADF mode (Fig. 6(b) and (d)). These phases were enclosed by thin boundaries, which exhibit different contrast from the small phases. The α -Mg in the alloys grows in a dendrite mode during casting due to the redistribution of the solutes. The dark phases and the white boundaries in the HAADF images were the dendrites and their boundaries, respectively. The distinct contrasts between the dendrites and their boundaries indicated

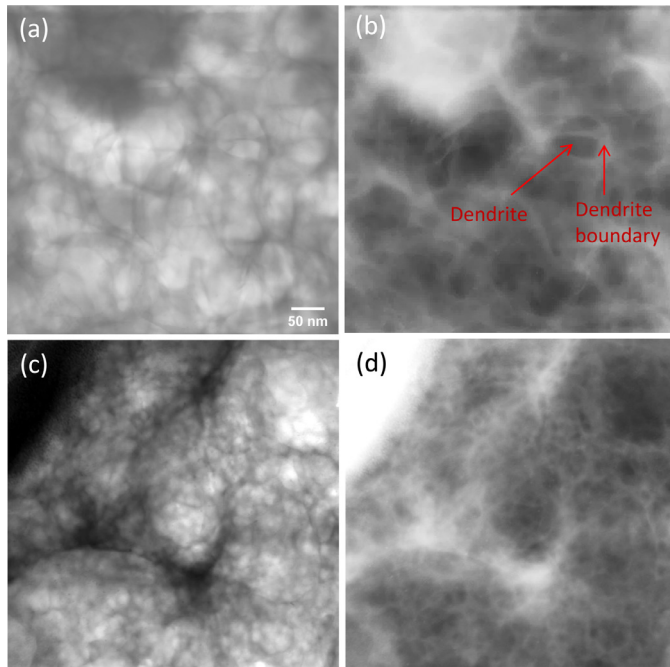


Fig. 6. STEM morphologies of grain microstructure in Mg-Al-RE alloys. (a) AE42, BF, (b) AE42, HAADF, (c) AE42Sr1, BF, and (d) AE42Sr1, HAADF.

a large difference in composition. There were more heavy elements in the boundaries than in the dendrites. Moreover, the dendrites of AE42Sr1 were finer than those of AE42, indicating that the addition of Sr in the Mg-Al-RE alloy refined the dendrite structure.

Element mapping was carried out in order to understand the difference in chemical composition between the different microstructure features. Fig. 7 shows the maps of Al, Ce and La for AE42 (the top and middle rows) and Al, Ce, and Sr for AE42Sr1 (the bottom row). There was more Al, Ce and La in the intermetallic phases than in the matrix (top row), which was consistent with the results of the SEM-EDS (Fig. 3). There was also more Al and rare earth elements at the dendrite boundaries than within the dendrites (Fig. 7 middle and bottom rows). The intermetallics and dendrite boundaries exhibited white contrast in the HAADF images (Fig. 5(b) and (d) and (Fig. 6(b) and (d))), indicating that there was no significant difference in Sr concentration between dendrites and their boundaries (bottom row in Fig. 7).

Al is the most common alloying element in Mg alloys and can promote precipitation strengthening. Al is partly in solid solution and partly precipitated in the form of intermetallic phases, such as β -Mg₁₇Al₁₂, along grain boundaries as a continuous phase as well as a part of the lamellar structure

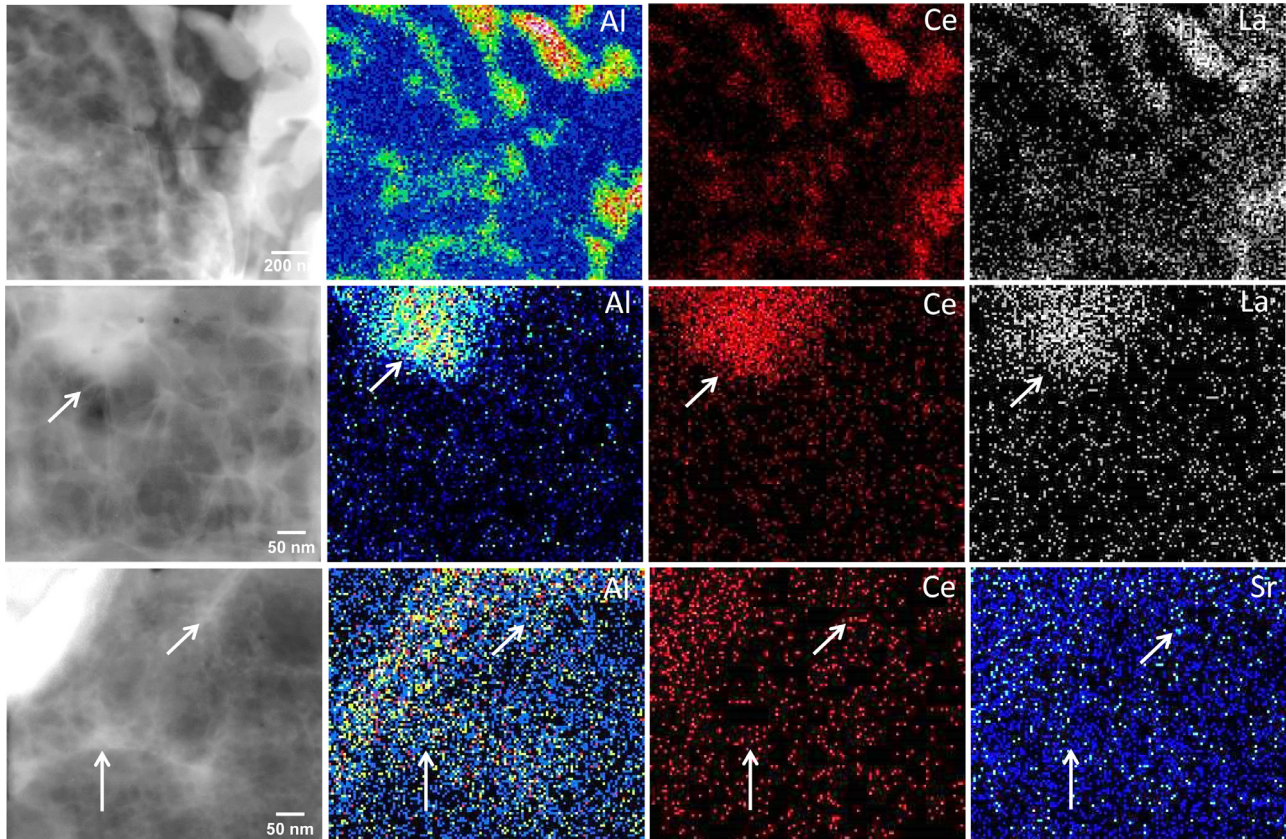


Fig. 7. The distribution of chemical elements in the Mg-Al-RE alloys of AE42 (top and middle rows) and AE42Sr1 (bottom row). Arrows show the white areas in the HAADF images.

for Mg–Al alloys such as AZ91 [45]. The eutectic Mg phase surrounded by the β -phase is richer in Al than the primary α -phase [45]. Al in combination with some of the rare earth elements can effectively refine grains [46]. Also, more intermetallic phases can form by the addition of RE elements, and Al_{11}Ce and Al_2Ce are present in the investigated alloys [42].

