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Mechanistic understanding of the corrosion behavior of Mg4Zn0.2Sn alloys: from the perspective view of microstructure

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Abstract

The corrosion behavior of as-cast and extruded Mg4Zn0.2Sn (wt.%) alloys was comprehensively compared in 0.5 wt.% NaCl solution. Microstructure and surface chemistry related corrosion performance has been revealed. Zinc-supersaturated solid solution is formed around the intermetallics in the as-cast alloy, but zinc alternately segregates between the $\alpha$-Mg matrix in the extruded alloy. According to Scanning Kelvin Probe Force Microscopy and immersion tests, micro-galvanic corrosion between the precipitates (intermetallics or impurity particles) or Zinc-rich area and the matrix resulted in severe localized corrosion in both conditions. However, alternation of microstructure induced by extrusion significantly enhanced the corrosion resistance of Mg4Zn0.2Sn alloy.

**Keywords:** Magnesium alloy; tin; corrosion behavior; extrusion; micro-galvanic corrosion.
1. Introduction

Since the early 20th century, magnesium (Mg) alloys have been used in industrial applications as structural materials [1]. The lowest density, about a quarter that of steel and two-thirds that of aluminum, imparts great potential to the application of Mg alloys as light-weighting materials in the areas of aerospace, portable electronics and automotive. Reducing the weight of structural components can efficiently decrease the emission of CO$_2$ and improve the energy efficiency. However, the inadequate formability, ductility and corrosion resistance mainly limit the wide applications of Mg alloys [2, 3]. Up to now, many efforts have been made to improve those properties of Mg alloys, including thermo [4, 5] and mechanical [6, 7] processing or integrated thermo-mechanical processing [8], optimization of alloy composition [9-12], and use of alternative fabrication routes [13].

The magnesium-zinc (Mg-Zn) system has been paid more and more attention recently. Studies revealed that the corrosion resistance of Mg-Zn alloys can be enhanced with the increment of Zn content up to 5 wt.% due to the homogenous distribution of Zn, refined microstructure and the formation of more protective film on the surface [14-16]. However, much higher addition of Zn (> 5 wt.%) results in more and larger intermetallics, which decreases the corrosion resistance of the alloy due to the enhanced micro-galvanic corrosion, and also deteriorates the strength of the alloy because of the formation of more crack sources (intermetallics) [14]. Therefore, it is suggested that 4 wt.% should be the limit of the Zn content in Mg to balance the corrosion rate and mechanical properties of Mg-Zn alloys [17].

For potential commercial applications, the corrosion resistance of Mg-Zn binary alloy are still not high enough to effectively prevent the deterioration of the alloys during service. Tin (Sn), as one of the further alloying elements, owns high overpotential for hydrogen evolution and thus has the potential to tailor the hydrogen release of Mg alloys [18]. The addition of Sn has been proven to adjust the corrosion and mechanical properties of Mg-Sn binary alloys via
variation of Mg$_2$Sn phase content and the homogeneity of microstructure [19]. Furthermore, Jiang et al. [18, 20] reported that serious localized corrosion of Mg4Zn alloy was weakened by the addition of 1 wt.% or 1.5 wt.% Sn, whereas 2 wt.% Sn strongly deteriorated the corrosion properties of the alloy because of the high number of Mg$_2$Sn intermetallics as pitting corrosion initiators. However, currently, studies about the Mg-Zn-Sn system are still limited, especially on the corrosion properties. Therefore, in this study, only a minor amount (0.2 wt.%) of Sn is added to the Mg4Zn (wt.%) base alloy aiming to obtain better corrosion performance by preventing the excessive formation of Mg$_2$Sn phases.

Although the majority of current commercial Mg components are cast products, thermo-mechanical processed Mg alloys are attracting increasing attention from industry. For example, hot-extruded Mg alloys can be used in automotive interior, luggage, motorcycle and bicycle applications [21]. Due to the severe plastic deformation during hot extrusions, refinement of the microstructure, dynamic precipitation as well as the redistribution of alloying elements can be achieved. This can help to improve the corresponding corrosion resistance and mechanical properties of Mg alloys [1]. Therefore, hot extrusion is applied in this study aiming to improve the corrosion properties of Mg4Zn0.2Sn alloy.

In the present study, the corrosion behavior of as-cast and extruded Mg4Zn0.2Sn alloys is compared in 0.5 wt.% NaCl solution. The Volta potential difference between the second phases and the matrix as well as the corrosion morphologies after immersion tests were determined to understand the corrosion mechanisms of the alloy before and after extrusion.

2. Experimental

2.1 Material preparation

Nominal Mg4Zn0.2Sn (wt.%) alloy was prepared with pure Mg (99.9 %), Zn (99.995 %) and Sn (99.963 %) using an indirect chill casting procedure [22]. Billets with a diameter of 49 mm and a length of 150 mm were machined for indirect hot extrusion experiment of the alloy. The
temperature for the homogenization process before extrusion and for the extrusion process was
320 °C and 375 °C, respectively, chosen according to the phase diagram of Mg4Zn-Sn system
shown in Fig. 1. The homogenization process lasted for 24 h and was followed by quenching
with warm water. A round bar with a diameter of 10 mm was extruded at 2.2 mm/s (ram speed).
The chemical compositions of the as-cast and extruded Mg4Zn0.2Sn alloys were analyzed by
spark optical emission spectroscopy (Spectrolab M9) and atomic absorption spectrometer
(Agilent 240FS AA) (for the analysis of Sn), listed in Table 1.

