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Review Article

Influence of β Phase on Corrosion Behavior of Mg-Al-Zn Alloys

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Abstract

There are numerous studies to understand the corrosion behaviors of AZ series Mg alloys and the results on the role of β phase in the corrosion of the AZ series Mg alloys are yet contradictory. In the literature, the β phase inhibits the corrosion by barrier effect or vice versa promotes corrosion by micro galvanic coupling. This review focuses on the influence of microalloying elements and the solidification rate on the β phase morphology, affecting the corrosion behavior of AZ series Mg alloys. Additionally, the oxide film-β phase relationship on the surface of the alloys also has been evaluated on their corrosion properties.

The review showed that the contradictory evaluations of the researchers about why the β phase prevents corrosion with the barrier effect or vice versa, why the β phase increases corrosion with micro galvanic coupling, attributed to variations in the production methods and related β phase morphology in microstructure.

Keywords: Mg alloy; AZ series; Intermetallic; Corrosion

Introduction

Mg-Al-Zn (AZ), Mg-Al-Mn (AM) and Mg-Al-Si (AS) series Mg alloys are used in many engineering fields from automotive industry to electronics and aerospace industry due to their high specific strength values [1-5]. As potential biodegradable implant material, it also has been attracted attention in recent years [6-11]. Mg alloys are designated by giving two letters following by two numbers. Letters presents main alloying elements (A=Al, Z=Zn, M=Mn, S=Si). Numbers indicate respective nominal compositions of main alloying elements in wt.%, e.g., AZ91 (Al ~9%, Zn ~1%).

Corrosion typically limits the use of the Mg in many applications, particularly those where it is expected to be exposed to aqueous solutions, as well as in corrosive environments from the marine atmosphere or salt on roads. Therefore, being an electrochemically highly active metal limits the use of Mg and its alloys without any protection [12,13].

There are many studies in the literature to understand the corrosion mechanisms of the AZ series Mg alloys [14-36]. However, opinions on the corrosion behavior of AZ series Mg alloys are still conflicting. Some researchers [14,15] argue that the corrosion resistance of AZ series Mg alloys noticeably improves as the amount of Al in the composition reaches to 8-9wt.%, which is due to the protective barrier effect of the $Mg_{17}Al_{12}$ (β) intermetallic phase. On the other hand, some researchers [22,23,26,30] report that the β phase does not act as a protective barrier, on the contrary, it acts as a microgalvanic cell with the alloy matrix accelerating the corrosion.

In this review, the literature with our previous and ongoing studies were compared, and the effects of production differences such as microalloying elements and solidification rate on the corrosion of AZ series Mg alloys on the β phase morphology and structure were examined. Additionally, oxide film-β phase relationship formed on the surface of the alloys were also evaluated in the frame of corrosion behaviors.

The relationship of β phase with corrosion in AZ series Mg alloys

Alloying elements and solidification rate are the main factors affecting the extend of secondary phases and its morphologies in cast metals. Therefore, parameters such as Al content, microalloying elements and their ratios, solidification rate and manufacturing methods should be considered together in the examination of corrosion behaviors of Mg alloys. In addition, the structure of the oxide film formed on the surface, related to the alloying elements, is another factor to be considered in the corrosion properties of the alloys.

β Phase

According to the Mg-Al phase diagram (Figure 1), the eutectic β phase appears to occur when Al content is above 13%. However, the eutectic β phase can also form at as low as 2wt.% Al under unstable solidification conditions during casting [26]. The morphology of the β phase is basically related to the amount of Al in the alloy [16,17,25,31,38,39], the solidification rate of the molten metal [24,32] and the addition of other alloying elements [18,21,28-35,38,39].