The addition of Sr has been found to refine the grains of Mg alloys [46,47]. Small additions of Sr are an effective grain refiner for pure Mg, low-Al-content Mg alloys (e.g., 1% Al), and for high-Al-content Mg alloys [46,47]. The present study found that the alloys have a dendrite structure under STEM-HAADF, and the addition of Sr refined the microstructure, including the dendrite grains and intermetallics in the Mg–Al–RE alloy (Figs. 2,4 and 5). The refinement of the microstructure can be explained by the formation of large amounts of the additional intermetallic phase of $\text{Mg}_8\text{Al}_4\text{Sr}$. The Al content in $\text{Mg}_8\text{Al}_4\text{Sr}$ is lower than in the other intermetallics Al_{11}Ce and Al_2Ce . During solidification of Mg alloys in die casting, the primary phase nucleates and grows, and then the eutectic phases form [48]. The redistributions of solutes Al and rare earth elements result in an increase in the Al and RE concentrations in front of the solidification regions of the α -Mg phase. When the Al content reaches a critical value, large amounts of nuclei of $\text{Mg}_8\text{Al}_4\text{Sr}$ form and grow as solidification continues. The critical value of Al content is lower for the formation of $\text{Mg}_8\text{Al}_4\text{Sr}$ than the formation of the other intermetallics such as Al_{11}Ce and Al_2Ce . Large amounts of $\text{Mg}_8\text{Al}_4\text{Sr}$ phases separate in the solidification regions into small areas and limit the growth of these areas, resulting in the formation of small grains. The formation of large amounts of additional $\text{Mg}_8\text{Al}_4\text{Sr}$ during solidification also reduces the concentration of Al solute in the Sr-added alloy [41,42]. More Al in the boundaries of the dendrites also refines the dendrite structure. Moreover, larger amounts of $\text{Mg}_8\text{Al}_4\text{Sr}$ nuclei refine the $\text{Mg}_8\text{Al}_4\text{Sr}$ phase, and also refine the other intermetallics due to the consumption of the excess Al. Hence, the addition of Sr refines the microstructure due to the formation of low-Al containing $\text{Mg}_8\text{Al}_4\text{Sr}$. In addition, the formation of large amounts of $\text{Mg}_8\text{Al}_4\text{Sr}$ between the massive Al_{11}Ce and Al_2Ce regions increases the total amount of intermetallics at boundaries, and also improved the network connection of AE42Sr1 compared to AE42 (Fig. 2). This more continuous network should have a positive influence on the corrosion performance of the alloy.

3.2. Effect of Sr addition on corrosion performance

3.2.1. Corrosion results from weight loss and hydrogen evolution

Fig. 8 presents the corrosion rates calculated from the weight loss for AE42 and AE42Sr1 after 7 day immersion in the 3.5 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$ at $24 \pm 2^\circ\text{C}$. The average corrosion rate of AE42 ($P_w = 0.66 \pm 0.10 \text{ mm y}^{-1}$) was slightly larger than that of AE42Sr1 ($P_w = 0.56 \pm 0.10 \text{ mm y}^{-1}$), although the data were relatively scattered. Fig. 9 shows the surface morphologies of the corroded AE42 and AE42Sr1 samples after 7 day immer-

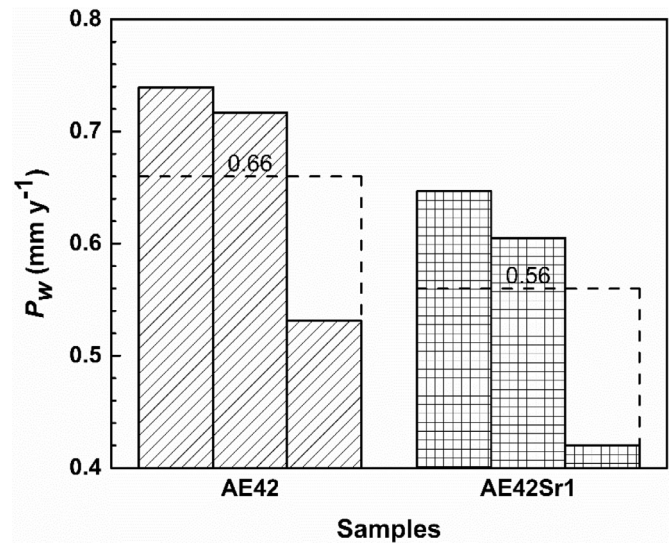


Fig. 8. Corrosion rate of AE42 and AE42Sr1 after 7 day immersion test in 3.5 wt.% NaCl + $\text{Mg}(\text{OH})_2$ solution at $24 \pm 2^\circ\text{C}$, dash line bar shows average value.

sion in the 3.5 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$. The corrosion morphologies of these two alloys were relatively uniform with a few spots of localised corrosion and filiform corrosion. There were more big pits and the corrosion surfaces were rougher for AE42 than AE42Sr1. This is more clearly shown by the high-magnification figures. The rougher surfaces of AE42 indicate that more material was removed from the surfaces during corrosion than from AE42Sr1. Fig. 10 shows the hydrogen evolution curves, the corrosion rate P_{AH} calculated from the daily hydrogen evolution rate, and pH vs P_w of AE42 and AE42Sr1 in the 3.5 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$ at $24 \pm 2^\circ\text{C}$. The hydrogen evolution volume for most of the specimens increased nearly linearly with time, but some hydrogen evolution rates changed with immersion time. The curves in Fig. 10(b) show that the corrosion rates of AE42 specimen decreased with time. The average corrosion rate for AE42 was $0.3 \pm 0.1 \text{ mm y}^{-1}$. The corrosion rates of all AE42Sr1 specimens also decreased with time. The average corrosion rate calculated from the hydrogen data for AE42Sr1 was $0.23 \pm 0.05 \text{ mm y}^{-1}$. The corrosion rate calculated from hydrogen evolution rate was lower than that from weight loss. This is attributed to some hydrogen dissolving in the samples or in the solution. Nevertheless, the corrosion rates calculated from both the weight loss and daily hydrogen evolution rate for AE42Sr1 were lower than those for AE42. These data indicated that addition of Sr decreased the corrosion rate of the Mg–Al–RE alloy in the $\text{Mg}(\text{OH})_2$ saturated 3.5 wt.% NaCl solution.