2.2 Microstructure characterization

The specimens for microstructure analysis were firstly wet ground with silicon carbide papers
from 800 to 2500 grit, and then polished in a mixture of 1 µm diamond suspension and oxide
polishing suspension (OPS). For optical observation, the polished samples were etched using
a picric acid-based etchant (150 mL ethanol, 20 mL deionized water, 6.5 mL acetic acid and 4
- 5 g picric acid). Protective glasses and gloves are required when dealing with picric acid and
the chromium trioxide (CrO3) solution mentioned later. After immersion in the etchant for
about 10 s, the sample surface was rinsed with ethanol to stop the etching process and dried in
an oil-free air stream. The optical images were utilized to calculate the average grain size using
a linear intercept method by AnalySIS pro (version 5) software. The microstructures were also
evaluated by scanning electron microscopy (SEM) (TESCAN Vega 3 SB). To facilitate the
observation of second phases, the backscattering electron (BSE) mode was utilized and the
compositions of the different phases in the alloys were determined by energy dispersive X-ray
spectroscopy (EDS) (Eumex). The acceleration voltage was 20 kV.

2.3 Electrochemical measurements

The Volta potential differences between different constituents and the matrix were measured
by scanning kelvin probe force microscopy (SKPFM) (JPK NanoWizard). Shortly before the
SKPFM measurements, the samples were polished with 1 µm diamond suspension in OPS and
subsequently with single OPS. After ultrasonically cleaning in an ethanol bath, the specimens were dried in air and immediately transferred to the measurements. A chromium/platinum (Cr/Pt) coated silicon probe (Budget Sensors) with resonance frequency of 75 kHz and force constant of 3 N/m was utilized for the measurements. The Volta potential difference maps were obtained in a resolution of 512 × 512 pixels with a hover height of 100 nm. Potentiodynamic polarization curves were collected in 0.5 wt.% sodium chloride (NaCl) solution after the samples were conditioned at open circuit potential (OCP) for 30 min and 48 h, respectively. A conventional three-electrode cell was utilized, which consisted of a Pt mesh as auxiliary electrode, a silver/silver chloride (Ag/AgCl) electrode as reference electrode and the specimen as working electrode. Ground samples (until 1200 grit) with 0.5 cm² exposed area were used for the measurements and the data was recorded from -150 mV vs. OCP using a Gill AC potentiostat at a scan rate of 0.2 mV/s at room temperature (air-conditioned at 21 ± 1 °C). The obtained data was analyzed using ACM Analysis software (version 4) and only the cathodic branches were considered. At least three specimens were tested for statistic purpose (this also applies for the following hydrogen evolution and weight loss tests).

2.4 Corrosion behavior investigation

To understand the corrosion mechanism of as-cast and extruded Mg4Zn0.2Sn alloys, two immersion tests for different durations were carried out in 0.5 wt.% NaCl solution. The first test was performed on polished samples for 6 h (short immersion). After immersion, the corroded surfaces were cleaned with 180 g/L chromium trioxide aqueous solution (chromic acid) and rinsed with deionized water and ethanol. SEM examination was performed to determine the role of each constituent in the alloy during immersion. Only polished specimens were used to check the possible risk of removal of second phases due to the cleaning process in chromic acid. No removal of material was observed on those sample surfaces. The second test with extended immersion period was performed on ground specimens for 48 h to study the
surface and cross-sectional morphologies after corrosion. Elemental distribution in the cross sections of the corrosion product layers was determined by EDS element mapping. The mapping was performed at a resolution of 191 × 256 pixels and 80 ms for each pixel. The surface in the transverse direction (perpendicular to the extrusion direction) of extruded Mg4Zn0.2Sn alloy was used for both immersion tests and the aforementioned potentiodynamic polarization measurements.

Hydrogen evolution and weight loss tests were performed to determine the corrosion rates (CR) of as-cast and extruded Mg4Zn0.2Sn alloys in 0.5 wt.% NaCl solution. The evolved hydrogen was collected using an inverted funnel and burette. After 168 h, the corrosion products were removed with chromic acid solution and the weight changes of the samples were measured.

3. Results

3.1 Microstructure analysis

Fig. 2 displays the OM images showing the microstructures of as-cast and extruded Mg4Zn0.2Sn alloys. Apparently, the as-cast Mg4Zn0.2Sn alloy reveals a coarse dendritic microstructure while the extruded Mg4Zn0.2Sn alloy exhibits significantly refined globular grains. The average grain sizes are 232 ± 20 µm and 34 ± 1 µm for as-cast and extruded Mg4Zn0.2Sn alloys respectively, demonstrating that the extrusion process greatly refines the microstructure of the alloy.

