Effect of Mn Modification on the Corrosion Susceptibility of Mg–Mn Alloys by Magnesium Scrap

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Received: 6 December 2019 / Revised: 23 January 2020 / Published online: 18 May 2020
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Abstract

The microstructure and anti-corrosion behavior of Mg–Mn alloys by magnesium scrap have been investigated in this study. The results show that the size of the Fe-rich particles in magnesium scrap decreases but the quantity increases with the Mn addition. Although the presence of Mn-containing Fe-rich particles with unique symbiotic structure can effectively weaken the micro-galvanic corrosion, the presence of more free Fe (Fe-rich particles) does not necessarily lead to severe corrosion of the alloy. The corrosion susceptibility of Mg–Mn–Fe alloy primarily depends on the solubility of iron in the Mg matrix, while it can be significantly reduced by suitable Mn addition. Besides, the tolerance limit of the Fe impurity can be expressed as $Fe_{\max} = 0.0083 \text{ Mn}$ (relative to the iron solubility). Only when the Fe/Mn ratio is below 0.0083 can the alloy have excellent corrosion resistance, with the corrosion rate changing in the scope of 0.38 ± 0.09 to $0.54 \pm 0.15 \text{ mg/cm}^2 \text{ day}$ and i_{corr} from 3 to $9 \times 10^{-4} \text{ A/cm}^2$.

Keywords Magnesium scrap · Mn modification · Fe impurity · Corrosion susceptibility · Corrosion resistance

1 Introduction

Magnesium and its alloys have the advantages of high specific strength, good machinability, excellent biocompatibility, etc., thus attracting more attention and enjoying a growing reputation when applied in many fields [1–4]. However, the extensive application of magnesium alloys was severely restricted by their relatively poor anti-corrosion ability.

It is well known that magnesium alloys are susceptible to galvanic corrosion caused by the second phase of impurities. Among the known impurities, the Fe element is the most common impurity and exists in almost every stage of the manufacturing process. Moreover, Fe impurity was proved to have significant toxic effect on the corrosion resistance of

the Mg alloys, causing increasing hydrogen evolution rate of the galvanic-type corrosion cell [5–8]. A lot of researches show that to keep the Fe impurity under an iron tolerance limit is a wise way to get excellent corrosion resistance and good mechanical properties [9–15]. As for pure Mg, the iron tolerance limit was reported to be 170 ppm [16, 17]. When the concentration of Fe impurities is lower than the tolerance limit, the adverse impact of Fe element on the corrosion resistance could be ignorable. But, it is very difficult to purify pure magnesium to a very high level in production practice.

Fortunately, the iron tolerance limit can be influenced by the third element and the casting process [4, 12, 18, 19]. Manganese element (Mn) can be found in the alloy brand standard of lots of commercial magnesium alloys (such as AZ series alloys, AM series alloys). One of the primary purposes of Mn addition is to combine Mn element with a certain amount of Fe element to form a higher density of Fe–Mn compound, decreasing the iron concentration and then settling the Fe element into the melting sludge. Moreover, in the melted alloy liquid, the temperature determines the relative proportion of the dissolved iron and undissolved iron content [18]. In other words, as the melt temperature decreases, the dissolved iron content decreases, but the undissolved iron content increases. So,

Available online at <http://link.springer.com/journal/40195>.

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reasonable control of the Mn content and casting process helps improve the corrosion resistance of the alloy further. Generally, the Mg–Mn alloy has good plasticity and corrosion resistance. However, with the increase in the proportion of magnesium scrap used in the Mg alloy production, it is important to study the corrosion resistance of Mg–Mn alloys prepared from magnesium scrap with high iron content. Although extensive researches have been conducted, the investigation on suitable quantitative relationship between Fe and Mn concentrations and the corrosion sensitivity of magnesium alloys was still insufficient. It is well known that Fe impurity mainly exists as a solid-solution form and free form in the alloy [12]. However, the different roles of the two existing forms of Fe in the corrosion process were not fully understood. In the present work, a series of Mg–Mn–Fe alloys with varying proportions of magnesium scrap and Mg–Mn master alloy were designed to get different Fe/Mn ratios. The modification effects of Mn on microstructure and anti-corrosion behavior of the alloy made from magnesium scrap, as well as the roles of different existing forms of Fe element in the corrosion process, were investigated.