3.2.2. Surface morphologies of corroded samples

Fig. 11 illustrates the surface morphologies of the corroded AE42 and AE42Sr1 after 7 days immersion testing. There were mud cracked corrosion products on the surfaces of AE42 and AE42Sr1. Fig. 11(c) – (f) are back scattered electron images, which show the bright skeleton network of the second

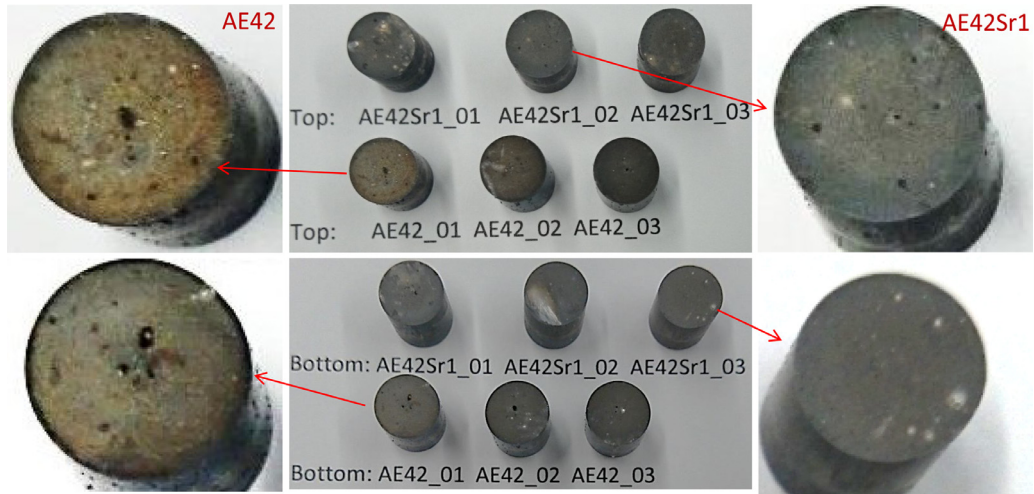


Fig. 9. Optical morphology of AE42 and AE42Sr1 after 7 day immersion test in 3.5 wt.% NaCl+Mg(OH)₂ solution at 24±2°C.

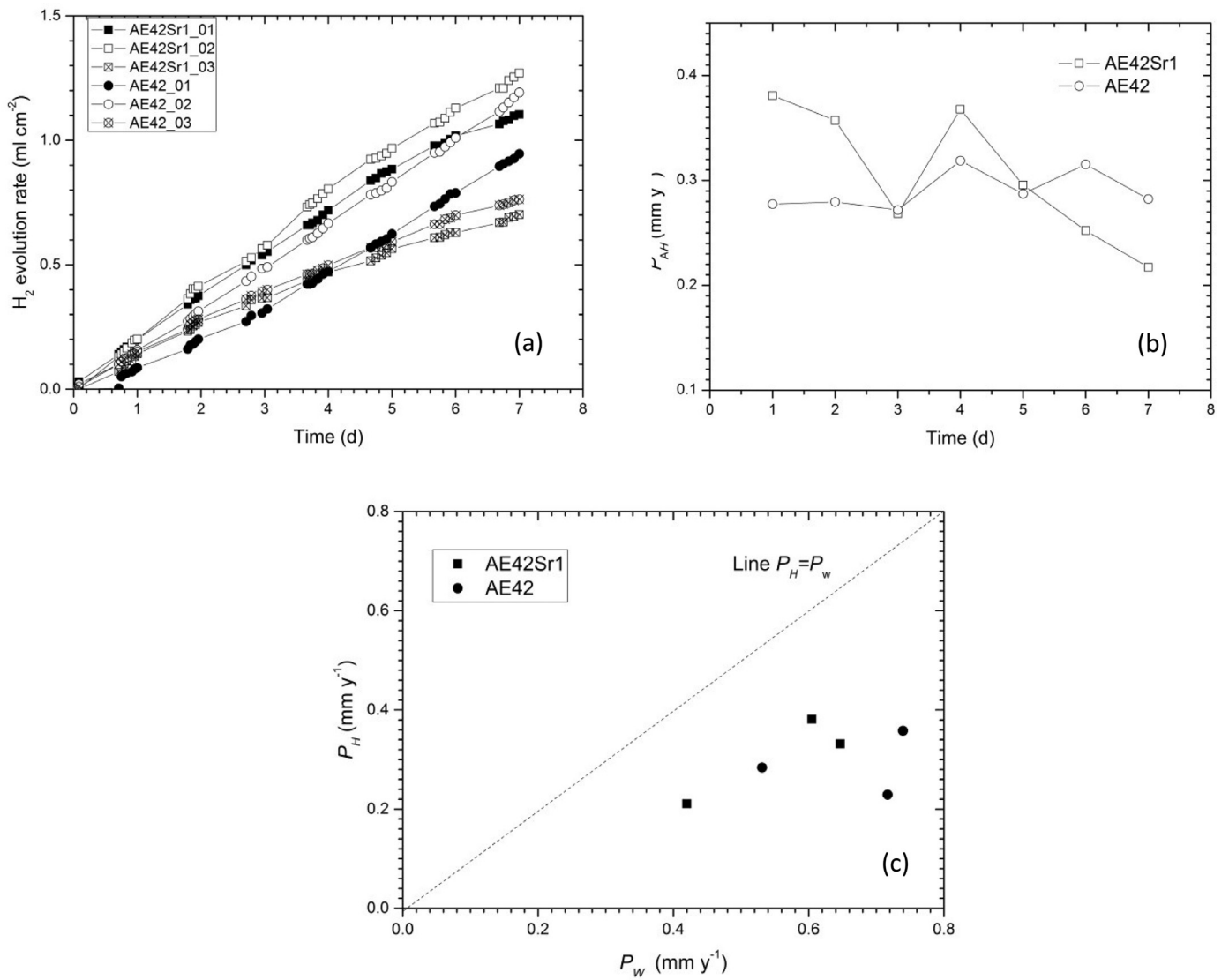


Fig. 10. Hydrogen evolution curves (a), average PAH curves vs time (b) and PHvs Pw (c) of AE42 and AE42Sr1 during 7 day immersion test in 3.5 wt.% NaCl+Mg(OH)₂ solution at 24±2°C.