According to Figs. 3a and 3b, divorced eutectic compounds in irregular and circular shapes are formed in the microstructure of as-cast Mg4Zn0.2Sn alloy. The morphologies of the eutectic phases are similar to those reported in as-cast Mg4Zn1Sn alloy [11]. Those micron-sized particles are distributed in the interdendritic regions. Moreover, the brighter contrast of the particle-free interdendritic regions indicates segregation of heavier elements at those places, which is consistent with enrichment of the remaining melt with Zn and Sn during solidification process. For extruded Mg4Zn0.2Sn alloy (Figs. 3c, 3d, 3e and 3f), those large particles
disappear after extrusion and sub-micron-scale precipitates are visible instead, which are mainly distributed at the grain boundaries. Similar microstructures of extruded Mg4Zn-Sn alloys were also revealed in reference [20]. However, a few larger particles (Fig. 3f) in polygonal shapes can also be revealed. Bright globular particles exist inside some of those polygonal particles. It is noticed that there are alternating bright and dark regions or bands in the microstructure of extruded Mg4Zn0.2Sn alloy, which are especially obvious in the transverse direction (Fig. 3e).

The phase compositions of as-cast and extruded Mg4Zn0.2Sn alloys were also determined by XRD (the XRD results are not shown here). However, only α-Mg phase was detected. The absence of possible Mg-Zn or Mg-Sn binary phases may be explained by the detection limitation of the instrument. Therefore, EDS was used to study the phase constituents in as-cast and extruded Mg4Zn0.2Sn alloys. As marked in Fig. 3b, letters A - C represent the second phases, brighter precipitate-free interdendritic regions and grey α-Mg dendrites in as-cast Mg4Zn0.2Sn alloy. In Figs. 3d and 3f, letters D - H refer to the darker matrix region, brighter matrix region, tiny particles, grey polygonal part (or single grey polygonal particles) and bright globular part of the larger particles in extruded alloy, respectively. At least ten sites were analyzed by EDS and the average compositions of the different phases are shown in Table 2 and Table 3. It is revealed that the compositions of the irregular and circular eutectic second phases in as-cast Mg4Zn0.2Zn alloy are similar. Those phases are rich in Mg and Zn with a very small amount of Sn, indicating that they are Mg-Zn binary phases. According to the atomic percentage composition, it seems that those second phases are Mg7Zn3. However, due to the contribution of the α-Mg in the eutectic phase (α-Mg + Mg-Zn phase) and the underlying α-Mg matrix, the real concentration of Mg in the second phase analyzed by EDS can be largely affected. Based on the EDS and XRD results reported by Cai et al. [14], those Mg-Zn binary phases should be MgZn phases, which are formed by the decomposition of Mg7Zn3 phases at
the eutectic temperature (325 °C). Similar results have also been reported in other studies. [15, 23, 24]. Herein, the Mg-Zn binary phases formed in the studied as-cast Mg4Zn0.2Sn alloy will be simply referred as Mg_xZn_y phases. As expected, a much higher content of Zn is detected in the brighter second phase-free interdendritic regions compared to the grey matrix dendrites. In the case of extruded Mg4Zn0.2Sn alloy, the difference of Zn content between the darker and brighter matrix regions is not so significant but the Zn content is still slightly higher in the brighter regions. For the tiny particles, considering such a small size, it is difficult to define the exact or even approximate composition by EDS. However, compared to Sn, the relatively higher amount of Zn may suggest that they are Mg-Zn phases (hereafter also referred as Mg_xZn_y phases) (more evidence is found in the element distribution of the cross sections after immersion tests). For the grey polygonal parts/particles, in comparison with Zn and Sn, much higher amount of Si was detected, which should be Mg_2Si phases. Because no ternary Mg-Sn-Si or Mg-Zn-Si can be formed [25-27]. Compared with the grey polygonal parts/particles, those bright globular parts inside the grey polygonal particles contain a similar amount of Zn, Sn and silicon (Si). However, the content of iron (Fe) and manganese (Mn) is evident, suggesting that they are Fe-Mn impurities. Furthermore, element mapping was recorded to confirm the element distribution in the microstructures of both Mg4Zn0.2Sn alloys, as shown in Fig. 4. This is especially important considering the different element compositions of the darker and brighter matrix regions of the extruded alloy. The EDS mapping results correlate well with the EDS analysis. As expected, those impurity elements (Si, Fe and Mn) enrich inside the second phases in the as-cast Mg4Zn0.2Sn alloy. For the extruded alloy, an obviously alternating distribution of Mg and Zn in the corresponding darker and brighter regions is observed, indicating that segregation of Zn still exists in the alloy after extrusion. Moreover, the existence of those Mg_2Si phases and Fe-Mn/Mg_2Si co-exited precipitates are also confirmed.

