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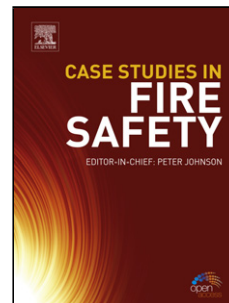
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Corrosion and Passivation of Magnesium Alloys

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Abstract

This paper reviews and discusses the possibility of the production of a passive magnesium (Mg) alloy through metallurgical approaches, such as purification, alloying, heat-treatment, mechanical processing and non-equilibrium sputter deposition. High-purity Mg and all existing Mg alloys produced by traditional methods are found to be active in a chloride containing solution. Passivity in a Mg alloy might be produced through a non-equilibrium technique with a sufficiently-high concentration of a strong passivating element supersaturated in the matrix phase. This paper clarifies important concepts regarding the passivity of Mg alloys, and suggests possible approaches to develop a passive, corrosion-resistant Mg alloy.

Keywords: A. Magnesium, A. Sputtered films, C. Passivity.

1. Introduction

Mg alloys are of industrial interest as structural metals due to their low density and high strength to weight ratio. However, their poor corrosion resistance limits their applications [1-11]. In the last two decades, the corrosion of Mg alloys has been intensively investigated with the aim to produce Mg alloys with improved corrosion resistance. The research has covered the fundamentals of Mg corrosion [3, 4, 12-18], alloying effects [15, 19-23], surface treatments, and coating technology [24-37]. These research efforts have produced many options for the improvement of the corrosion resistance of Mg alloys. However, none of the studied Mg alloys has adequate corrosion resistance in NaCl containing solutions, and no practical alloy has been produced with a corrosion rate in 3 wt.% NaCl lower than that of high-purity Mg.

The application of Mg alloys is still limited to the components which are used in mild service environments, such as pedal brackets, instrument panel frames and integral seat frames [38]. If a Mg alloy is to be used in a service application where the alloy is in contact with water and chloride solutions (e.g. AM50 and AM60 die castings used in the car body), the Mg alloy needs a coating system, although the cost of the magnesium component can be increased by up to 25% [5].

Inspired by the high corrosion resistance of stainless steels in corrosive environments, and the suggestion of Song and Atrens [3], researchers have explored the development of a Mg alloy [15, 22, 39, 40] much more resistant than all current Mg alloys. Song and Atrens [3] indicated that a “stainless” Mg alloy much more corrosion resistant than any current Mg alloy could be developed if an alloying element could produce a passive film on Mg.

Mg is an active metal. The oxide, MgO, on the surface has a Pilling-Bedworth ratio < 1 resulting in an incomplete coverage of the surface oxide or a porous film [41]. Some alloying elements may form oxide films with Pilling-Bedworth ratio > 1 , but the oxides often have too high solubility in aqueous solutions to form a stable and protective surface film on Mg, or the alloying elements cannot be easily dissolved in

Mg to form a solid solution with Mg. Therefore, no successful corrosion resistant Mg alloy has been reported so far. Nevertheless, a more corrosion resistant Mg alloy remains a research goal.

This paper discusses the possibility of forming a passive, corrosion-resistant Mg alloy through metallurgical techniques, based on a review of recent research. This paper also clarifies some important concepts associated with the possibility of passivity of Mg alloys, and proposes some possible approaches to the production of Mg alloys that are much more corrosion resistant.

2. High-purity magnesium

The corrosion behaviour of high-purity Mg has been widely studied, and the corrosion rate of high-purity Mg is considered as a benchmark against which to compare the corrosion rates of other Mg alloys [15, 22, 42-46].

High-purity Mg is single phase. The impurity concentrations are below the impurity tolerance limits [14]. The corrosion rate in 3.5 wt.% NaCl solution saturated with Mg(OH)₂ was measured to be $\sim 0.38 \text{ mm y}^{-1}$ [44]. The corrosion took the form of shallow pits, which gradually linked up. There was filiform corrosion in some specimens. Some high-purity Mg specimens also suffered some localized corrosion, exhibiting somewhat deep pits in some areas, and had a somewhat higher corrosion rate $\sim 1.0 \text{ mm y}^{-1}$. For example, Zainal Abidin *et al.* [47] found some localized corrosion for high-purity Mg in buffered Hanks' solution; two specimens exhibited only general corrosion, while the third specimen suffered some localized corrosion. Cao *et al.* [42] found somewhat similar behaviour in the study of the corrosion of ultra-high-purity Mg in 3.5 wt.% NaCl solution saturated with Mg(OH)₂. The average corrosion rate was $\sim 0.25 \text{ mm y}^{-1}$, slightly lower than that of high-purity Mg. Most of the ultra-high-purity Mg specimens suffered uniform corrosion as shown in Fig. 1(a), but some suffered some localized corrosion as shown in Fig. 1(b).

Williams *et al.* [48] used an in-situ scanning vibrating electrode technique to investigate the corrosion of pure Mg (99.9+ wt.%) samples in aqueous sodium

chloride solutions. The localized corrosion featured by a strongly cathodically active centre surrounded by a 0.5 mm anodic ring.

These studies indicate that both localized corrosion and uniform corrosion can occur on high-purity Mg. The corrosion rate associated with localized corrosion has been somewhat higher than the corrosion rate measured for uniform corrosion. The cause of the localised corrosion is attributed to chance contamination increasing the corrosion rate by micro-galvanic corrosion. The uniform corrosion is considered to be the intrinsic corrosion, and the corresponding corrosion rate is considered to be the intrinsic corrosion rate.

The higher corrosion rates for some high-purity Mg samples could also be because (i) different crystal planes have somewhat different corrosion rates [49-51], (ii) localised corrosion usually initiates from a non-closely packed crystal plane [52], and (iii) casting pores can activate the Mg surface during immersion, leading to localized corrosion [53].

Localized corrosion also occurs frequently for Mg alloys [15, 22, 54-58]. Cao *et al.* [15] and Shi *et al.* [22], for Mg alloys immersed in 3.5 wt.% NaCl solution saturated with Mg(OH)₂ at their open circuit potentials, observed localized corrosion on binary Mg alloys attributed to the presence of second phase particles. Recently, localized corrosion and micro-galvanic corrosion of Mg alloys has been studied using new approaches, such as scanning vibrating electrode technique (SVET), scanning ion-selective electrode technique (SIET) and scanning vibrating probe method (SVP) [54-58]. For example, Gnedkov *et al.* [54] found that micro-galvanic corrosion was crucial for the corrosion of MA8 (Mg-Mn-Ce) and VMD10 (Mg-Zn-Zr-Y) based on SVP measurements. Williams *et al.* [56] used SVET to investigate localized corrosion of AZ31, and found that cathodic activation was associated with an enrichment in noble Al-Mn particles.

High-purity Mg does not exhibit passivity. Fig. 2 [59] presents typical polarisation curves for pure Mg in NaCl and Na₂SO₄ solutions. There was no passivity in any of these curves. This is consistent with the finding from another study that high-purity Mg is active in all experimental conditions except in chromic acid solution [15, 42,

60].

Stainless steel corrosion may change from active to passive on anodic polarization. To find out if Mg can become passive, Song *et al.* [16] anodically polarized pure Mg to the hydrogen equilibrium potential, and found that Mg dissolution rate steadily increased with potential. This experiment confirmed that Mg does not become passive on anodic polarization.