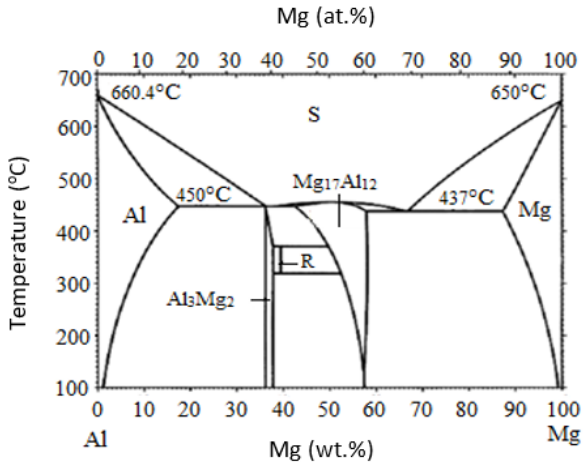


Figure 1: Mg-Al equilibrium diagram [37].

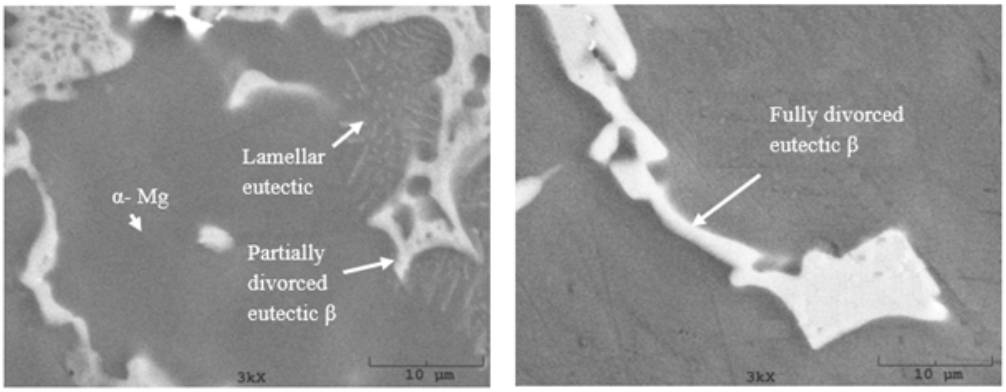


Figure 2: Morphologies of β phases in (a) AZ91 and (b) AZ91+0.5Ti alloys [21].

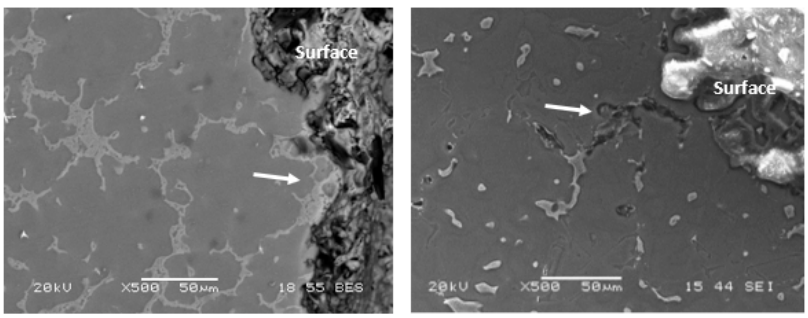


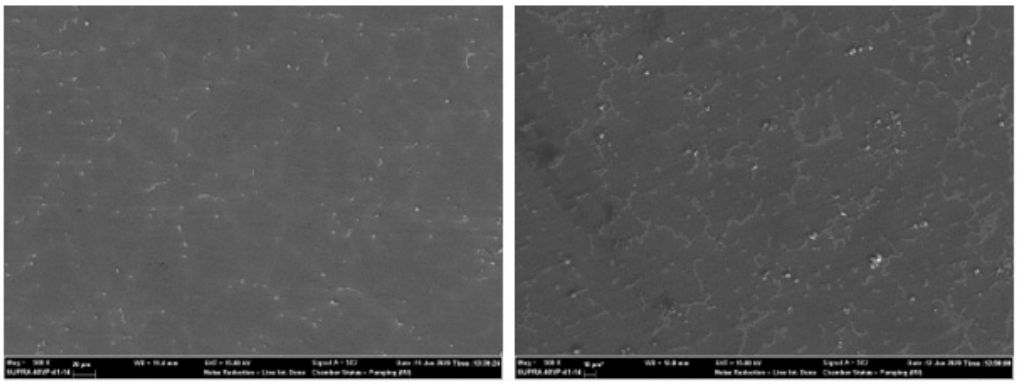
Figure 3: Corrosion in AZ91 alloy showing (a) fully eutectic β phase interrupting the corrosion progress (solidified at 8 °C/sec) and (b) corrosion progresses via lamellar eutectic β phase (solidified at 1.4 °C/sec). Environment: 3.5% NaCl, dark areas show corrosion products.