3.2 Corrosion performance
3.2.1 SKPFM measurement

To facilitate the understanding of the corrosion behavior of Mg4Zn0.2Sn alloy and the influence of different microstructure, the distribution of surface Volta potential difference over different constituents of the as-cast alloy was measured by SKPFM, as shown in Fig. 5. Obviously, according to Fig. 5b, the divorced Mg₅Zn₇ phases exhibit higher Volta potential compared with the surrounding matrix. The average Volta potential difference between the Mg₅Zn₇ phase and the matrix is 86 ± 26 mV. Interestingly, slightly higher Volta potential can be noted also for the matrix surrounding the second phases when compared with the matrix that is a bit further away from the second phases. Combining the SKPFM results with the microstructure of as-cast Mg4Zn0.2Sn alloy, the matrix around the Mg₅Zn₇ phase should be those Zn-rich interdendritic regions. Therefore, the Mg₅Zn₇ phases possess the highest nobility, followed by the Zn-rich interdendritic regions and the α-Mg dendrites (matrix) respectively. Accordingly, from kinetic interpretations, galvanic couples can be formed between Mg₅Zn₇ intermetallic as possible cathode with both intermetallic-free regions (Zn-rich interdendritic region and α-Mg matrix) as possible anode and between Zn-rich interdendritic area (cathode) and α-Mg matrix (anode) when the alloy is immersed in corrosive electrolyte.

The extremely fine second phases (sub-micron-scale) in extruded Mg4Zn0.2Sn alloy and the low content and small size (about 3 µm) of those impurity particles pose great difficulty to the successful SKPFM measurement of a desired position (place with impurity particle). Nevertheless, it has been widely accepted that a Fe-containing impurity particle plays a critical role in the corrosion performance of Mg alloys when exposed to corrosive environment [28]. Moreover, Fe-containing impurity particles possess much higher standard electrode potential than Mg and the high Volta potential difference between an Fe-containing impurity particle and α-Mg matrix has also been determined in pure Mg in refs. [29-31]. Thus, it can be speculated that galvanic coupling may be formed between the Fe-Mn/Mg₃Si co-existed particle
and the surrounded α-Mg matrix besides the Mg$_x$Zn$_y$ phases when the extruded Mg4Zn0.2Sn alloy is exposed to corrosive electrolyte. However, the presence of Mn can suppress the detrimental effect of Fe on the corrosion behavior of Mg alloys. Therefore, the relative galvanic activity of the couple between the Fe-Mn/Mg$_2$Si particle and the matrix and that between the tiny second phase and the matrix has to be considered.

3.2.2 Short-term immersion

The respective role of each phase in both as-cast and extruded Mg4Zn0.2Sn alloys is revealed during the corrosion process. Short immersion tests (6 h) in 0.5 wt.% NaCl solution were conducted on polished alloy surfaces and the corrosion products were removed with chromic acid, as displayed in Fig. 6. For as-cast Mg4Zn0.2Sn alloy (Figs. 6a and 6b), the α-Mg dendrites and the α-Mg inside the eutectic phase dissolve preferentially, while the Mg$_x$Zn$_y$ phases and the surrounding Zn-rich interdendritic regions seem to remain intact. This suggests that micro-galvanic corrosion occurs between the components of the eutectic phase and between the α-Mg dendrites and the interdendritic area (second phase + Zn-rich interdendritic region). It is worth mentioning that, due to the degradation, many small particles are visible along the boundaries between the α-Mg dendrites and the interdendritic regions. The EDS analysis (Table 4) demonstrated that those particles are considerably rich in Zn, which is even higher than the original Zn-rich interdendritic regions (shown in Table 2). In the case of extruded Mg4Zn0.2Sn alloy (Figs. 6c and 6d), the brighter Zn-rich matrix seems to be less corroded than the darker matrix. Moreover, a dark circle is formed around the Fe-Mn/Mg$_2$Si particle, revealing the occurrence of micro-galvanic corrosion between the impurity containing particle and the surrounding matrix. In comparison, much milder micro-galvanic corrosion can be noticed between the nearby Mg$_x$Zn$_y$ phases and the matrix (Fig. 6d), indicating the weaker galvanic effect. Some small holes are observed on the corroded surface (Fig. 6c),
which may be explained by the detachment of those impurity particles or tiny second phases as a result of undermining caused by the galvanic attack.

3.2.3 Surface and cross-sectional analysis after long-term immersion

Fig. 7 shows the surface and cross section morphologies of as-cast and extruded Mg4Zn0.2Sn alloys after exposure to 0.5 wt.% NaCl solution for 48 h. Apparently, localized corrosion occurs for both alloys but is more severe for the as-cast alloy. To be specific, for the as-cast alloy, the layer of corrosion products (Fig. 7a) formed on the surface is less compact. More and much deeper corrosion cavities can be observed in the cross-sectional morphology (Fig. 7b). Besides, some detached second phases (denoted by blue arrows in Fig. 7b) remain in the corrosion product layer. The partially protruded second phases in the corrosion product layer indicate that the surrounding Zn-rich interdendritic regions also dissolve to some extent. Moreover, small particles are noticed at the Zn-rich interdendritic region/corrosion product layer interface. The immersion test results of the as-cast Mg4Zn0.2Sn alloy agree well with the SKPFM and short immersion tests. The least noble α-Mg matrix dissolves first, followed by the Zn-rich interdendritic regions, while the more noble MgₙZnₙ phases serve as micro-cathodes during immersion. For the extruded Mg4Zn0.2Sn alloy, generally, shallow corrosion cavities appear at those dark matrix regions (denoted by yellow arrows in Fig. 7d), while the brighter matrixes (denoted by red arrows in Fig. 7d) remain as stilts. Small particles (denoted by blue arrows in Fig. 7d) are embedded in the corrosion product layer or aggregate at the interface of the bulk alloy and the corrosion products.