Nevertheless, there is typically a film on the surface of a Mg alloy immersed in an aqueous solution. The surface film on pure Mg consists of a MgO inner layer and a porous Mg(OH)₂ outer layer [16, 60-63]. This surface film is not as protective as the passive films on stainless steels, but much thicker.

The corrosion rate of commercial-purity Mg can be decreased by reducing the impurity concentration [3, 64]. However, the research by Cao *et al.* [42] indicated that for Mg with purity 99.85 wt.% further reducing the impurity level did not lead to a significantly decreased corrosion rate. To further decrease the Mg corrosion rate, or to make Mg passive, an alloying approach needs to be considered.

3. The possibility of passivity

From a thermodynamic viewpoint [65], it is possible to decrease the Mg corrosion rate through alloying with inert noble elements. Due to the high chemical activity of Mg, the addition of noble alloying elements would need to be in large amounts. Unfortunately, the solubility of noble elements in Mg is low. Furthermore, the noble elements are much heavier than Mg, so that only a small amount could be added and still retain the low-density advantage of Mg. Therefore, it is not feasible to develop a low-density Mg alloy [66] through alloying with noble elements.

However, a corrosion resistant material does not need to contain thermodynamically stable phases. A kinetically passivated metal can also have a low corrosion rate. Stainless steels have corrosion rates orders of magnitude lower than steels [67-75]. Iron (Fe) can become stainless steel when Fe is alloyed with more than 10.5 wt.% Cr [76]. Thus, there may be a possibility to obtain a corrosion resistant Mg alloy through

alloying with passivating elements, such as Cr, Ti, Al, Ni, Zr, etc. [40, 77]. Alloying can modify the matrix phase composition, and change the amounts and distribution of the second and other phases in an alloy. In Mg alloys, the matrix phase is the most critical constituent that is most susceptible to corrosion attack. If the corrosion resistance of the matrix phase could be significantly improved, or if the matrix phase could be made passive by alloying with an element, then a corrosion resistant Mg alloy would be achievable.

Metal passivity refers to kinetic stability. A passive surface is in a steady state when the formation and dissolution of the passive film are equal. The passive film must be able to be repaired while the metal is in a corrosive environment.

Some Mg alloys may form a protective surface film in a special environment or solution. For example, a Mg alloy after anodization in a bicarbonate solution can survive more than 500 hours in the ASTM B117 salt spray [78]. It is not surprising that a specially treated (including chemically and mechanically treated) surface has a low corrosion rate. However, the surface film initially formed under certain conditions is usually unsustainable in corrosive solutions, and hence it is not a passive film. A Mg alloy with such a surface film may initially have a low corrosion rate, but once the original surface film is dissolved, changed or damaged during service, if the film cannot be repaired, the Mg alloy corrodes rapidly [23].

A highly corrosion resistant Mg alloy which can become passive in the service environment must have sustainable passivity. This would be achieved if the surface film is protective, and more importantly can self-repair after being damaged in the service environment. This is an important concept that should be borne in mind in developing corrosion resistant Mg alloys.

4. Influence of alloying elements

4.1 Measurements of corrosion rates

Alloying is one of the important methods of improving the corrosion resistance of Mg, as it could be possible in theory to produce a passive Mg alloy through forming a

stable, sustainable, repairable, protective passive film mainly consisting of the alloying element oxides rather than a Mg based film on the Mg alloy surface [3, 42].

On the other hand, a small amount of an alloying element might modify the microstructure [79], leading to formation of a Mg based solid solution and even some new intermetallic phases that can act as cathodic sites. It may also reduce the impurity tolerance limits in Mg. The side effects of alloying on corrosion should also be considered in exploring the passivity of alloyed Mg.

There has been a lot of research focused on the influence of alloying elements on Mg corrosion [1, 3, 13, 38, 41, 80-83]. The findings from these studies can be summarized as follows.

(1) Some alloying elements can mitigate the detrimental effect of impurities on Mg corrosion. For example, Zr can remove Fe and purify Mg alloys by precipitation of Fe_2Zr or FeZr_2 from the alloy melt [84, 85]. Mn, Al and Si can also decrease the Fe content and decrease the corrosion rates of Mg alloys, but not as effectively as Zr [14, 86].

(2) Some alloying elements can significantly alter the surface film of a Mg alloy, and thus affect the corrosion behavior. For example, two Al^{3+} ions can replace three Mg^{2+} ions in tetrahedral $\text{Mg}(\text{OH})_2$ lattice in the surface film on Mg-Al alloys [87]. Velikokhatnyi *et al.* [88], based on first principle calculations, indicated that alloying with Ca, Y and Al would form a more stable chemically-less-reactive hydroxide film due to the stronger cohesive energy. Furthermore, the addition of RE and Y improved the corrosion resistance of Mg alloys and their mechanical properties at temperatures up to 250°C [24, 85, 89-93]. Takenaka *et al.* [83] found that the surface oxide film consisted of both Mg and RE (La, Nd or Ce) and provided good corrosion resistance to Mg. Liu *et al.* [94] found that Mg-Y alloys had a good protective film in a dilute sulphate solution. Rosalbino and co-workers [81, 82] reported that decreased corrosion rates were produced by the incorporation of Er in the $\text{Mg}(\text{OH})_2$ lattice. Furthermore, the influence of Zr on corrosion behavior of rare-earth containing Mg alloys has also attracted attention. The addition of Zr produces Zr-rich regions in grain

centers, resulting in a corrosion resistance for these regions higher than the remainder of the grains [21, 91, 95-97]. This could be attributed to the fine distribution of Zr particles, which could produce a more robust oxide film on the Mg alloy surface [91]. However, Neil *et al.* [98] found that Zr-rich regions in the ZE41 grain centers suffered serious corrosion attack because of the relatively large sizes of the Zr-rich particles in the grains.

(3) Some alloying elements can modify the exchange current density of the cathodic or anodic reaction on Mg alloys, which could either increase (e.g. Cu) or decrease (e.g. Al, Lu and As) the corrosion rate [41, 99, 100]. For example, Hagihara *et al.* [99] found that the addition of Al in single crystal Mg decreased the anodic current density while the addition of Cu increased the cathodic current density. Hence, the single crystal Mg-Al alloy had a lower corrosion rate, while the single crystal Mg-Cu had a higher corrosion rate than that of single crystal Mg [99]. Samaniego *et al.* [41] reported that the addition of lutetium to AZ31 reduced cathodic kinetics in the initial stages of corrosion for as-cast specimens. Birbilis *et al.* [100] reported that the poisonous element As retarded the cathodic hydrogen reaction on Mg and thus reduced the corrosion rate of Mg.

(4) When the alloying element exceeds its solubility in Mg, a second phase containing this element may precipitate from the Mg matrix. The second phase typically accelerates the corrosion rate due to the micro-galvanic effect between the second phase and the Mg matrix. Neil *et al.* [98] found that the matrix of ZE41 suffered galvanic corrosion because of the T-phase ($\text{Mg}_7\text{Zn}_3\text{Re}$) when the specimen was immersed in 0.001M NaCl solution at the open circuit potential for 18 hours (see Fig. 3). Coy *et al.* [101] also reported that the matrix of ZE41 suffered micro-galvanic corrosion because of the cathodic phases, Zr_4Zn rich phase and T-phase. However, when the second phase is in the form of continuous network, it can decrease the corrosion rate of Mg alloy due to its barrier effect [38]. This barrier effect has also been confirmed by Zhao *et al.* [45], although some Ca-Zn phases in their study may not be inert [102].