Fully divorced, partially divorced and/or lamellar eutectic β-phase morphologies in Mg alloys could occur depending on amount of Al, microalloying elements and solidification conditions [21,25]. In Figure 2, the microstructures of AZ91 alloy and its Ti microalloyed version are shown. Since the presence of Zn in AZ series alloy, formation of eutectic morphology in the alloy is possible. Due to the high segregation tendency of Zn during solidification and the structural undercooling in front of the solid-liquid interface in the early stages of solidification, the increase in the growth of primary dendrites reduces the distance between the dendrites and thus helps the formation of a fully divorced β eutectic [40,41]. The lamellar eutectic forms in a supersaturated α-Mg solid solution juxtaposed with the fully divorced β phase.

Predominantly lamellar and partially divorced β morphology is formed at slow solidification and high Al content, whereas under die casting or at low Al content fully divorced β morphology is formed in large extend. Figure 3 shows advance of corrosion front in AZ91 alloy having lamellar, partially divorced and fully divorced eutectic β phases. Evidently, corrosion progresses through lamellar and partially divorced eutectics whereas the fully eutectic β interrupts the progress of corrosion.

Al content-β phase relationship

The etxtend of β phase increases with increasing Al content and transformed to a coarsened net-like structure as shown in Figure 4. It has been reported [25] that the globular shaped β phase in the alloy turned into a coarser lamellar or partially divorced β eutectic structure with increasing Al content.



(a) (b)

Figure 4: Microstructures of (a) AZ31 alloy and (b) AZ91 alloy.

It has been reported [16,17,19] that the corrosion resistance of AZ91 alloys was better than AZ21 and AZ31 magnesium alloys. Pardo et al. [17], in his study on the effects of Al content in AZ31, AZ80 and AZ91D alloys, concluded that the barrier effect of the β phase increased with the amount of Al, and that it was the highest in the AZ91D alloy. Wang et al. [27] observed that AZ61 alloy has better corrosion resistance when compared to AZ31 alloy in their study. Researchers [16,17,19,27] attributed the higher corrosion resistance of AZ91 alloy to two key factors; the enrichment of Al in the matrix and the presence of β phases that acting as a protective barrier during corrosion. Contrary to the above researchers [16,17,19,27], some researchers [22,23,26,30] reported that β-phases increase corrosion by forming microgalvanic cells with the alloy matrix. Studies on the corrosion behavior of the above mentioned [17,19,22,23,27] AZ series Mg alloys have not been comprehensively evaluated. For example, in references [17,27], the AZ31 and AZ61 alloys are compared with the AZ91 alloy and discussed only by considering the Al content of the alloys, regardless of their production method. In the evaluated studies [17,27], AZ91 alloy is in billet form and AZ31 alloy is in rolled plate form, and it is inevitable that their microstructures will be different. However, it is known that alloying elements [18,21,25,28-35], solidification rate [20,24,32] and production methods [33] significantly affect the microstructure and therefore have serious effects on the corrosion behavior of the alloys.

Candan and Candan [25] conducted systematic comparative studies on the corrosion behavior of AZ21, AZ41, AZ61 and AZ91 Mg alloys (with similar solidification rate and impurity content). Their results showed that the corrosion resistance was weaker in studies with Al addition above 4wt.%. The reduction in corrosion resistance of the alloys was attributed to the presence of lamellar and partially divorced β eutectics promoted by high Al content. Therefore, these results showed that β caused micro galvanic corrosion rather than a barrier effect.

Microalloying

Corrosion properties of AZ series Mg alloys can be improved by microalloying with Y, Ce, Sb, Bi, Si, Ca, Ho, Sr, Sc, Pb or Ti [5,18,21,24,28,29,32,34,35,38,42-65].