Element mappings (Fig. 8) were performed for the cross sections (the same positions shown in the inserted images in Figs. 7b and 7d) of both alloys to investigate the element distribution at the corroded interfaces. As expected, the corrosion product layers formed on the surfaces of both alloys are rich in oxygen (O). For the as-cast Mg4Zn0.2Sn alloy, it is revealed that the α-Mg matrix dissolves preferentially, while the second phases together with the Zn-rich
interdendritic regions serve as a kind of barrier for the interior α-Mg matrix. Moreover, those small particles located at the corroded interface are rich in Zn. They should be similar to the small particles (distributed along the boundaries of the α-Mg matrix and the interdendritic regions) observed after short immersion tests (Figs. 6a and 6b). For the extruded alloy, the small particles in the corrosion product layers or at the alloy/corrosion product interfaces are also rich in Zn, which may be the remaining tiny second phases after corrosion. In addition, enrichment of Zn is noticed at the interface of the bulk material and the corrosion products layer, while the distribution of Sn is quite homogeneous. No Mg$_2$Si phases or Fe-Mn/Mg$_2$Si particles were detected in the selected region for analysis probably because of the low content of them in the alloy (Fe, Si and Mn mapping results are not shown here).

3.2.4 Potentiodynamic polarization curves

To compare the corrosion resistance of as-cast and extruded Mg$_4$Zn$_{0.2}$Sn alloys, potentiodynamic polarization curves were recorded after conditioning at OCP for different time intervals (see Fig. 9). When the conditioning time is 30 min, the polarization curves are quite noisy for both alloys, which may be a result of the active surface evolution during immersion. The corrosion potential ($E_{corr}$) is slightly more positive after hot extrusion due to the higher cathodic current density. With extended conditioning time, both the cathodic and anodic current densities of the extruded alloy are lower than those of the as-cast alloy. Meanwhile, in all cases, the anodic current density increases rapidly with increasing potential and no retarded dissolution, e.g. by protective film formation, is observed in the anodic parts, which is typical for most of the Mg alloys [32-34]. This indicates that the corrosion product layers formed on both alloy surfaces are not protective enough to the anodic dissolution of the alloys.

According to the measured and calculated parameters listed in Table 5, as-cast Mg$_4$Zn$_{0.2}$Sn alloy possesses higher corrosion resistance than the extruded one when the OCP conditioning
time is 30 min. However, after 48 h, the extruded alloy shows a lower corrosion rate in 0.5 wt.% NaCl solution at room temperature.

3.2.5 Hydrogen evolution and weight loss

Hydrogen evolution and weight loss tests were also carried out to assess the integral corrosion rates of as-cast and extruded Mg4Zn0.2Sn alloys after exposure to 0.5 wt.% NaCl solution for up to 168 h at room temperature. According to the hydrogen evolution curves in Fig. 10a, generally, the as-cast Mg4Zn0.2Sn alloy evolves much more hydrogen than the extruded one during immersion. Moreover, the hydrogen evolution of the as-cast alloy follows an exponential growth, while it is a logarithmic growth (a slower increase at longer time) for the extruded alloy, indicating a much faster hydrogen evolution of as-cast alloy. As a result, the gap between the evolved volumes of hydrogen from the Mg4Zn0.2Sn alloy in the two different processing conditions becomes wider with extension of immersion time. The corrosion rates calculated according to the total volume of evolved hydrogen agree well with those determined by the weight loss, revealing that the long-term corrosion rate of Mg4Zn0.2Sn alloy is significantly reduced after hot extrusion.

4. Discussion

The solid solubility of Zn and Sn in Mg matrix is similar, dropping rapidly when the temperature is decreased from the eutectic temperature. For the Mg-Zn binary system, the solubility of Zn decreases from 6.2 wt.% at 325 °C to 1.6 wt.% at 25 °C [23, 35]. While in the Mg-Sn binary system, the equilibrium solid solubility of Sn declines substantially from 14.85 wt.% at 561 °C to only 0.17 wt.% at room temperature [36, 37] Supersaturation of solute atoms in α-Mg can still occur during casting due to the non-equilibrium solidification process [11]. For the Mg-Zn-Sn ternary system, no ternary phases have been reported or confirmed neither by experimental nor by thermodynamic calculation [38-40]. However, a small amount of Zn can dissolve in the Mg2Sn binary phase [11, 41] and Sn can dissolve in the MgZn2 phase [41,
but not in Mg4Zn7 or MgZn precipitates according to the work of Sirkin et al. [43] and Mingolo et al. [38]. Therefore, the microstructure of the as-cast Mg4Zn0.2Sn alloy is composed of α-Mg, Zn-supersaturated region and divorced eutectic phase (α-Mg matrix + MgxZny phase) (Figs. 3a and 3b). After homogenization treatment and hot extrusion, most of the MgxZny phases in the as-cast alloy are dissolved into the matrix as verified by the significantly decreased volume fraction of second phases (Fig. 3a), leading to the exposure of some Fe-Mn/Mg2Si particles in the matrix. A small amount of tiny Mg-Zn binary phases dynamically precipitate on the grain boundaries and those Fe-Mn/Mg2Si and single Mg2Si particles are redistributed in the microstructure (Figs. 3c-3f). This is associated with the homogenization treatment which was applied prior to extrusion. Furthermore, it occurs concurrently due to the microstructure changes during the forming process, which includes the reformation of the microstructure due to dynamic recrystallization and also dynamic precipitation [1]. Thus, the coarse dendritic grains in the as-cast billets are substituted by fine recrystallized globular grains in the extruded alloy. Apart from the refinement of microstructure, redistribution of alloying elements is also concomitant with the extrusion process. Moreover, element segregation still exists, but only little attention has been paid in other reports regarding to the influence of distribution of segregated solute atoms on the corrosion behavior of wrought Mg alloys.