2 Experimental

2.1 Material Preparation and Microstructure Characterization

The magnesium scrap (0.0423% Fe, mass fraction) and Mg–Mn master alloy (0.0123% Fe and 3.25% Mn) were used as raw materials in this test. The Mg–Mn–Fe alloys were fabricated in a low carbon steel crucible under the protection of a shield gas consisting of SF₆ and CO₂ (1:100). After adding the Mg–Mn master alloy into the crucible, the melt was kept at 750 °C for 30 min and then slowly cooled down to 650 °C and held for 90 min (with a temperature fluctuations of ± 15 °C, and cycle duration of 20 to 25 min). After that, the crucible was quenched into cold water to obtain the solidified ingot. The chemical compositions of alloy samples cut from the half-height position of their as-cast alloy ingots were determined by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy), as listed in Table 1. Specimens for microstructure characterization were ground with SiC emery papers and then dried in a cold air stream. The SEM (Tescan Vega 3 LMH and JEOL JSM-7800F field emission scanning electron microscope) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to characterize the microstructure. The average size of the particles was evaluated by using Image-Pro Plus software, and the results were determined by averaging the values taken from at least five separate SEM images.

Table 1 Chemical composition of the Mg–Mn–Fe alloy samples (wt%)

Alloys	Mn	Fe	Si	Mg
1# (Mg–0Mn–0.023Fe)	0	0.0236	0.0179	Bal
2# (Mg–0.1Mn–0.023Fe)	0.1090	0.0232	0.0188	Bal
3# (Mg–0.3Mn–0.020Fe)	0.2780	0.0201	0.0203	Bal
4# (Mg–0.5Mn–0.018Fe)	0.5030	0.0182	0.0171	Bal
5# (Mg–1.0Mn–0.018Fe)	0.7610	0.0172	0.0206	Bal
6# (Mg–2.0Mn–0.010Fe)	1.4890	0.0079	0.0200	Bal

2.2 Constant Immersion Testing and Corrosion Morphology Characterization

The corrosion rate was evaluated by measuring the weight loss of alloy samples at room temperature in 3.5 wt% NaCl solution for two days. The specimen's surface was mechanically ground to 1000 grit SiC paper, washed with distilled water and then dried in a stream of cold air. After the immersion test, the samples were washed with a chromic acid solution (200 g/L CrO₃ + 10 g/L AgNO₃) at ambient temperature for about 15 min to remove the corrosion products and then quickly rinsed with distilled water and dried in the cold air. The measured metal weight loss (WL, mg) was used to calculate the corrosion rate (CR, mg/cm² day) as follows:

$$CR = \frac{WL}{At},$$

where t is the exposure period in days and A is the total surface area in square centimeters. The corrosion morphology of the tested specimens was further characterized using scanning electron microscopy.

2.3 Electrochemical Measurement

The electrochemical test was conducted using a Metrohm Autolab PGSTAT 302 electrochemical workstation in a three-electrode cell composed of a reference electrode (a saturated calomel electrode), a counter electrode (a platinum foil) and a working electrode. The area of the working electrode was 0.785 cm². EIS measurements were carried out at a certain corrosion potential in a frequency range from 100 kHz to 0.01 Hz using a 10 mV amplitude perturbation. Potentiodynamic polarization curves were plotted at a scanning rate of 1 mV/s. The above reagents used were of GR grade or better. No stirring was applied to the solution during the experiments.

To get better understanding of the relationship between the iron content (including the dissolved and undissolved

iron contents) and corrosion rate, the solid solubility of Fe in trial samples with different additions of Mn was got from Mg–Mn–Fe phase diagram. The content of free Fe is difference between the measured value (tested by ICP) and solid solubility of Fe.

3 Results

3.1 Microstructure of Fe-Rich Particle

The morphology and EDS results of the Fe-rich particles in 1# (0.0236% Fe, 0Mn) and 4# (0.0182% Fe, 0.503% Mn)

alloys after mechanical grinding are shown in Fig. 1. Fe impurities in the alloy mainly exist in the form of solid solutions and free forms (Fe-rich particle). As seen in Fig. 1a, c, e, 1# alloy has several Fe-rich particles with an average size of 0.72 μm . Sharing similar structure as particles of sample 1# alloy, the Fe-rich particles in 2# alloy have a brighter inner layer and slightly darker outer layer. However, the Fe-rich particle of 4# alloy has a more pronounced flocculating structure than that of the 1# alloy. Moreover, with Mn addition, the size of Fe-rich particles decreases but the number increases, indicating that the Mn element inhibited the coarsening process of the Fe-rich particles in the melt, and its details will be reported in future research.