(5) Some alloying elements can alter the characteristics of an existing phase, forming a different second phase, which is less detrimental to the Mg corrosion behavior. Lunder *et al.* [80] found that AE42 after addition of Mn showed a lower micro-galvanic corrosion rate, which was attributed to the fact that the $\text{Al}_{11}\text{Mn}_3$ phase formed by Mn addition was a passive cathode over a wide pH range.

Recent studies [2, 14, 15, 22] have indicated that the corrosion rates of most Mg alloys containing alloying elements were higher than that of high-purity Mg (see Fig. 4), although the addition of some alloying elements did decrease the corrosion rates of their low-purity parent metals. Fig. 4 shows that the vast bulk of Mg alloys have corrosion rates higher than that of high-purity (99.85 wt.%) Mg (0.38 ± 0.24 mm/y). It should be noted that in this figure, the corrosion rate for Mg alloys evaluated from hydrogen evolution measurements are to some extent underestimated, especially at low corrosion rates, as some hydrogen resulting from Mg corrosion is absorbed into Mg specimen or dissolved in the solution and is not be collected during hydrogen measurement [15, 42]. The loss in hydrogen volume is relatively small for high corrosion rates. However, the loss of hydrogen can become important for low corrosion rates. Fig. 4 shows that most of the Mg alloys have corrosion rates higher than that of high-purity Mg in the $\text{Mg}(\text{OH})_2$ saturated 3.5 wt.% NaCl solution. Furthermore, the addition of As does not decrease the corrosion rate much below that of high-purity Mg, either.

4.2 Understanding corrosion rates

These following considerations help to explain these corrosion rates of Mg alloys. The considerations suggest that a Mg alloy, that is more corrosion resistant than high-purity Mg, should have (a) low impurity levels, (b) a passive matrix, and (c) inert secondary phase and other precipitates if these phases cannot be avoided.

(1) Many studies [23, 103-111] investigated the influence of alloying elements on the corrosion performance of impure Mg alloys (which contained relatively high levels of impurities). The impure Mg or low-purity Mg alloy actually had a much

higher corrosion rate than that of high-purity Mg. Therefore, even when alloying improved the corrosion resistance, the improved corrosion rate after alloying was nevertheless still higher than that of high-purity Mg.

(2) Many alloying elements do not have a strong passivating ability under the conditions studied, and the surface films formed on the Mg alloys have not been protective. For example, Cao *et al.* [15] did not find passivity with the following alloying elements: Zr, Sr, Si, Ca, Nd, La, Ce, Mn, Zn, Y, Sn, Gd and Al.

(3) Many alloying elements do not completely dissolve into the Mg matrix, but can locally precipitate as particles, forming a heterogeneous microstructure, even if the concentration of the alloying element is lower than its solubility in Mg. The micro-galvanic effect of the precipitated particles typically increases the corrosion rate.

(4) Some alloying elements may significantly reduce the impurity tolerance limits. For example, the Fe tolerant limit is about 170 ppm for pure Mg, but is reduced to a few ppm by alloying with Al [46, 49, 112, 113]. Therefore, there is a possibility that the parent alloy has an impurity level below the tolerance limit, but after alloying the impurity tolerance limit is lower. In this case, alloying decrease the corrosion resistance of the Mg alloy.

(5) Some passivating elements have too low solubility in Mg to make the Mg matrix phase passive [114]. They precipitate as other phases, and their concentrations in the matrix phase are insufficient to form a passive film.

5. Heat-treatment

Heat treatment can significantly affect the corrosion resistance of a Mg alloy through modifying the alloy microstructure [45, 46, 115-120]. It is a possible approach to formation of a passive Mg matrix, and thus corrosion resistant Mg alloys. The corrosion rate of Mg or a Mg alloy can be different after heat treatment.

For high-purity Mg, Liu *et al.* [46] reported that heat treatment of as-cast, high-purity Mg led to precipitation of an Fe-rich phase from the Mg matrix, which

significantly increased the corrosion rate, and this behaviour could be explained by the Fe-Mg phase diagram. The as-cast Mg alloy was high-purity because the Fe content was below the tolerance limit (~180 ppm) for as-cast Mg, and all the Fe was in super-saturated solid solution in the Mg matrix. Heat treatment caused the precipitation of the Fe into an Fe-rich phase and the increased corrosion rate. The tolerance limit for Fe after heat treatment was ~2ppm.

For Mg alloys, especially the commercial AZxx series alloys (such as AZ91), heat-treatment can alter the second phase amount and distribution. The second phase in a Mg alloy typically has two effects on corrosion [38, 121]. (i) The second phase accelerates corrosion of the matrix by micro-galvanic corrosion when the second phase concentration is low and the second phase occurs as isolated precipitates. (ii) The second phase retards corrosion as the second phase acts as a corrosion barrier, if the second phase forms a continuous network. Because of the dual-effect of the second phase, the influence of heat treatment on corrosion performance of a Mg alloy can sometimes be complicated [119].

Cao *et al.* [15] and Shi *et al.* [22] studied the influence of heat-treatment on corrosion behaviour on a series of binary Mg-X (wt.%) alloys: Mg0.1Zr, Mg0.1Sr, Mg0.3Si, Mg0.3Ca, Mg0.6Nd, Mg0.7La, Mg0.9Ce, Mg1Mn, Mg5Zn, Mg5Y, Mg5Sn, Mg5Gd and Mg6Al. The amount of alloying was (i) 5 wt.% for alloying elements that have solubility higher than 5 wt.% in Mg, and (ii) close to their maximum solubility for all other alloying elements. All the Mg alloys were solution heat-treated at a temperature close to the eutectic temperature for 42 hours and quenched in cold water. The heat treatments were designed to dissolve each of the alloying elements into the Mg solid solution, and it was expected that the elements would remain in solid solution after quenching to room temperature. The aim was to study the passivating ability of these elements. However, there was no passivity for these Mg alloys under the conditions studied.

Fig. 5 shows the corrosion rates by weight loss measurement in 3.5 wt.% NaCl solution saturated with Mg(OH)₂ for these Mg-X (wt.%) alloys before and after solution heat-treatment. The corrosion rates of the Mg-X alloys after solution

heat-treatment are plotted on the Y-axis against the corrosion rates of the corresponding as-cast Mg-X alloys on the X-axis. The figure shows that different alloying elements led to different corrosion rates, and the corrosion rates ranged widely over more than one order of magnitude. For example, the corrosion rate of Mg-Gd was more than 10 times higher than those of Mg-Ca, Mg-Mn and Mg-Al.

Fig. 5 also shows that Mg_{0.3}Ca, Mg₆Al, Mg_{0.6}Nd, Mg_{0.1}Sr, Mg_{0.3}Si and Mg₅Y had increased corrosion rates, while the corrosion rates of Mg₁Mn, Mg₅Sn, Mg_{0.9}Ce, Mg_{0.7}La, Mg₅Zn and Mg₅Gd decreased after solution heat-treatment, and the change in corrosion rate of Mg_{0.1}Zr by heat-treatment was relatively small. The decreased corrosion resistance by heat-treatment could be attributed to the precipitation of some harmful particles during the solution heat-treatment and quenching, which overwhelmed the beneficial effect of the alloying elements. The decreased corrosion rates by solution heat-treatment could be caused by the dissolution of the second phases in the matrix. Mn and Zr are generally believed to be purifiers for Mg, which can reduce the harmful effect of the Fe impurity through reacting with it to form heavier precipitates that were removed from the alloys before casting. The decreased corrosion rate of Mg-Mn by solution heat-treatment could result from the reaction of Mn with the Fe remaining in the alloy, forming inert harmless Mn and Fe containing intermetallics. The Zr and Fe containing particles precipitated in the Mg-Zr alloy should be less harmful than the Fe impurity, but they could still be cathodic to Mg. Hence, solution heat-treatment might result in slightly more Zr and Fe containing particles precipitated, and thus a slightly increased corrosion rate.