The corrosion process of Mg4Zn0.2Sn alloys in 0.5 wt.% NaCl solution is schematically illustrated in Fig. 11. In dry air, magnesium oxide (MgO) is instantaneously formed on Mg alloy surface at room temperature, which imparts good corrosion resistance to Mg alloys in such circumstance. In the presence of water, MgO reacts with it, generating magnesium hydroxide (Mg(OH)2). However, both MgO and Mg(OH)2 are water-soluble, resulting in the exposure of the underlying substrate to the solution [2, 44, 45]. Additionally, In the presence of Cl-, local breakdown of the corrosion products layer can also occur, resulting in the exposure of the underneath substrate to the corrosive electrolyte and triggering localized corrosion. This
may be achieved by the formation of metal-hydroxyl-chloride complex compounds [46]. The highly negative electrode potential of Mg and the poor protection ability of the oxide/hydroxide surface film render Mg intrinsically prone to corrosion in aqueous environment. Moreover, when the nobler second phases, impurities and some other compounds, for example, noble inclusions, which can be locally polarized, are exposed due to the defective surface film, localized corrosion can be triggered [45]. As disclosed by the SKPFM study for as-cast Mg4Zn0.2Sn alloy (Fig. 5), the Mg2Zn1 phases show higher Volta potential compared to the nearby α-Mg matrix, which can form micro-galvanic couples with the matrix. Although the Volta potential map of the extruded alloy is lacked in this study, the short immersion tests (Figs. 6c and 6d) and literature review [47, 48] demonstrate that the Fe-Mn/Mg2Si and single Mg2Si particles are nobler than α-Mg matrix and may induce micro-galvanic corrosion. Therefore, localized corrosion was detected for both processing conditions according to the surface and cross-section morphologies after immersion (Figs. 6 and 7). The different relative Volta potential of each constituent influences the dissolution precedence during immersion, which is clearly revealed by observation of the cross section of the as-cast Mg4Zn0.2Sn alloy (Fig. 7b). Furthermore, the cross-section morphology of the extruded Mg4Zn0.2Sn alloy (Fig. 7d) reveals that galvanic effect also exists between the Zn segregated matrix and the normal α-Mg matrix owing to the heterogeneous distribution of elements. After extrusion, fine second phases dynamically precipitate and either second phases or impurity particles are uniformly distributed in the alloy. Considering the low amount and the detachment of impurity particles after certain immersion time, the intensity of micro-galvanic coupling is reduced in the extruded Mg4Zn0.2Sn alloy compared to the as-cast one. More importantly, the presence of Mn favors the formation of Fe-Mn solid solution (Mn encapsulates Fe) instead of pure Fe particles as revealed in this study. Since the galvanic activity between Mn and Mg is less than that between Fe and Mg, the Fe-Mn particles would exhibit significantly lower electrocatalytic activity.
towards hydrogen reduction reaction compared with pure Fe impurities [49-52]. Accordingly, the re-deposition process observed in the case of pure Fe impurities [53] can also be affected due to the altered self-corrosion behavior of Fe-Mn particles after detachment. The surrounding less active Mg$_2$Si phases may also contribute to that to some extent. Consequently, the corrosion rate of the alloy greatly decreases in spite of the micro-galvanic effect between the impurity particles and the α-Mg matrix. Besides, the refined grain size of Mg alloys after extrusion has also been reported to enhance the corrosion resistance of Mg alloys, which is thought to be a result of the formation of more coherent surface layer on the refined microstructure [1, 54-56].