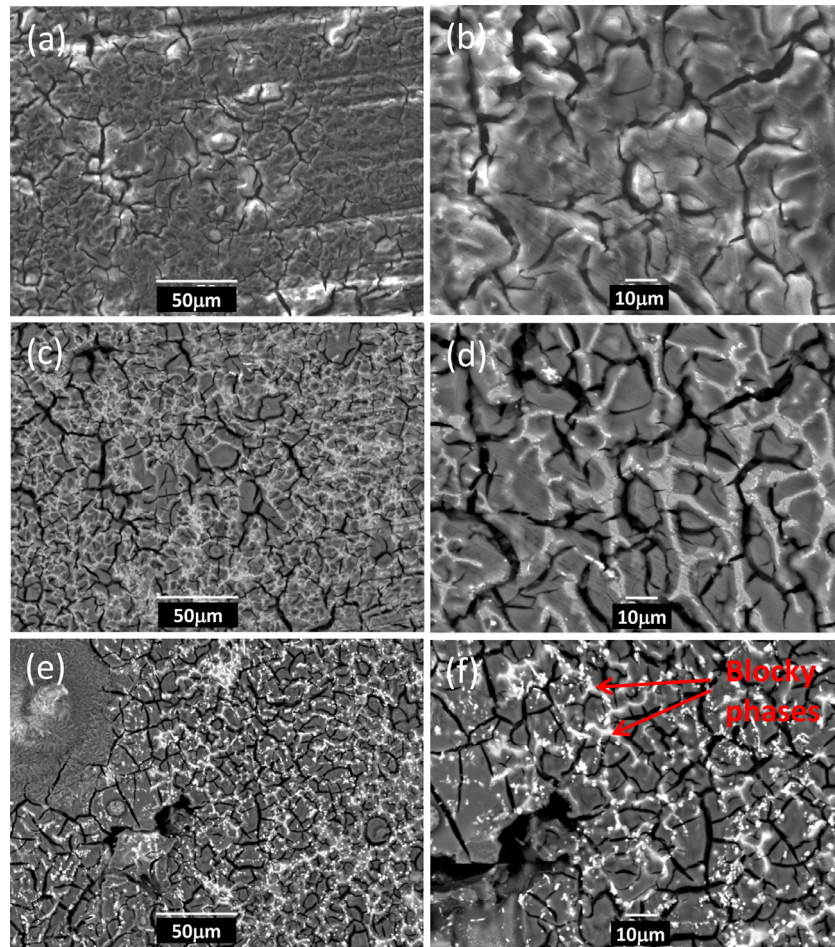


Fig. 11. Morphologies of Mg-Al alloys after 7 day immersion test in 3.5 wt.% NaCl + Mg(OH)₂ solution at 24 ± 2 °C. (a) and (b) SEM, AE42, (c) and (d) SEM-BSE, AE42, and (e) and (f) SEM-BSE, AE42Sr1.

phases under the corrosion products. The cracks on AE42 were bigger than on AE42Sr1, indicating that the corrosion product layer on AE42 was thicker than on AE42Sr1. Moreover, many cracks penetrate/cross through the intermetallic network (break the network) on the Sr free alloy (Fig. 11(d)), while most of the cracks were stopped by the blocky intermetallic phase on the Sr-containing alloy (Fig. 11(f)). These results were confirmed by an examination of the cross-section morphologies of the corroded samples for the two alloys as illustrated in Fig. 12. The corrosion of Sr free AE42 alloy reached inside the substrate about 4 or 5 grain size depth from the surface until being blocked by the continuous second phase. But the corrosion product of AE42 containing Sr reached inside the substrate only about one or two grain size depths until being locked by the second phase. The total corrosion rate was limited by the blocking effect caused by the second phase. The microgalvanic effect caused by rich second phases enhanced the fast formation of a tight barrier of the corrosion product layer at the beginning and the role of the micro-galvanic effect was eliminated gradually by the blocking effect of the continuous second phases. Some corrosion behaviour changed into partially localised corrosion as shown in Fig. 12(c) for the non-continuous second phase locations.

In the corroded surface layers, less intermetallic phases and cracks remain than in the uncorroded substrates. The corroded surface layer on AE42 (Fig. 12(a) and (c)) was thicker, had more and larger cracks, and contained much smaller amounts of intermetallics than that on AE42Sr1 (Fig. 12(b) and (d)).

3.2.3. EDS analysis of corrosion products

Fig. 13 presents various EDS spot analyses on the corroded AE42 and AE42Sr1. The EDS analysis results of the selected spots are listed in Table 2. The dark area is the corrosion product on the matrix, consisted of mainly Mg(OH)₂ with alloying elements Al, Si and the ions from the sodium chloride solution. The bright spots were on the thin corrosion products formed on the second phases. It was clearly shown that the Mg₈Al₄Sr blocky phase under spot 8 (Fig. 13(b)) stopped the propagation of the cracks contains a large amount of Sr. The composition of the second phases and the matrix changed after the corrosion. Moreover, there was a much higher oxygen content for both the second phases and matrix in the AE42 sample than in the AE42Sr1 sample. This also indicated that the corrosion layer was thicker on the AE42 than the AE42Sr1. The EDS results indicated that the corrosion