Fig. 1 SEM images and EDS results of Fe-rich particles: **a, c, e** 1# alloy, **b, d, f** 4# alloy

To better analyze the trend of element intensity (Fe, Mn and Mg) around Fe-rich particles, EDS line scanning was employed, with its results being shown in Fig. 2. The intensity of Fe element of Fe-rich particles in 1# alloy reaches the maximum peak value at the core (see Fig. 2a) and then decreases gradually along the radial direction, while the intensity of Fe and Mn elements of the Fe-rich particles in 4# alloy reaches the peak value at the same site (the center of the brighter inner layer), both of which have the same changing trend along the radial direction of the particle (see Fig. 2b). Hence, the particles containing Fe and Mn should be a coupled growth microstructure (symbiotic structure), which is consistent with the previous hypothesis of Kim's [20]. The presence of Mn in Fe-rich particles may cause Mn and Fe to create a buffer zone and form the symbiotic structure, thus contributing to weakening the effect of micro-galvanic corrosion.

3.2 Corrosion Rate and Surface Morphology

The corrosion rate can be used to evaluate the corrosion susceptibility of magnesium scrap. The corrosion rate of 1# alloy (0.0236% Fe) is as high as 144.88 ± 5.22 mg/cm² day, while with 0.1% Mn addition as 2# alloy, it decreases sharply to 70.09 ± 3.60 mg/cm² day. When the Mn content continues to increase as 3# alloy (0.3% Mn, 0.0201% Fe), the corrosion rate decreases further to 13.79 ± 1.17 mg/cm² day. However, as 4#, 5#, 6# alloys, when the Fe content is less than 0.0182%, and the Mn content is more than 0.5%, their corrosion rate remains at a low level, just about 0.38 ± 0.09 to 0.54 ± 0.15 (mg/cm² day). It was well known that even a small amount of iron impurities can reduce the corrosion resistance of magnesium alloys. However, reasonable control of Mn addition can weaken the adverse effects of iron impurity and reduce the corrosion susceptibility of magnesium scrap, which will also be discussed later.

Figure 3 shows the typical morphology of the surfaces of the alloy samples after immersion in 3.5 wt% NaCl solution

Fig. 2 EDS element line scanning spectrums of Fe-rich particles: **a** 1# alloy; **b** 4# alloy

Fig. 3 Scanning electron micrographs showing typical corrosion morphology of the Mg–Mn–Fe alloy samples after immersion in 3.5 wt% NaCl solution for 48 h with the corrosion products removing: **a** 1#, **b** 2#, **c** 3#, **d** 4#, **e** 5#, **f** 6#, **g** high magnification of the marked area A in **a**, **h** high magnification of the marked area B in **c**, **i** high magnification of the marked area C and D in **d**, **k** high magnification of the marked area E in **e**

for two days and removal of corrosion products. Severe corrosion was observed on the surface of 1#, 2# and 3# alloy specimens for the significant reduction in volume, as shown in Fig. 3a–c. The severe localized corrosion sites formed on the surface of these alloys have the same morphological features, exhibiting a honeycomb-like structure composed of

crisscrossed and interconnected holes. Besides, some striated features proceeding along specific directions are naturally found, as indicated by the yellow arrow in Fig. 3a, c. At high magnification, the striated regions show a layered structure (see Fig. 3g, h), which is formed due to different dissolution rates of crystal plane with different orientations

[13, 14, 21, 22]. Slight corrosion was observed on the surface of 4#, 5#, 6# alloy specimens, as shown in Fig. 3d–f. As for 4# alloy specimen, pitting corrosion with the average diameter of 99.83 μm (see Fig. 3d, i) was observed, and the slight filiform corrosion was randomly distributed on the surface (see Fig. 3d, j). The corrosion of magnesium alloys typically takes the form of micro-galvanic corrosion, which could germinate along the second phase of the alloy due to the potential difference between the second phase (Fe impurity) and the magnesium matrix. The filiform corrosion morphology is caused by an active corrosion cell that moves across a metal surface [23]. As for 5# and 6# alloys, the average diameter of corrosion pits decreases to 64.89 and 48.28 μm , which is attributed to a reduction in galvanic potential difference between the α -Mg phase and Fe–Mn particle with symbiotic structure [20, 24]. However, the increase of galvanic couple consisting of Mn phase and α -Mg phase could promote the initiation of pitting corrosion, causing a significant increase in the number of corrosion pits, as shown in Fig. 3e, f.