To better understand the different alloying effects on the corrosion rates of these solution-heat-treated Mg alloys, their anodic and cathodic current densities are plotted versus their total contents of impurities in Fig. 6. The total impurity content is the amount of all the impurities in the alloy (including all the elements except the alloying elements X and Mg). Fig. 6 shows the anodic current densities at potentials 20 mV more positive than the open circuit potentials (OCPs) and the cathodic current densities at potentials 70 mV more negative than the OCP of ultra-high-purity Mg, as-cast high purity Mg and solution-heat-treated Mg-X (wt.%) alloys after 7 days of

immersion in 3.5 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$ [15, 22]. The Mg alloys were arranged according to their impurity concentrations (wt.%) on the X axis. The anodic and cathodic current densities of the solution-heat-treated Mg-X alloys were higher than the corresponding current densities of high purity Mg.

Fig. 6 indicates that the anodic and cathodic current densities increased as the total impurity content increased. Based on the dependence of current densities on impurity content, these alloys could be classified into two groups. The first group included Mg0.3Ca, Mg6Al, Mg0.6Nd, Mg0.1Sr, Mg0.1Zr, Mg5Y and Mg5Gd; the anodic and cathodic current densities increased with increasing significantly total impurity content. Mg0.3Si, Mg5Sn, Mg0.9Ce, Mg0.7La, Mg5Zn were in the second group. Their anodic and cathodic current densities did not increase much with total impurity content. It appears that these two groups of alloys corresponded well to the two categories in Fig. 5; the first group contained mainly the alloys (except Mg0.3Si and Mg5Gd) that had increased corrosion rates after solution heat-treatment, while the second group had those whose corrosion rates decreased by solution heat-treatment. It is unclear why the alloying effect and the impurity content effect on the corrosion of these solution-heat-treated alloys exhibited these two different trends. There may be an interaction between the alloying elements and impurities, and two different mechanisms may dominate the corrosion of these Mg alloys. Further systematic investigations are needed to understand these interesting alloying and impurity effects.

The solution heat-treatment results suggest that the Mg matrix, if alloyed with some alloying elements below their solubility limits, does not become passive, and instead may become even more active.

6. Hot rolling

In addition to heat-treatments, the microstructure of a Mg alloy can also be modified by mechanical working, which may consequently influence the corrosion behavior. It has been reported that hot rolling can improve the corrosion resistance of Mg alloys

[50, 122-124]. Gu *et al.* [122] found that binary Mg alloys after hot rolling evolved less hydrogen during immersion in both simulated body fluid and Hanks' solution. Wang *et al.* [123] also found that hot rolling decreased the corrosion rate of AZ31 in Hanks' solution. Cao *et al.* [124] found that the corrosion rates, in 3.5 wt.% NaCl solution saturated with Mg(OH)₂, decreased after hot rolling for most of the investigated Mg-X (wt.%) alloys, including Mg5Gd, Mg0.3Ca, Mg6Al, Mg1Mn, Mg5Sn, Mg0.1Sr, Mg0.6Nd, Mg0.7La, Mg0.9Ce, but not for Mg0.1Zr and Mg0.3Si whose corrosion rates increased significantly (see Fig. 5).

However, rolling of AZ31 sheet can cause the Mg alloy surface to pick up Fe-containing particles, and consequently can cause increased corrosion rates [125]. Surface grinding can effectively remove the Fe-containing particles and dramatically decrease the corrosion rates of AZ31 [125].

Moreover, hot-rolling Mg alloys can develop a strong basal texture; most of the basal planes become parallel to the rolling surface [50]. The basal plane of Mg is the most closely-packed plane that exhibits the lowest corrosion rate [49, 51]. Therefore, the cleaned rolling surface of a Mg alloy sheet has a lower corrosion rate.

Hot rolling also refines the grains of Mg alloys due to recrystallization during rolling [124, 126]. Grain refinement can improve the corrosion resistance of a Mg alloy [126]. For example, grain refined AZ31 Mg and pure Mg produced by equal channel angular pressing have been found to have decreased the corrosion rates [123, 127, 128]. Argade *et al.* [129] found that the corrosion rates of Mg-Y-RE alloy was significantly decreased by friction stir processing through grain refinement. The relationship of grain size and corrosion rate is analogous to the Hall-Petch relationship [130]. Similarly, Pu *et al.* [29, 131] indicated that grain refinement and grain orientation obtained by surface burnishing decreased the corrosion rate of a Mg alloy, but the beneficial effect became smaller when grain size decreased down to around 1 μm . However, contradictory findings have also been reported for pure Mg [132] and AZ91D [133] that grain refinement after equal channel angular pressing led to higher corrosion rates in a NaCl solution.

Hot rolling may also help form a coherent and protective film on Mg alloys in

chloride solutions. Cao *et al.* [124] found that most of the hot rolled Mg-X (wt.%) alloys suffered uniform corrosion, while the as-cast Mg-X (wt.%) alloys suffered localized corrosion [15]. Hot rolling can change the distribution of second phases and produce a more homogeneous microstructure. This might be helpful for forming a more coherent and protective film on the hot-rolled Mg alloys than on the corresponding as-cast Mg alloys.

Although there have been many reports on the influence of grain refinement on corrosion behaviour of Mg alloys, so far convincing explanation for the phenomenon are limited [51, 125, 134, 135]. Recently, Song [50] proposed a mechanism that appeared to be successful in explaining the complicated corrosion behaviour influenced by hot-rolling, in which hot rolling introduced dislocations and severely distorted lattice at the grain boundaries, and as a result, the solubility of impurity or intermetallic precipitates became larger in the distorted lattice (particularly in dislocations and grain boundaries) [50, 125, 135]. According to this model, on one hand, more impurities or intermetallic precipitates can be dissolved in the hot-rolling induced dislocations and refined grain boundaries. On the other hand, dislocations and grain boundaries are more active than the inner grain area and easier to be corroded. Therefore, over grain-refinement (i.e., grains become too fine) is not beneficial to the corrosion resistance of Mg alloy. This explains that the equal channel processed AZ31 has finer grains but did not have lower corrosion rate than hot-rolled AZ31 [123].

In summary, hot rolling can refine grains, modify crystallographic orientation, homogenise the matrix phase, and enhance impurity tolerance limits [50]. The homogenised surface and enhanced impurity tolerance are helpful for forming a protective film on Mg alloys [50, 124]. Although hot rolling can improve the corrosion resistance of a Mg alloy to some degree, the film formed on a hot-rolled specimen mainly consists of porous and non-protective MgO and Mg(OH)₂ [61, 62, 136]. It is not a passive film and cannot make the Mg alloy passive. However, the highly distorted lattice may offer a short-cut for passivating alloying elements to rapidly diffuse from the substrate to the surface film, which might be helpful to the growth and repairing of a film on the Mg alloy in a corrosive environment.