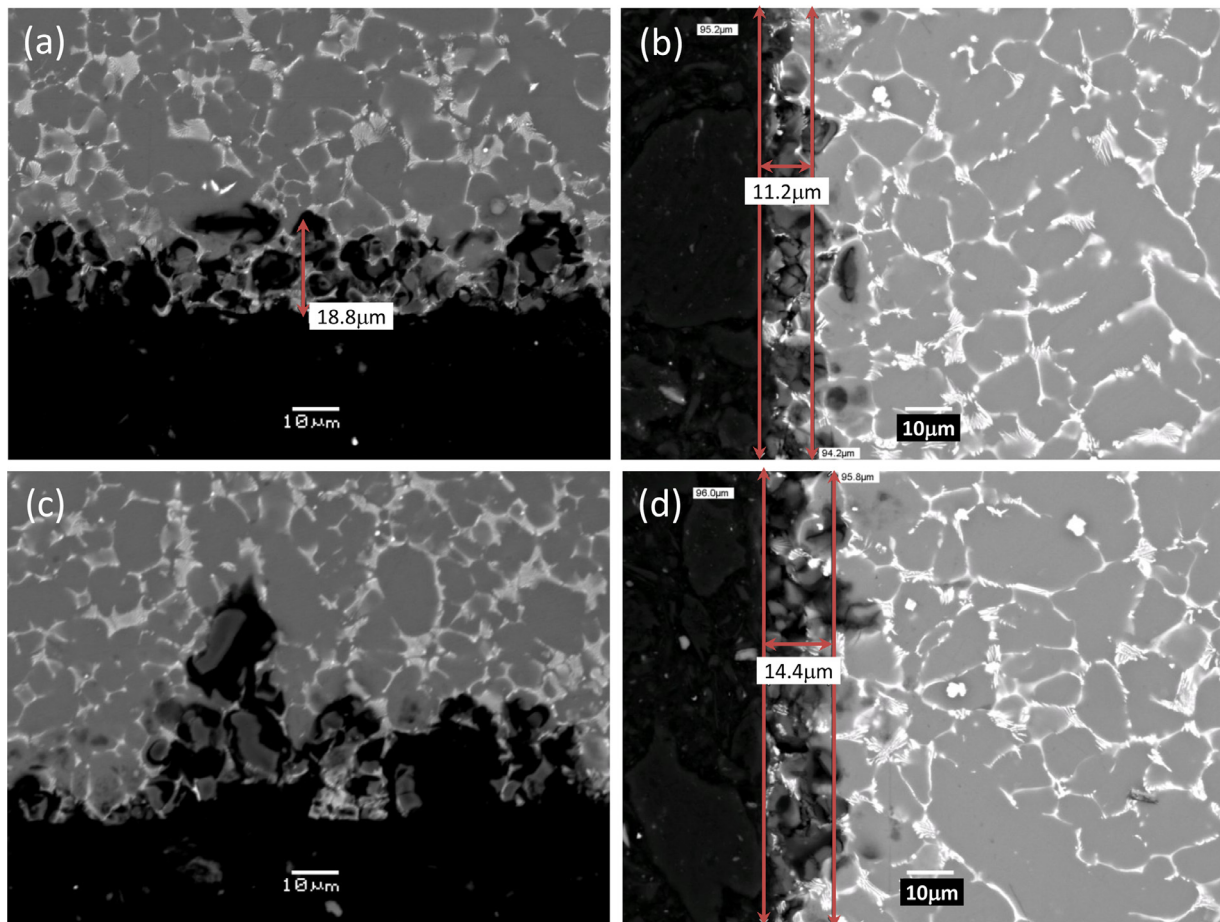


Fig. 12. Cross sections of the corroded (a) and (c) AE42 and (b) and (d) AE42Sr1 samples after 7 day immersion test in 3.5 wt.% NaCl+Mg(OH)₂ solution at 24±2°C.

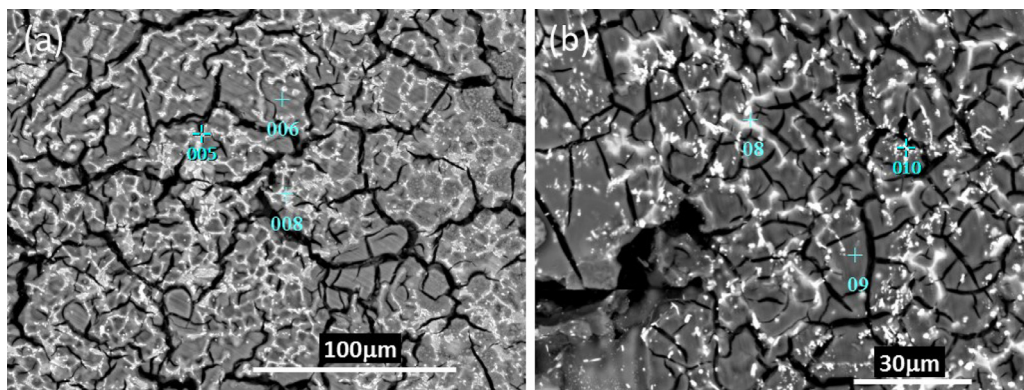


Fig. 13. Spots for EDS composition analysis (wt.%) of (a) AE42 and (b) AE42Sr1 samples after 7 day immersion test in 3.5 wt.% NaCl+Mg(OH)₂ solution at 24±2°C, see results in Table 2.

products were mainly Mg(OH)₂, Al₂O₃, La₂O₃, and CeO₂ [49–51].

3.2.4. Analysis of cross-section of corroded samples

The effect of the grain size generated from the high-pressure die-cast for AE42 and AE42Sr1 alloys, had been also compared using the cross-section images of the traverse

and lateral direction of the corroded samples as shown in Fig. 14. There were similar corrosion behaviours on both directions for AE42 and AE42Sr1 alloys as shown in Fig. 14. Corrosion of both alloys penetrated into the substrate from the surface and stopped at a continuous network like second phase. Localised corrosion may exist due to the break in the network.

Table 2

Chemical composition (wt.%) of the spots on the corroded samples of AE42 and AE42Sr1 alloys analysed by EDS after 7 day immersion test in 3.5 wt.% NaCl + Mg(OH)₂ solution at 24±2°C.

Alloy	Spot	Location	C	O	Mg	Al	Si	Cl	La	Ce	Sr
AE42	005	Second phases	3.28	36.50	38.7	9.89	0.45	3.08	2.76	5.28	–
	006	Matrix		36.84	42.1	7.28	2.28	11.4	–	–	–
	008	Second phases	3.48	34.3	31.1	11.5	1.36	8.21	3.24	6.65	–
AE42Sr1	08	Second phases		6.07	63.3	10.89	–	–	–	–	19.69
	09	Matrix	6.97	34.3	48.87	7.35	1.55	0.91	–	–	–
	010	Second phases	4.14	12.20	50.61	12.11	–	0.62	4.98	13.63	1.70