As revealed by the cross-section element mapping results (Fig. 8), Zn enriches at the surface film/substrate interface for both alloys, especially for the extruded one. Similar enrichment of alloying elements at the film/Mg alloy interfaces have been reported for Electron 717 alloy (Unocic et al.) [57, 58], AZ31 alloy (Cristóbal et al.) [59] and Mg5Sn3Zn alloy (Yang et al.) [60]. Moreover, according to the investigations carried out in refs. [58, 59, 61], it is speculated that the uniform enrichment of Zn at the entire film/alloy interface is related to the enhanced corrosion resistance of Mg alloys possibly by suppressing the outward migration of Mg. According to these literature, the segregation of Zn at the interface of Mg matrix and corrosion products is mainly attributed to two reasons. On the one hand, as corrosion proceeds in a relatively aggressive electrolyte, the active Mg atoms are selectively dissolved, leaving behind the inert Zn atoms [60]. Sn segregation can also occur for Mg5Sn3Zn alloy. However, given the much lower content of Sn in Mg4Zn0.2Sn alloy studied herein, only Zn segregation was detected at the surface film/substrate interface. On the other hand, in comparison with MgO, the lower thermodynamic stability of ZnO favors the enrichment of unreacted Zn at the corroding interface as corrosion proceeds [58]. Unocic et al. and Cristóbal et al. considered that the enriched Zn existed in metallic form based on EDS line profile (the peaks of O and Zn did
not correlate with each other) and XPS analysis. While Yang et al. identified the XPS region spectra of Zn 2p\textsubscript{3/2} to be the mixture of ZnO and metallic Zn, which might be ambiguous because of the strong overlap between the binding energy of Zn\textsuperscript{2+} and Zn\textsuperscript{0}. This was also mentioned by Cristóbal et al. and they determined the chemical state of Zn more effectively by measuring both FWHM value and the splitting value (2p\textsubscript{1/2}-2p\textsubscript{3/2}). The concentrated Zn behaves differently at the interfaces of the two alloys, i.e., existing as dispersed Zn-rich particles in the as-cast Mg\textsubscript{4}Zn\textsubscript{0.2}Sn alloy (Figs. 6a and 6b) while continuously distributed along the film/substrate interface in the extruded alloy (Fig. 8). This may be a result of the almost perfect solid solution state of the alloy reached after homogenization and extrusion. Therefore, it can be concluded that the extrusion process refines the microstructure (grain size and second phases) of Mg\textsubscript{4}Zn\textsubscript{0.2}Sn alloy, leads to more homogenous distribution of alloying elements (Zn and Sn) and impurities (Fe, Mn and Si), thereby resulting in a weakened micro-galvanic effect and an enhanced Zn segregation at the corrosion interface. Finally, this contribute to slightly denser corrosion products layer during immersion and weaker localized corrosion. The nobler second phases are the main driving force for the severe localized corrosion in the as-cast alloy, while mainly the Fe-Mn/Mg\textsubscript{2}Si particles are the cause for the extruded alloy.

5. Conclusion

In this study, the corrosion behavior of as-cast and extruded Mg\textsubscript{4}Zn\textsubscript{0.2}Sn alloys in 0.5 \textit{wt.}\% NaCl solution was compared. After extrusion, the microstructure of the as-cast alloy is greatly refined. The micron-sized eutectic phases (α-Mg + Mg\textsubscript{x}Zn\textsubscript{y} phase) are replaced by tiny Mg-Zn precipitates and a few Fe-Mn/Mg\textsubscript{2}Si impurity particles. Interestingly, even after homogenization and extrusion, Zn segregated regions which are alternately distributed between α-Mg matrix still exists in the extruded alloy. Micro-galvanic couples are formed as expected from the Volta potential differences of those second phases, precipitates, Zn-rich areas and the
α-Mg matrix, resulting in localized corrosion behavior of both alloys. The localized corrosion is more severe for the as-cast alloy because of the large volume fraction of eutectic phases (α-Mg matrix + Mg$_x$Zn$_y$ phase). However, hot extrusion significantly refines the microstructure of the alloy and homogenizes the distributions of alloying elements (Zn and Sn), which largely weakened the localized corrosion of extruded Mg$_4$Zn$_{0.2}$Sn alloy.

**Declaration of interests**

The authors declare that there is no conflict of interests.

**Data availability**

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

**Acknowledgement**

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Reference


https://doi.org/10.1002/adem.200310405.


Figure Captions

Fig. 1. Phase diagram of Mg4Zn-Sn system calculated by Pandat.

Fig. 2. Microstructures of (a) as-cast and (b) extruded Mg4Zn0.2Sn alloys determined by optical microscope (ED: extrusion direction).

Fig. 3. Microstructures of (a, d) as-cast Mg4Zn0.2Sn alloy and (b, c, e, f) extruded Mg4Zn0.2Sn alloy along (b, e) extrusion direction and (c, f) transverse direction taken by SEM in BSE mode (ED: extrusion direction).

Fig. 4. Element distribution for the microstructure of as-cast and extruded (in transverse direction) Mg4Zn0.2Sn alloys determined by EDS mapping.

Fig. 5. (a) Topography, (b) surface Volta potential map and (c) a line-profile analysis of a second phase for as-cast Mg4Zn0.2Sn alloy studied by SKPFM.

Fig. 6. Surface morphologies of (a) as-cast and (b) extruded Mg4Zn0.2Sn alloys after immersion in 0.5 wt.% NaCl solution for 6 h at room temperature with removal of corrosion products. (c) and (d) are the enlarged details of the marked regions in (a) and (b) respectively.

Fig. 7. Surface and cross-sectional morphologies of (a, c) as-cast and (b, d) extruded Mg4Zn0.2Sn alloys after immersion in 0.5 wt.% NaCl solution at room temperature for 48 h (ED: extrusion direction).

Fig. 8. Element mappings for the cross sections of as-cast and extruded Mg4Zn0.2Sn alloys after immersed in 0.5 wt.% NaCl solution at room temperature for 48 h (ED: extrusion direction).

Fig. 9. Potentiodynamic polarization curves of as-cast and extruded Mg4Zn0.2Sn alloys after conditioned at OCP for different time at room temperature.