7. Sputter deposition

The above results and discussion suggest that alloying, including solution heat-treatment and hot-rolling, could not make Mg matrix passive. Particularly, passivity is unlikely when the alloying element concentrations are below their solubility limits. It is of scientific interest to know if a passive Mg matrix can be produced if the concentration of the passivating element is much higher than its solubility in Mg. Such a Mg matrix is super-saturated single phase which can be obtained through a non-equilibrium process, such as sputter deposition or rapid solidification.

Sputter deposition of binary thin film Mg alloys can extend the solubility of alloying elements in Mg [114, 137, 138] and can produce single-phase Mg alloys with a wide composition range. For Mg, the required minimum amounts of passivating elements could be much larger than that for a stainless steel due to the high activity of Mg. However, the solid solubility of the strong passivating elements is low in Mg matrix. For example, the solid solubility of Ni in Mg is only a few ppm, and Cr and Ti cannot be dissolved in Mg under equilibrium conditions [40]. These elements that are difficult to alloy with Mg can be produced dissolved in Mg through non-equilibrium sputter deposition.

The sputter technique has been employed to produce corrosion resistant Mg alloys. Schluter *et al.* [138] found that for sputtered MgY and MgGd single phase alloys, even after the content of Y and Gd reached 40 wt.% and 20 wt.%, respectively, there was no significant change in corrosion rate on these alloys. Furthermore, the corrosion rates of sputter-deposited Mg5Y (wt.%) and Mg5Gd (wt.%) were significantly lower than those of solution heat-treated Mg5Y (wt.%) and Mg5Gd (wt.%) [22].

Recently, the threshold level of Ti to passivate Mg was measured by Song *et al.* [40]. The corrosion potential of the magnetron sputtered Mg-Ti alloy increased with increasing Ti content (see Table 1 and Fig. 7). The $Mg_{28}Ti_{51}C_{11}O_{10}$ alloy had the lowest current density and there was a continuous protective thin Mg and Ti oxide

film formed on its surface after immersion. In contrast, the films on the other Mg-Ti alloys containing less Ti were thick, discontinuous and non-protective.

Yao *et al.* [139] studied melt-spun glassy Mg alloys containing supersaturated amounts of the alloying elements Ni, Nd, Y and Cu. These amorphous Mg alloys formed under rapid solidification conditions showed a distinct passive region when anodically polarized in a dilute chloride solution as shown in Fig. 8. Similar passivity results have also been reported for magnetron-sputtered Mg-Ti single-phase alloy [140]. Fig. 8 shows that Ni and Cu could lead to passivity if in solid solution, even though these are well known impurities in Mg, and dramatically increases the corrosion rate of a Mg alloy when present as Ni-rich and Cu-rich particles [141].

So far, research work on non-equilibrium Mg-A (A-strong passivating elements) alloys has appeared to be promising. For example, the alloys with multi-passivating alloying elements have showed clear passive regions with low passivating current densities ($<0.01\text{mA/cm}^2$). In fact, the passivity of Mg alloys shown in Fig. 8 might lead to a permanent solution to galvanic corrosion, a critical problem with Mg alloy components in practical service. This is understandable, as passivation can significantly nobly shift the corrosion potential and dramatically inhibit the anodic dissolution. A passive Mg alloy does not have a high galvanic corrosion rate when in contact with cathodic metals. The mitigation of galvanic corrosion based on passivation of Mg alloys would be more reliable than any surface treatments, because the repairable passive film can self-heal if it is damaged.

8. Research suggestions

The corrosion and passivation of Mg alloys are electrochemical behavior. Corrosion is the electrochemical dissolution of Mg metal. Passivation would be caused by the formation of a protective surface film. The substrate alloy influences the corrosion and passivation behaviour through influencing the composition of the surface film. The composition of the surface film during corrosion on Mg alloys has been investigated recently [60, 142-148]. Most of the published investigations mainly

focused on the MgO and Mg(OH)₂ constituents in the film. The influence of the alloying elements on the film stability has not been systematically examined. There is a lack of fundamental understanding of the electrochemical reactions and processes in the surface films and at the film/substrate interfaces.

In order to develop a passive corrosion resistant Mg alloy, the following critical question need to be answered: “what are the most suitable and effective passivating elements that can alloy with Mg to form a passive film”. Alloying elements that may passivate Mg should meet the following 3 criteria:

- i) The elements must be non-toxic and environment-friendly.
- ii) The elements should have strong passivating ability and small amounts of the elements in Mg should be enough to form a protective surface film on a Mg alloy, and thus the resultant alloy will not become too heavy.
- iii) The alloying elements from the bulk of the Mg alloy can continuously diffuse to the surface to react with the environment to form a protective passive film, i.e., the surface film can be directly formed and repaired (if damaged) in the service environments, particularly chloride containing aqueous solutions.

Requirement iii) could be the most difficult. It is relatively easy to form or even apply a surface film or layer on Mg under specific conditions (e.g., phosphating, carbonating, anodizing, or even organic coating). However, these initially formed surface films or layers cannot survive in the service environments for a long time, particularly when the service environments are aggressive. Once the films are damaged during service, severe localized corrosion attack occurs.

Surrounding the core issue, i.e. selection of suitable passivating elements for Mg, there are 3 important research topics that should be discussed:

1. Is there a threshold concentration for a passivating element dissolved in the Mg matrix solid solution to cause passivation?
2. How do the alloying elements from the substrate Mg alloy influence the composition and microstructure of the corrosion product film or passive film?
3. How is the substrate Mg alloy dissolved or passivated under the surface film?

9. Concluding Remarks

A corrosion resistant Mg alloy has been pursued by researchers for decades, and would be a useful light-weight material. It is still not clear if a passive corrosion resistant Mg alloy is achievable and this review on recent progress indicates that there is still a long way to go.

Nevertheless, some understanding has been obtained from the efforts to develop passive corrosion resistant Mg alloys as follows.

1. High-purity or ultra-high-purity Mg does not exhibit passivity in a concentrated chloride solution.
2. The corrosion rate of ultra-high-purity Mg is 0.25 mm y^{-1} in 3.5 wt.% NaCl saturated with Mg(OH)_2 , which can be set as a benchmark. A Mg alloy would need a corrosion rate significantly lower (e.g. 10 times lower) than this benchmark to be passivated.
3. A passive corrosion resistant Mg alloy would require a protective surface film and a surface film which can self-repair if damaged.
4. Solution heat-treatment has a dual effect on the corrosion of Mg alloys. Heat-treatment can reduce the amounts of the second phase and other particles that have a galvanic effect on the Mg matrix phase, and thus lead to less galvanic corrosion. Heat-treatment may also result in precipitation of impurity containing particles in the Mg matrix, accelerating the corrosion of the matrix through the micro-galvanic effect of the impurity precipitates.
5. Hot rolling can improve the corrosion resistance of a Mg alloy through modifying the crystallographic orientation, enhancing the impurity tolerance limit, homogenising the composition and microstructure, and possibly facilitating the formation of a protective film.
6. Sputter-deposited and rapidly solidified single phase Mg alloys containing supersaturated alloying elements Ti, Ni, Nd, Y and Cu have shown a passivation tendency in a dilute chloride containing solution.

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Figure captions:

Fig. 1 Typical surface appearances of ultra-high-purity Mg specimens (a) showing uniform corrosion, typical of most surface of most specimens, and (b) a specimen with some localized corrosion. The appearances shown were after immersion at the open circuit potential (OCP) in 3.5 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$ for 14 days at $25 \pm 2^\circ\text{C}$ and after removal of the corrosion products [42].