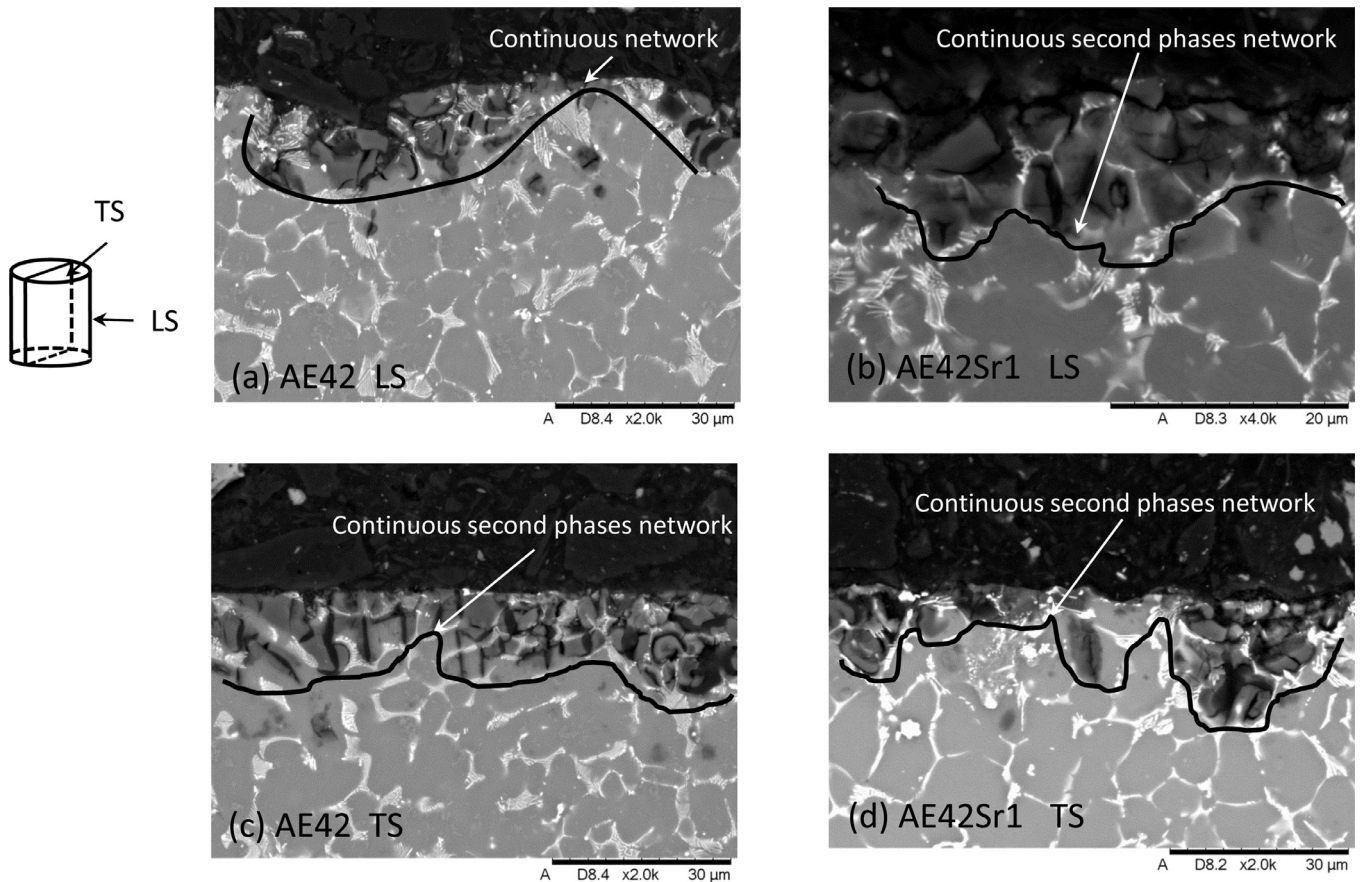


Fig. 14. Cross-section of corroded AE42 and AE42Sr1 along the lateral direction (a) and (b) and traverse direction (c) and (d) after 7 day immersion test in 3.5%NaCl+Mg(OH)₂ solution at 24±2°C .

Fig. 15 shows the surface morphologies of the corroded AE42 and AE42Sr1 after the corrosion products have been removed by cleaning. The corrosion was mainly uniform with a few spots of localised damage for both the two alloys. The bright net shape structure of the second phase area can be seen easily after the corrosion product have been removed. The composition of the bright area has been analysed by EDS, which confirmed that the bright skeleton-like net left after the cleaning process consisted of the second phases. There were grain grooves on the corroded surface. These results indicated that the dissolution rate of the grain matrix was higher than those of the grain boundaries, i.e. the grain boundaries were more corrosion resistant than the grain matrix. There were small grooves in the big grain grooves as shown in Fig. 15(g)

and (h). These small grooves could be formed due to the dissolution of the dendrites, which contain less Al and rare earth elements than the dendrite boundaries.

3.2.5. Electrochemical evaluation

The electrochemical impedance spectra (EIS) for AE42 and AE42Sr1 after 2-hour immersion and 2-day immersion in the NaCl solution saturated with Mg(OH)₂ are presented in Fig. 16. The EIS data were simulated with the equivalent circuit in Fig. 16(c) which has been used previously to simulate EIS data [52,53] to evaluate the polarisation resistance. The polarisation resistance of AE42 increased from 1400 Ω cm² at the beginning to 2200 Ω cm² after 2 days immersion as shown in Fig. 16(a). The polarisation resistance of AE42Sr1