3.3 Macro-Corrosion Process

Figure 4 shows the macroscopic corrosion morphology evolution of the alloy samples in 3.5 wt% NaCl solution with different immersion times. When the specimen was immersed in the solution, many small hydrogen bubbles were immediately formed on the surface of Mg. After

soaking for a period of time (0.3 h), the hydrogen stream bubbles were generated at some points of the surface of 1# and 2# alloy samples, while the bubbles on the surface of other alloys (3#, 4#, 5# and 6# alloys) were relatively weak, as shown with the red arrow in Fig. 4. That means that the corrosion rate of 1# and 2# alloys is faster than that of 3#, 4#, 5# and 6# alloys. In general, the localized corrosion occurred at the sites with corroded dark surface, and the hydrogen stream appeared. As for the 1#, 2# and 3# alloys, with the further extension of immersion time as 4.0 h, these localized corrosion sites developed gradually, with dark corrosion products and a strong hydrogen stream on the surface. In addition, the formation of corrosion products underneath the $\text{Mg}(\text{OH})_2/\text{MgO}$ film catalyzes the corrosion process of Mg alloys [25], making the contribution of reactions in dark areas to the global hydrogen evolution rate stronger. When immersion time is longer than 12 h, the dark corrosion zone extended to the whole surface of the alloy and to the depth at the same time. After immersion for about 24 h, the rough and thin corrosion products fell off obviously to the periphery, with its color becoming light. However, as for 4#, 5# and 6# alloys, when the immersion time varied from 4 to 24 h, the silvery surface changed little but only with a few localized corrosion sites (see Fig. 4), indicating that a more protective surface film was formed on the surface of these alloys.

Figure 5 shows the SEM of corrosion morphology and EDS results of 1# and 4# alloy samples after immersion in

Fig. 4 Optical images showing the macro-corrosion morphology evolution on the surfaces of the Mg–Mn–Fe alloy samples during immersion in 3.5 wt% NaCl solution

Fig. 5 SEM of corrosion morphologies and EDS results of alloy samples in 3.5 wt% NaCl solution for 1 h: **a** 1# alloy; **b** 4# alloy

3.5 wt% NaCl solution for 1 h. It can be seen that the localized corrosion morphology of 1# alloy was severe as the corrosion products fell off seriously, with the diameter of localized corrosion holes being larger, as indicated by the white arrow in Fig. 5a. The Fe-rich particles, mainly composed of Fe, O, and Mg elements, can be found at the bottom of the localized corrosion hole. Compared with the corrosion morphology of 1# alloy, the localized corrosion of 4# alloy was relatively mild, and the diameter of localized corrosion holes was smaller, as shown in Fig. 5b. Similarly, the Fe-rich particles are mainly composed of Mg, Mn, Fe, and O elements. The hydrogen evolution reaction mainly occurs at these Fe-rich sites (active cathode), which is because of

the more significant standard electrode potential difference between Mg and Fe (more than 1 V). Therefore, in some cases, only localized corrosion holes can be found because of the detachment of Fe-rich particles.

3.4 Electrochemical Behavior

DC potentiodynamic polarization measurements of the specimens with different levels of Mn and Fe content were performed scanning from OCP to 400 mV and -400 mV for characterizing the current response from alloy substrate in 3.5 wt% NaCl solution at room temperature. The polarization curves are shown in Fig. 6a, and cathodic Tafel extrapolation

Fig. 6 **a** Potentiodynamic polarization curves, **b** EIS spectra of alloys in 3.5 wt% NaCl solution