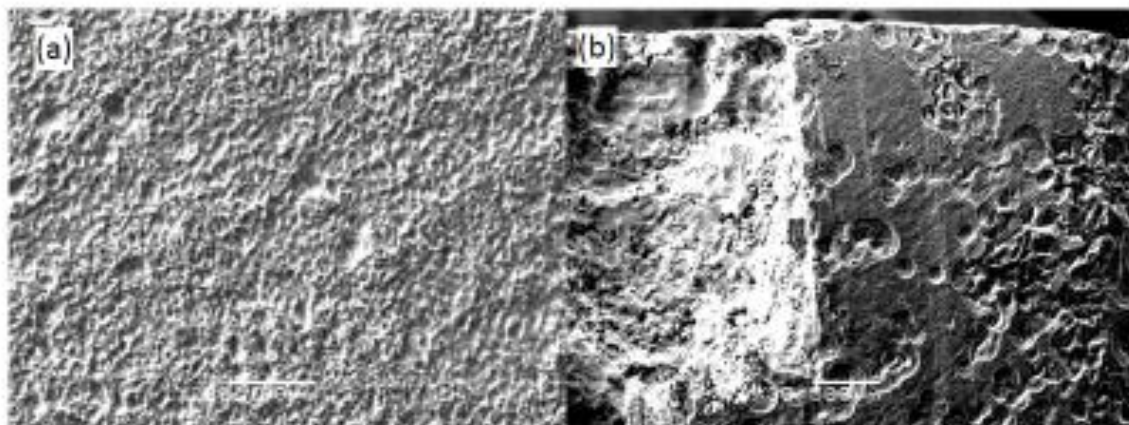


Fig. 2 Typical polarisation curves for pure Mg (99.96 wt.%) in the following solutions: (A) 1 M NaCl, pH = 11, (B) 0.5 M Na₂SO₄, pH = 11, (C) 1 M NaCl, pH = 13, (D) 0.5 M Na₂SO₄, pH = 13 [59].

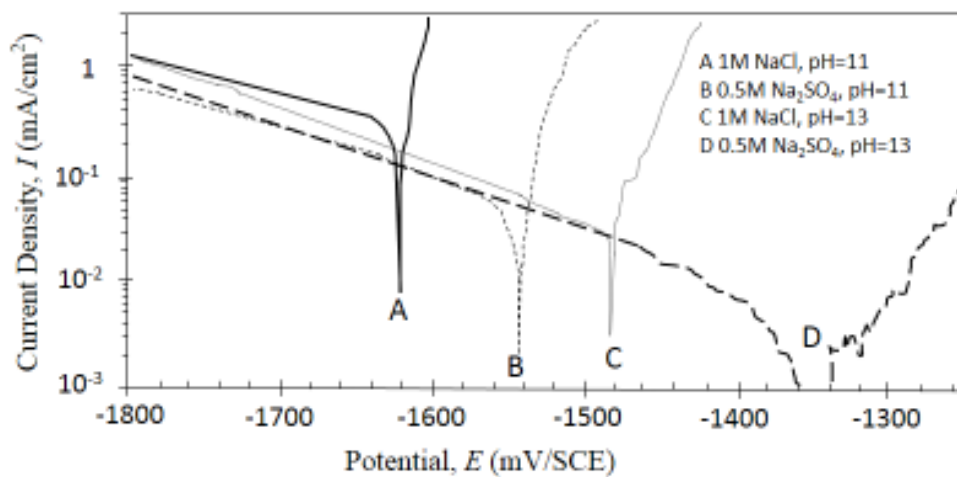


Fig. 3 A cross-section of WE41 after 18 h immersion in 0.001 M NaCl solution at the open circuit potential [98]. The corrosion product of the specimen has been removed.

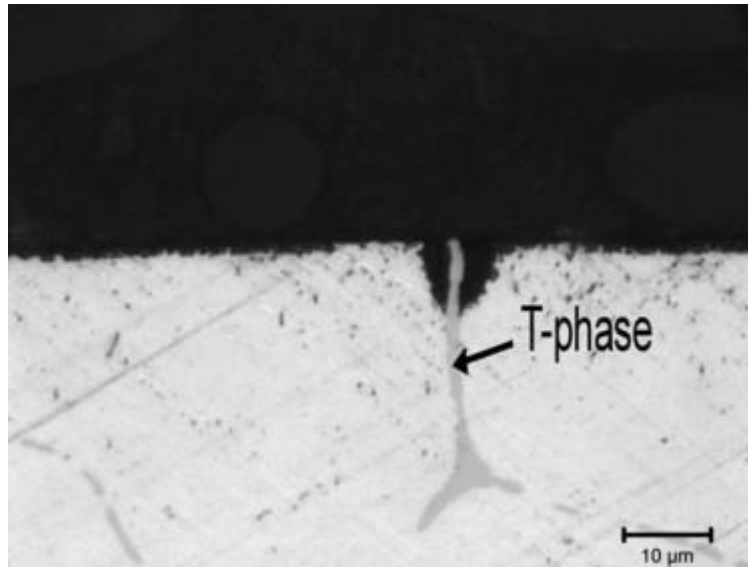


Fig. 4 Compilation of corrosion rates for ultra-high-purity Mg (UP), high-purity Mg (HP) and Mg alloys after immersion in NaCl containing solutions at the open circuit potentials [2, 14]. The corrosion rates (P_w) of the Mg alloys as measured by weight loss were significantly higher than the intrinsic corrosion rate ($0.38 \pm 0.24 \text{ mm y}^{-1}$) of high-purity Mg in the 3.5 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$. In some cases, the corrosion rates (P_H) measured by hydrogen evolution were lower than that of high-purity Mg as indicated by the circle; however, such corrosion rates under-estimate the real corrosion rates.