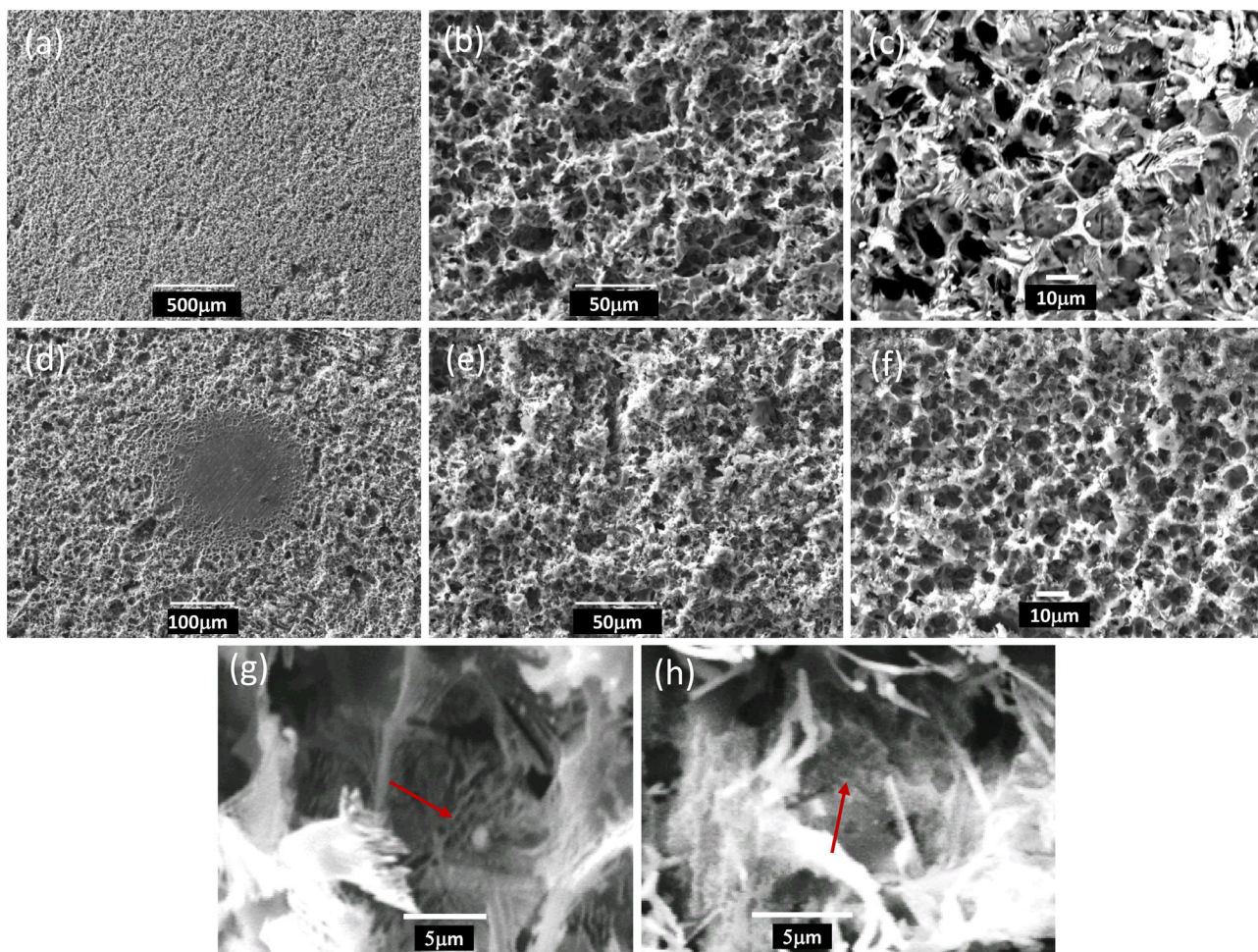


Fig. 15. SEM morphologies of Mg-Al alloys (corrosion products have been removed) after 7 day immersion test in 3.5 wt.% NaCl+Mg(OH)₂ solution at 24±2°C. (a), (b), (c) and (g) AE42, and (d), (e), (f) and (h) AE42Sr1.

increased from 1500 Ω cm² to 2500 Ω cm² as shown in Fig. 16(b). The observation that the polarisation resistance increased with immersion time means corrosion products were built up on the surface. The polarisation curve of AE42 and AE42Sr1 alloys after 2-day immersion test in the 3.5 wt% NaCl solution saturated with Mg(OH)₂ are shown in Fig. 17. A film breakdown potential can be found on both polarisation curves which means the built-up corrosion product film acts as a protective film on the surface. Comparison of the anodic branch of polarisation curves of both alloys, indicates that the current density of AE42 was higher than that of AE42Sr1. The open circuit potential of AE42Sr1 was also nobler than that of AE42. This means that the polarisation curves indicate that the corrosion resistance of AE42Sr1 was higher than that of AE42, in agreement with the EIS data and the weight loss data.

An increase in Al content in Mg alloys has been found to reduce the activity of Mg in dilute NaCl solutions and improve the corrosion resistance of Mg alloys [45,54]. The formation of Al₂O₃ and Al(OH)₃ compounds on the metallic surfaces during corrosion plays a significant role to limit fur-

ther progress of corrosion in Mg alloys [45]. The additions of rare earth elements to Mg alloys have also been found to enhance the corrosion resistance [55,56]. Therefore, the larger amounts of refined intermetallic phases due to additions of rare earth elements result in suppression of micro-galvanic couples and the formation of oxide films containing rare earth elements during corrosion can enhance the protective effectiveness of the corrosion products [55,56].

Since more Sr and rare earth elements are present in the intermetallic phases, dendrites and grain boundaries as shown in Figs. 3 and 7, the corrosion resistance of the intermetallic phases and boundary areas should be enhanced, as indicated by the dendrite grooves after corrosion (Fig. 15). Moreover, the Sr-containing intermetallic phase may stop the propagation of corrosion (Figs. 11 through 14), and reduce the possibility of the alloy being in contact with the corrosive media and thus retards further corrosion. Hence, the formation of large amounts of the additional intermetallic phase of Mg₈Al₄Sr improved the protectiveness of the oxide films in AE42Sr1, and the continuous phase networks improved the corrosion resistance of AE42Sr1. As the refined