is applied for analyzing the experimental polarization curves. The cathode reaction in the polarization curves corresponds to the evolution of the hydrogen, while the anodic polarization curve shows important features related to the corrosion resistance [26]. The corrosion potential E_{corr} of 1# alloy (0.0236wt% Fe) is -1707 mV, which reveals a positive shift of corrosion potential E_{corr} to -1686 , -1605 , -1550 , -1584 , -1572 mV for 2# (0.1% Mn, 0.0232% Fe), 3# (0.3% Mn, 0.0201% Fe), 4# (0.5% Mn, 0.0182% Fe), 5# (1.0% Mn, 0.0172% Fe), 6# (2.0% Mn, 0.0079% Fe) alloys, respectively. It indicates the collective effect of Mn and Fe on the respective corrosion reactions in anodic and cathodic domains. The fitted i_{corr} of the 1# and 2# alloys is kept the same order of magnitude as 5.3×10^{-4} and 5.2×10^{-4} A/cm², while the i_{corr} of 3# alloy is more than one order of magnitude higher than that of 1# and 2# alloy. It should be noted that no obvious passivation transition region can be distinguished in the anodic zones of these alloys, indicating that the coordination of Mn and Fe content does not completely change the weak corrosion resistance of hydro(oxide). In other words, this cooperation of Fe and Mn cannot effectively reduce the toxic effects of Fe impurities, with the corrosion resistance being poor. To be specific, the i_{corr} of 4#, 5#, and 6# alloys ranges from 3 to 9×10^{-4} A/cm² and is about two orders of magnitude lower than that of 1# and 2# alloys, which means that these alloys have better corrosion resistance. Also, for the alloy with Mn content more than 0.5% and Fe content less than 180 ppm, the passivation transition region can be easy to find from the anodic branch, indicating the enhancement of barrier properties of the formed corrosion products by the pure Mg. During the refining process, with the Mn addition, the solubility of Fe in the Mg matrix decreases, and a higher density of Fe–Mn compound forms and then settles to the melting sludge. Both of them contribute to the formation of a more protective surface film, which ultimately increases the polarization resistance in the corrosive electrolyte.

Electrochemical impedance spectroscopy (EIS) was conducted after the stabilization of the OCP immersion in 3.5 wt% NaCl solution at room temperature, and the EIS spectra (Nyquist plots) are given in Fig. 6b. From a general view of the Nyquist plots, the enhancement of the corrosion resistance of the 4#–6# alloys is relatively apparent, as indicated by the larger semicircles in comparison with the 1# alloy. It is easy to find that the corrosion resistance of 1#, 2# and 3# alloys is almost equivalent and minor (approx. 300 Ω cm²), which can be explained by the lower standard electrode potential of Mg (-2.37 V) and the insufficient protection of the corrosion products as hydro(oxide) layers. Moreover, the existence of a large amount of Fe impurities included the dissolved iron content (iron solubility) and undissolved iron content could aggravate the effect of the micro-galvanic corrosion. However, with the further increase in Mn content and decrease in Fe content, the increase in the diameters of

the large semicircles circle may be caused by the increase in compactness/thickness of the hydroxide layer on the Mg surface blocking the micro-galvanic corrosion between Fe impurities and Mg substrate [4]. In addition, it is clear that all the Nyquist plots include an inductive loop, indicating that the Mg electrode is experiencing localized corrosion [27]. All the obtained results of electrochemical measurement agree well with the immersion test and the following surface observation.

4 Discussion

4.1 Corrosion Susceptibility

According to Mg–Fe phase diagram [28], the solubility of Fe decreases with the decrease in temperature, so the low-temperature treatment (650 °C with intentional fluctuation of ± 15 °C) can accelerate the precipitation of Fe-rich particles from supersaturated solid solution. Moreover, according to the Mg–Mn–Fe phase diagram [29], the addition of Mn can also decrease the solubility of Fe in the melt. However, the low-temperature treatment (90 min) can promote the formation and growth of the Fe-rich particles [30, 31], including the Fe–Mn particles which has a symbiotic structure due to good affinity of Mn and Fe elements [20, 32, 33].

As for 1# alloy, the Fe-rich particles can form a robust micro-galvanic couple with the Mg matrix. The Fe-rich particles and the Mg matrix together create a mixed potential, which leads to the anodizing and dissolving of Mg matrix and to the cathodic polarization of the particles of pure insoluble elements such as Fe and Mn. The difference in corrosion resistance between the 4#–6# alloy and the 1#–3# alloy is quite obvious, as shown in Figs. 3, 4 and 6. That means that iron has a particularly harmful effect on magnesium alloy when the iron content exceeds its specific tolerable limit. The total iron content in the alloy includes the dissolved iron content (iron solubility) and undissolved iron content (the free iron). But it is not clear which part of the iron plays an important role in corrosion. According to Reichek et al. [9], the Fe/Mn weigh ratio of the alloy must be within the value of 0.032 (so called critical factor) to ensure that the alloy has better corrosion resistance. In other words, the corrosion rate of magnesium alloy could be controlled with a low value when the Fe/Mn ratio is lower than the critical factor.