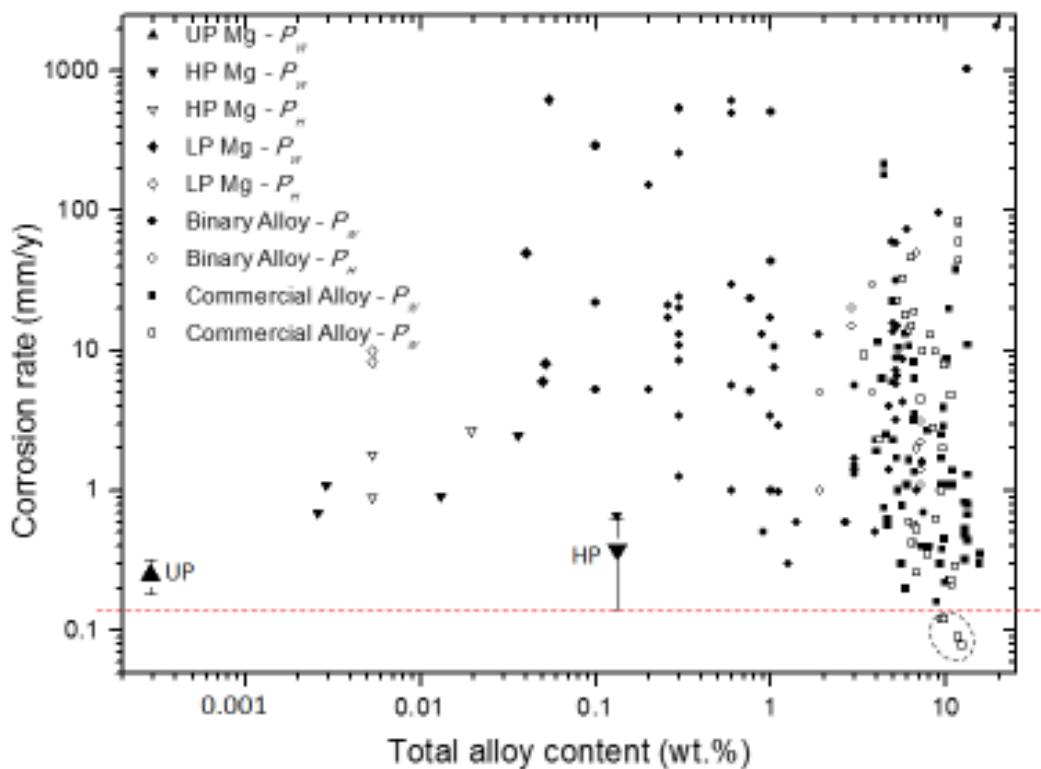


Fig. 5 Corrosion rates (P_w) obtained from weight loss measurements after 7 days of immersion in 3.5 wt.% NaCl solution saturated with $Mg(OH)_2$ at the open circuit potentials for as-cast and solution-heat-treated Mg-X (wt.%) alloys: Mg0.1Zr, Mg0.1Sr, Mg0.3Si, Mg0.3Ca, Mg0.6Nd, Mg0.7La, Mg0.9Ce, Mg1Mn, Mg5Zn, Mg5Y, Mg5Sn, Mg5Gd and Mg6Al; and for hot-rolled Mg-X (wt.%) alloys: Mg0.1Zr, Mg0.1Sr, Mg0.3Si, Mg0.3Ca, Mg0.6Nd, Mg0.7La, Mg0.9Ce, Mg1Mn, Mg5Sn, Mg5Gd and Mg6Al. The data are extracted from [15, 22, 124].

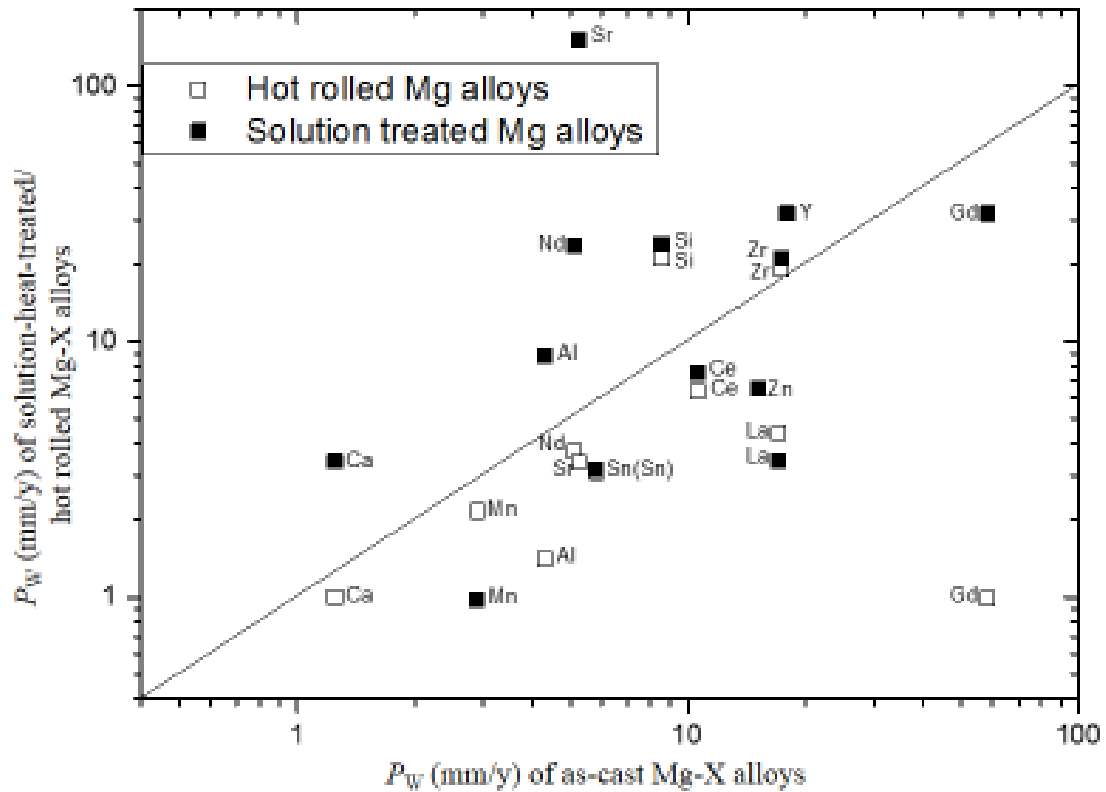


Fig. 6 Anodic current densities at potentials 20 mV more positive than the open-circuit potentials (OCPs) and cathodic current densities at potentials 70 mV more negative than the OCPs after 7 days of immersion in 3.5 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$ for ultra-high-purity Mg (UP), as-cast high-purity Mg (HP) and solution-heat-treated Mg-X (wt.%) alloys: Mg0.1Zr, Mg0.1Sr, Mg0.3Si, Mg0.3Ca, Mg0.6Nd, Mg0.7La, Mg0.9Ce, Mg1Mn, Mg5Zn, Mg5Y, Mg5Sn, Mg5Gd and Mg6Al. The x axis label “Impurity concentration” refers to the total amount of all the impurity elements in the alloy (including all the elements except the alloying elements X and Mg). The data are extracted from [15, 22, 42].

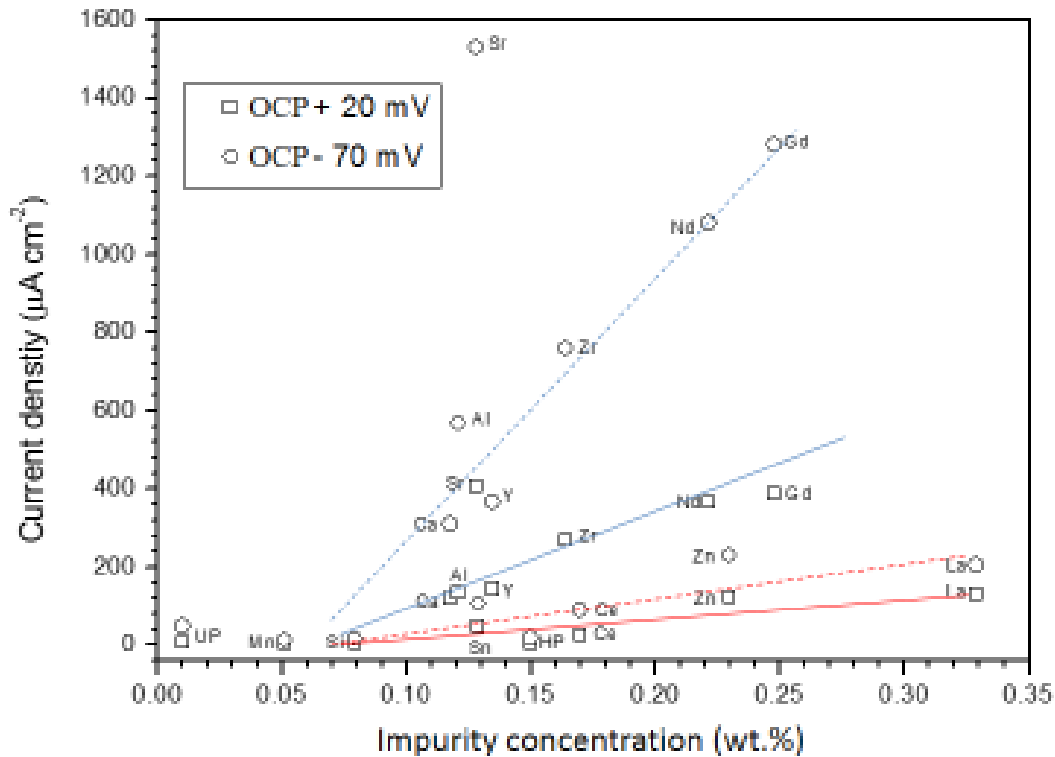


Fig. 7 Polarization curves for magnetron-sputtered Mg-Ti alloys in 0.1 wt.% NaCl solution saturated with $\text{Mg}(\text{OH})_2$ [40].