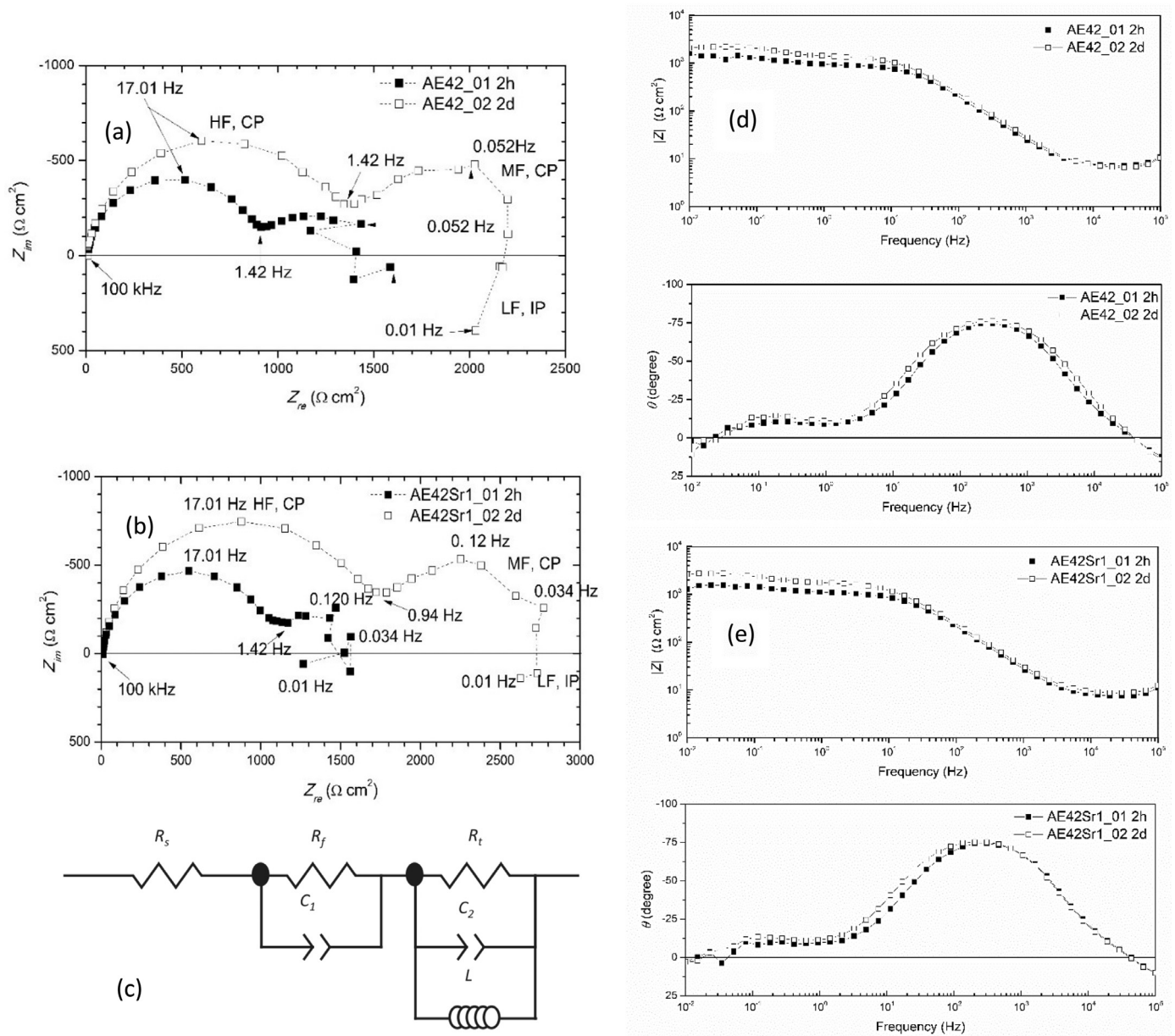


Fig. 16. EIS of (a), (d) AE42 and (b), (e) AE42Sr1, of the two alloys after 2 h and 2 days immersion test in 3.5 wt.% NaCl+Mg(OH)₂ solution at 24±2°C, and (c) the equivalent circuit used to simulate all EIS data [38,39].

microstructure has more intermetallic phases and boundary areas, it improves the protective effectiveness of the oxide films in AE42Sr1 compared to those in AE42. Therefore, the observation of the addition of 1% Sr into the Mg-Al-RE alloy enhances the corrosion performance of the alloy can be summarily attributed to the following mechanisms: (1) The formation of an oxide film on the metallic surfaces during corrosion limits the progress of corrosion in Mg alloys [45]. The alloys containing more Sr and rare earth elements in the dendrites and grain boundaries exhibit more protective oxide films in these solute rich regions [55,56]. (2) The Sr-containing intermetallics suppress the micro-galvanic effect and stop the further development of corrosion. (3) The

continuous Mg₈Al₄Sr phase networks increase the protective barrier effect of the intermetallic phases, and hence improve the corrosion resistance of AE42Sr1, (4) The addition of Sr can refine the microstructure, resulting in more intermetallic phases and boundary area, and improving the effectiveness of the oxide films in the AE42Sr1 compared to those in AE42.

The corrosion rates of both alloys ($P_W = 0.6$ to 0.7 mm y^{-1}) were comparable to that of High-Purity Mg ($P_W = 0.4 \text{ mm y}^{-1}$) [11] [9], indicating that the protective nature of the essentially continuous second phase network was more important than that of the influence of corrosion acceleration by micro-galvanic interaction between the matrix and the second phase particles.

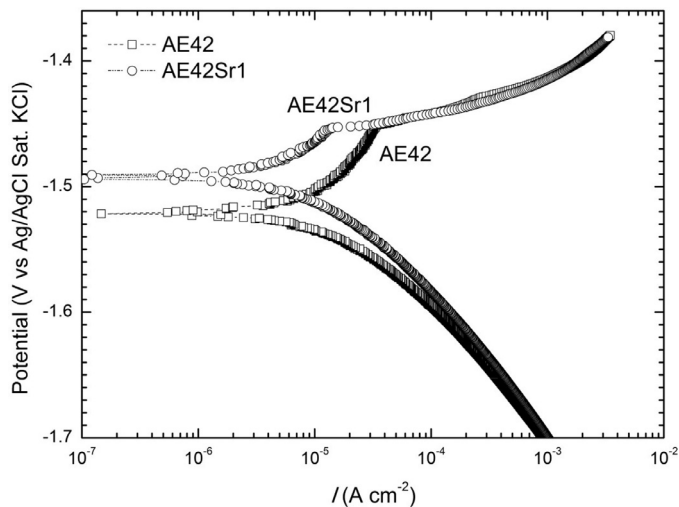


Fig. 17. Polarisation curves of AE42 and AE42Sr1 alloys after 2 days immersion test in 3.5 wt.% NaCl+Mg(OH)₂ solution at 24±2°C.

4. Conclusions

1. The addition of strontium introduced a Sr-containing intermetallic phase (Mg₈Al₄Sr) into the AE42 alloy, which extended and increased the volume fraction of the intermetallic network, and also improved the continuity of the intermetallic network.
2. The corrosion rate of the Sr-containing alloy ($P_W = 0.56 \pm 0.10 \text{ mm y}^{-1}$) was somewhat lower than that of the Sr free alloy ($P_W = 0.66 \pm 0.10 \text{ mm y}^{-1}$), according to the weight loss, hydrogen evolution rate and EIS measurements, attributed to the greater continuity of the second phase network.
3. The corrosion rates of both alloys were comparable to that of High-Purity Mg, indicating that the protective nature of the essentially continuous second phase network was more important than that of the influence of corrosion acceleration by micro-galvanic interaction between the matrix and the second phase particles.
4. The corrosion rate of the surface was the same as that of the interior, indicating that there was no skin effect for these diecastings, with a much lower corrosion rate.

Data availability

The raw data required to reproduce these findings are available to download from <https://doi.org/10.14264/uql.2018.522>. The processed data required to reproduce these findings are available to download from <https://doi.org/10.14264/uql.2018.522>.

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