Figure 7 and Table 2 show the iron content and corrosion performance of the alloy samples. The black curve (a) in Fig. 7 represents the iron solubility as a function of Mn content in the Mg–Mn–Fe system at 650 °C. Due to the addition of Mg–Mn master alloys with a certain Fe impurities, the total iron content in the melt maintains a downward trend, as shown in the blue curve (c). As for the alloy without Mn

Fig. 7 Changes in iron solubility, the free iron, the total iron and corrosion performance of the Mg–Mn–Fe alloy samples

addition (1# alloy), despite the fact that the free Fe content (56 ppm) is low, the solubility of Fe in the Mg matrix is high (about 180 ppm), resulting in a high corrosion rate as 144.8 ± 5.22 mg/cm² day. With the increase in Mn content from 0 to 0.1%, the solubility of Fe decreases sharply from 180 to 105 ppm, while the content of free Fe increases from 56 to 127 ppm. However, the corrosion rate decreases to 70.09 ± 3.60 mg/cm² day, indicating that the addition of

Mn significantly reduces the galvanic corrosion between the Fe particles and the Mg matrix. When the Mn content increases to 0.3%, the free Fe content is almost unchanged, but the solubility of Fe decreases. The final corrosion rate decreases significantly as 13.79 ± 1.17 mg/cm² day, indicating that the solubility of Fe is the main factor affecting the corrosion rate. Although the free Fe content of 4# and 5# alloys remains at a higher level as about 140 ppm, their corrosion rates are just 0.40 ± 0.12 mg/cm² day (4# alloy) and 0.54 ± 0.15 mg/cm² day (5# alloy), due to their low solubility of Fe (only about 40 ppm). As for 1# and 6# alloys, the free Fe content of them is close to each other, but the iron solubility of 6# alloy is lower than that of 1# alloy. So, the corrosion rate of 6# alloy is much lower than that of 1# alloy. It fully reflects the decisive role of the solubility of Fe on the corrosion rate. In summary, the corrosion rate of the alloy mainly depends on the solubility of Fe, and the presence of more free Fe (Fe-rich particles with Mn) does not necessarily lead to severe corrosion of the alloy. As more Fe atoms dissolve in the Mg matrix, the stability of the film can be decreased and the corresponding mechanism will be reported in future research.

Figure 8 further illustrates the effect of Fe solubility and the total Fe content on the corrosion rate. It can be seen from Fig. 8a that when the iron solubility is less than 40 ppm, the

Table 2 Iron content and corrosion performance of the alloy samples

Alloy	Mn (wt%)	The total iron (ppm)	Iron solubility (ppm)	The free iron (ppm)	Corrosion rate (mg/cm ² day)
1#	0	236	180	56	144.88 ± 5.22
2#	0.109	232	105	127	70.09 ± 3.60
3#	0.278	201	75	126	13.79 ± 1.17
4#	0.503	182	42	140	0.40 ± 0.12
5#	0.761	172	30	142	0.54 ± 0.15
6#	1.489	79	20	59	0.38 ± 0.09

Fig. 8 Corrosion performance vs. the iron content and Fe/Mn ratio of Mg–Mn–Fe alloy samples

alloy maintains excellent corrosion resistance. As we know, the critical factor concerning the Fe impurity is the Fe/Mn ratio rather than the absolute level of Fe concentration. Figure 8b shows the relationship between the Fe/Mn ratio and the corrosion rate. As indicated in Fig. 8b, the corrosion rate of the cast from the region below the tolerance limit is just about 0.38 ± 0.09 to 0.54 ± 0.15 (mg/cm² day), while the corrosion rate of the cast from the region above the tolerance limit increases gradually. Based on the above analysis, the tolerance limit of Fe impurities can be expressed as $Fe_{\max} = 0.0083 \text{ Mn}$ (relative to the iron solubility). Moreover, when the critical Fe/Mn ratio is superimposed on the plot of mutual solubility limits, the results (see Fig. 9) can provide convenient guidance for the production of Mg–Mn alloys. Since the solubility of Fe is mainly affected by the refining temperature and the Mn addition, it is possible to indirectly decrease the detrimental effect of Fe impurities by controlling the Mn content with a specific melt refining temperature. Tolerance limits may also be related to the boundary

Fig. 9 Fe–Mn solubility limits and the iron tolerance limit. The red numbers adjacent to the data points are the corrosion rates of the Mg–Mn–Fe alloy samples

between active and passive forms of iron precipitates. Only when the compositions are below the tolerance limits, both the Fe and Mn contents can decrease at the same time.