Fig. 10. (a) Hydrogen evolution curves and (b) corrosion rates calculated by evolved hydrogen volume and weight loss of as-cast and extruded Mg4Zn0.2Sn alloys after immersion in 0.5 wt.% NaCl solution for 168 h at room temperature.

Fig. 11. Schematic illustration for the corrosion process of as-cast and extruded Mg4Zn0.2Sn alloys in 0.5 wt.% NaCl solution.
Figure 1

Figure 2

(a) Grain size: 232 ± 20 μm  (b) Grain size: 34 ± 1 μm
Figure 3

![Figure 3 Image](image)

Figure 4

![Figure 4 Image](image)
Figure 5

Topography

Volta potential

Line-profile analysis

- Matrix
- Mg$_2$Zn$_4$ phase

position/ µm

Volta potential / mV
Figure 6

As-cast alloy

Extruded alloy
(transverse direction)

Low magnification
(BSE image)

(a)  

(b)  

High magnification
(BSE image)

20 µm

20 µm

5 µm

Holes

rich in Zn

Fe-Mn/Mg$_2$Si particle

Mg$_x$Zn$_y$

(c)  

(d)
Figure 8

As-cast Mg4Zn0.2Sn

Extruded Mg4Zn0.2Sn

Figure 9

Current density / mA cm²

Potential / mV (vs. Ag/AgCl)
1 Tables

2 Table 1. Chemical compositions of as-cast and extruded Mg4Zn0.2Sn alloys.

<table>
<thead>
<tr>
<th></th>
<th>Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>As-cast</td>
<td>0.22</td>
</tr>
<tr>
<td>Extruded</td>
<td>0.17</td>
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</tbody>
</table>

3 Table 2. Chemical compositions for different constituents in the microstructure of as-cast Mg4Zn0.2Sn alloy analyzed by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>As-cast Mg4Zn0.2Sn alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A-Second phase</td>
</tr>
<tr>
<td></td>
<td>at.%</td>
</tr>
<tr>
<td>Mg</td>
<td>77.9 ± 1.1</td>
</tr>
<tr>
<td>Zn</td>
<td>22.0 ± 1.1</td>
</tr>
<tr>
<td>Sn</td>
<td>0.1 ± 0.0</td>
</tr>
</tbody>
</table>

4 Table 3. Chemical compositions for different constituents in the microstructure of extruded Mg4Zn0.2Sn alloy analyzed by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Extruded Mg4Zn0.2Sn alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matrix</td>
</tr>
<tr>
<td></td>
<td>D-Darker region</td>
</tr>
<tr>
<td></td>
<td>at.%</td>
</tr>
<tr>
<td>Mg</td>
<td>98.8 ± 0.3</td>
</tr>
<tr>
<td>Zn</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td>Sn</td>
<td>0.1 ± 0.0</td>
</tr>
<tr>
<td>Si</td>
<td>11.9 ± 2.5</td>
</tr>
<tr>
<td>Mn</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>4.0 ± 0.2</td>
</tr>
</tbody>
</table>
Table 4. EDS analysis of the constituents in as-cast Mg4Zn0.2Sn alloy after immersion in 0.5 wt.% NaCl solution for 6 h followed by the removal of corrosion products.

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix at.%</th>
<th>Matrix wt.%</th>
<th>Second phase at.%</th>
<th>Second phase wt.%</th>
<th>Small particles at.%</th>
<th>Small particles wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>1.6</td>
<td>1.0</td>
<td>5.4</td>
<td>2.4</td>
<td>10.5</td>
<td>6.6</td>
</tr>
<tr>
<td>Mg</td>
<td>97.4</td>
<td>96.4</td>
<td>63.7</td>
<td>42.3</td>
<td>83.7</td>
<td>79.2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>0.6</td>
<td>0.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Zn</td>
<td>0.9</td>
<td>2.3</td>
<td>30.4</td>
<td>54.3</td>
<td>4.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0</td>
<td>0.2</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 5. Measured and calculated parameters from potentiodynamic polarization curves recorded in 0.5 wt.% NaCl solution at room temperature.

<table>
<thead>
<tr>
<th>OCP conditioning time</th>
<th>Alloy</th>
<th>$CR$ / mm year$^{-1}$</th>
<th>$i_{corr}$ / mA cm$^{-2}$</th>
<th>$E_{corr}$ / mV vs. Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>As-cast Mg4Zn0.2Sn</td>
<td>0.90 ± 0.10</td>
<td>0.039 ± 0.004</td>
<td>-1556 ± 6</td>
</tr>
<tr>
<td></td>
<td>Extruded Mg4Zn0.2Sn</td>
<td>2.30 ± 0.26</td>
<td>0.101 ± 0.010</td>
<td>-1536 ± 4</td>
</tr>
<tr>
<td>48 h</td>
<td>As-cast Mg4Zn0.2Sn</td>
<td>1.64 ± 0.24</td>
<td>0.072 ± 0.010</td>
<td>-1496 ± 12</td>
</tr>
<tr>
<td></td>
<td>Extruded Mg4Zn0.2Sn</td>
<td>0.76 ± 0.06</td>
<td>0.040 ± 0.002</td>
<td>-1443 ± 25</td>
</tr>
</tbody>
</table>