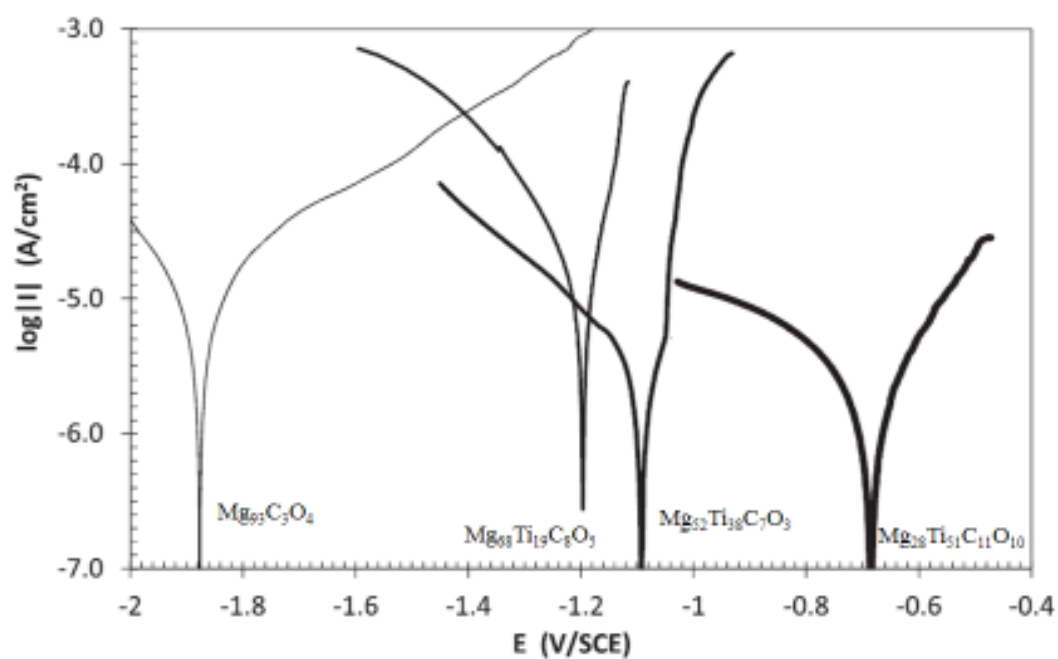


Fig. 8 Polarization curves of melt-spun glassy Mg alloys and pure Mg in 0.01 M NaCl (pH = 12) [139]. The Mg alloys $Mg_{65}Cu_{25}Y_{10}$, $Mg_{65}Ni_{20}Nd_{15}$, $Mg_{82}Ni_{18}$ show a distinct passive region.

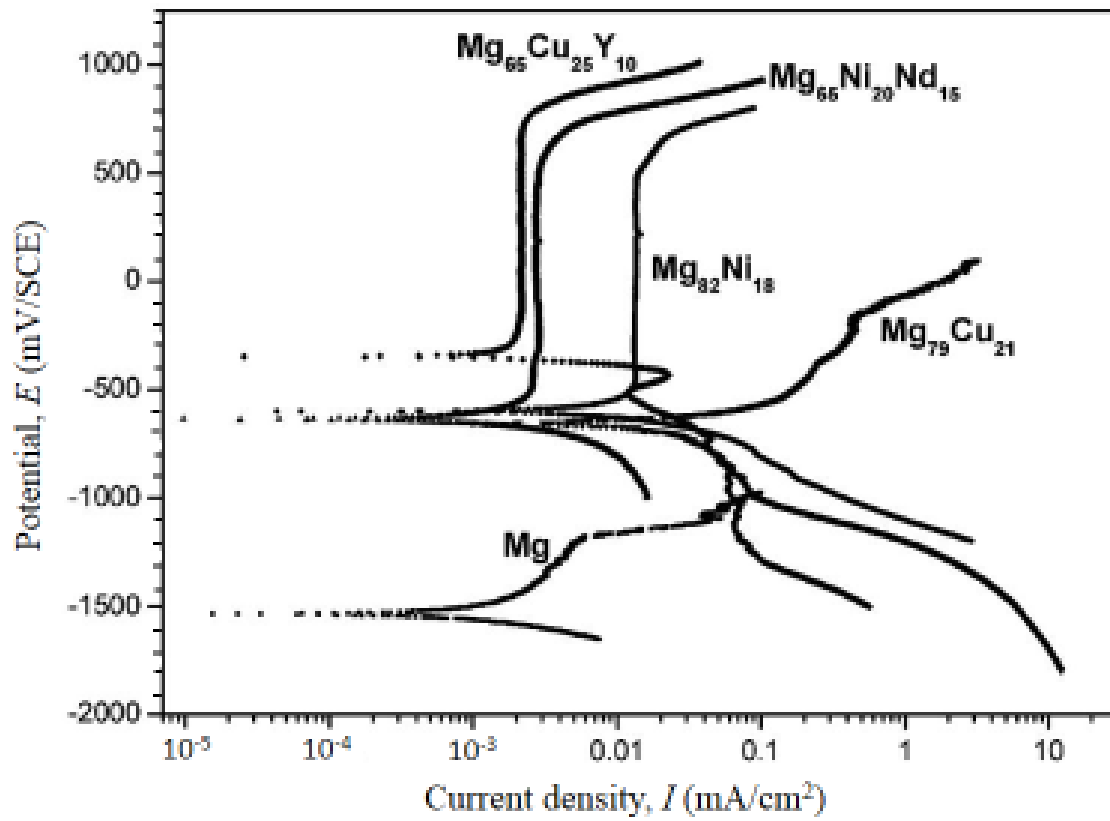


Table caption:

Table 1 Corrosion potentials (E_{corr}) and corrosion current densities (I_{corr}) estimated from measured potentiodynamic polarization for sputtered Mg-Ti alloys immersed in 0.1 wt.% NaCl solution saturated with Mg(OH)₂. The data are extracted from [40].

Sputtered alloy name*	Mg (at.%)	Ti (at.%)	O (at.%)	C (at.%)	E_{corr} (V/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)
Mg ₉₃ C ₃ O ₄	93.4	0.0	3.8	2.8	-1.88	7.9
Mg ₆₈ Ti ₁₉ C ₈ O ₅	68.5	19.3	4.7	7.5	-1.20	15.8
Mg ₅₂ Ti ₃₈ C ₇ O ₃	52.3	38.0	3.3	6.4	-1.10	2.5
Mg ₂₈ Ti ₅₁ C ₁₁ O ₁₀	28.3	51.4	9.9	10.4	-0.68	1.6

*The Mg-Ti alloy names are different from those in the original reference [40].