4.2 Corrosion Mechanism

According to the literature [34], the standard reduction potential of Fe is by far more positive than that of Mg ($Fe: -0.78 V_{\text{nhe}}$; $Mg: -2.37 V_{\text{nhe}}$), which significantly promotes the occurrence of galvanic corrosion. In general, due to the low solubility of Fe in the Mg matrix, the Fe-rich particles tend to precipitate during the melt solidification process, which can be distinguished by SEM and EDS in this study (see Fig. 1). The schematic illustration of pure Mg during the corrosion process is shown in Fig. 10a. During the dissolution of anodic magnesium, hydrogen evolution reaction [35] mainly occurs at these Fe-rich sites (active cathode). The anodic oxidation kinetics is primarily supported by the cathodic reaction of Fe-rich particles. As the surface area of Fe-rich particles increases and the cathode reaction kinetics increases during Mg dissolution (see Figs. 3, 4), the Fe-rich particles are usually located at the center of the corrosion sites and buried under the layer of the film (see Fig. 5). Exposure of 1# alloy (pure Mg) in 3.5 wt% NaCl solution leads to rapid corrosion with extensive, thick and porous $Mg(OH)_2$ formation covering the thin MgO film, which are attributed to the relatively high solubility of Fe in the Mg matrix [36, 37]. This highly porous nature of the $Mg(OH)_2$ film formed in the solution does not protect the alloy at all, as it does not inhibit the solution from infiltrating into the inner regions of the film and the film–metal interface.

However, as for the alloy with a Fe/Mn ratio higher than 0.0083, the corrosion resistance is inadequate because the coordination of Mn and Fe contents does not entirely change the weak corrosion resistance of hydro(oxide). Only when the Fe/Mn ratio is in a specific relationship, the alloy has excellent corrosion resistance (see Fig. 6). During the corrosion of Mg, Fe impurity may dissolve into the solution and get reduced to a simple substance by magnesium. Finally,

Fig. 10 Schematic illustrations of **a** Mg–Fe, **b** Mg–Mn–Fe alloy during the corrosion process

the Fe element re-deposits on the surface of magnesium and then promotes the occurrence of micro-galvanic corrosion [38]. Experimental evidence shows that the increase in the cathodic area is related to the re-deposition of dissolved iron species at the Mg surface. Therefore, with the decrease in Fe solubility, the adverse effects of the dissolved Fe will be significantly reduced. Mn itself cannot improve the corrosion resistance of magnesium, but it can effectively reduce the harmful effect of Fe impurity, probably by the following mechanism. On the one hand, Mn addition can not only reduce the solubility of Fe in the melt, but also form a higher density of Fe–Mn compound, which then settles to the bottom of the melt and purifies the melt. On the other hand, the Fe–Mn particles with a symbiotic structure can act as a barrier for the electrochemical potential difference between Mg and Fe, reducing the deleterious effect of Fe impurities on the alloy, as shown in Fig. 10b. In other words, this lower influence of micro-galvanic corrosion is attributed to an increased resistance between the α -Mg phase and Fe–Mn particles, thereby improving the corrosion resistance of Mg–Mn–Fe alloy.

5 Conclusion

In this study, the microstructure of Fe-rich particle and anti-corrosion behavior of magnesium scrap by Mn modification have been investigated. The results show that the corrosion resistance of magnesium scrap can be further controlled by the Mn addition. The Mn-containing Fe-rich particles with unique symbiotic structure can effectively reduce the toxic effects of Fe impurities, and the presence of more free Fe (Fe-rich particles) does not necessarily lead to severe corrosion of the alloy. The corrosion susceptibility of Mg–Mn–Fe alloy mainly depends on Fe solubility, which can be significantly reduced by suitable Mn addition. Only when Fe/Mn ratio is below 0.0083 (relative to the iron solubility) can the alloy have better corrosion resistance, with a corrosion rate of 0.38 ± 0.09 to 0.54 ± 0.15 mg/cm² day and an i_{corr} of 3 to 9×10^{-4} A/cm².

Acknowledgements This work was financially supported by the National Key Research and Development Program of China (No. 2016YFB0301100), the Fundamental Research Funds for the Central Universities (No. 2018CDJDCD0001) and the Key Nature Science Foundation of Chongqing (No cstc2017jcyjBX0040).

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