Zhang et al. [45] reported that 0.8% Y addition has a significant effect on the improvement of corrosion resistance of AZ91 alloy

due to its grain refining effect. Adding Y element to AZ series alloys formed the Al_2Y phase. At the same time, it not only reduced the extent of β phase with its grain refiner feature, but also encouraged the formation of more homogeneously distributed β in the matrix. As a result, Y addition (up to 0.8%) has a positive effect on the corrosion resistance of AZ91 alloys. On the other hand, an increase in the corrosion rate of AZ91E alloy containing high amount of Y (2%Y) has been reported [46]. Witte et al. [5], compared in vivo corrosion behavior of WE43 and LAE442 (containing rare earth elements) Mg alloys with AZ31 and AZ91 Mg alloys. As a result of this study, it was stated that the corrosion resistance was highest in the LAE442 alloy, while the AZ31, AZ91 and WE43 alloys dissolved at similar rates. In the studies carried out to improve corrosion resistance of the AZ91 alloys [43,63,64], the effect of Ce addition was investigated. The addition of Ce to the AZ91D alloy resulted in a net-like β-phase that acted as a corrosion barrier [63]. In a study on the effect of Ho on AZ91D alloys [35], it was reported that the corrosion resistance of the alloy improved. Limited research on Ho to date [35] suggested that the addition of 0.2% and 0.4% Ho to the AZ91D alloy could improve the corrosion resistance by reducing extent of the β phase due to the formation of Al and Ho-containing intermetallic phases. It was reported [52] that the addition of Sc in AZ91 alloys refined the microstructure with the formation of Al_3Sc phases, which suppressed the formation of the β phase. In the comparison between AZ91E and AZ91E alloy containing 0.1% Sc [46], it was reported that an increase in corrosion resistance occurred in alloys with Sc added.

Addition of Sb or Bi to AZ91 alloy caused the formation of Mg_3Sb_2 or Mg_3Bi_2 phases [48]. Therefore, these phases, which are the cathode relative to the matrix, reduced the corrosion resistance of the alloy [48]. It has been reported [48] that the addition of Sb and Bi to the alloy together caused a significant decrease in the corrosion resistance of the alloy. Addition of Bi to Mg-Al alloy, needle-shaped Mg_3Bi_2 phase had been formed even if the Bi concentrations were below the solubility limit [61]. In another studies [46,62] on the effect of adding Bi to AZ91 alloy, presence of Mg_3Bi_2 in the structure decreased the corrosion resistance. In a study, carried out by Srinivasan et al. [42], it was observed that the addition of Si and Sb together on the corrosion behavior of AZ91 Mg alloy increased the corrosion resistance. They attributed this to the formation of thin polygonal shaped Mg_2Si phases and being more effective in preventing corrosion than the Chinese script shaped Mg_2Si phases.

It has been reported [47,49] that addition of Ca to the AZ91 Mg alloy increased the corrosion resistance of the alloy due to the mesh Al_2Ca phase that acted as an effective barrier against corrosion. Wu et al. [34] in their study, effects of Ca and RE elements on the corrosion behavior, microstructure and mechanical properties of AZ91 were investigated. The addition of Ca has increased the corrosion resistance compared to the addition of RE. The increase in corrosion resistance of AZ91 alloy with 1% Ca added was based on the formation of Al_2Ca phase. Although these studies [34,47,49] support each other, in general, when Ca additions are close to or above the solubility limit (1.35%), acceleration in the corrosion rate has also been reported [65-67].

When Sr is added above the solubility limit (>0.1wt.%) in AZ series alloys, it increased grain size, binary eutectic Al_4Sr, $Mg_{17}Sr_2$ and Mg_2Sr structures [68]. These phases reduced the β phase ratio and homogenized its distribution which increased the corrosion resistance of the alloy [54,68,69].

Pb microalloying changed the microstructure of AZ series cast Mg alloys and caused a more homogeneous β phase distribution [18,70]. In our previous studies [18] on mechanical and corrosion behaviors of AZ91 Mg alloys containing Pb (0.2-1.0 wt.%), the corrosion resistance of the alloy increased significantly with the addition of trace amounts of Pb. The results showed that the addition of Pb suppressed the formation of the β phase (Figure 5), resulting in better corrosion resistance and mechanical properties in the AZ91 alloy [18].

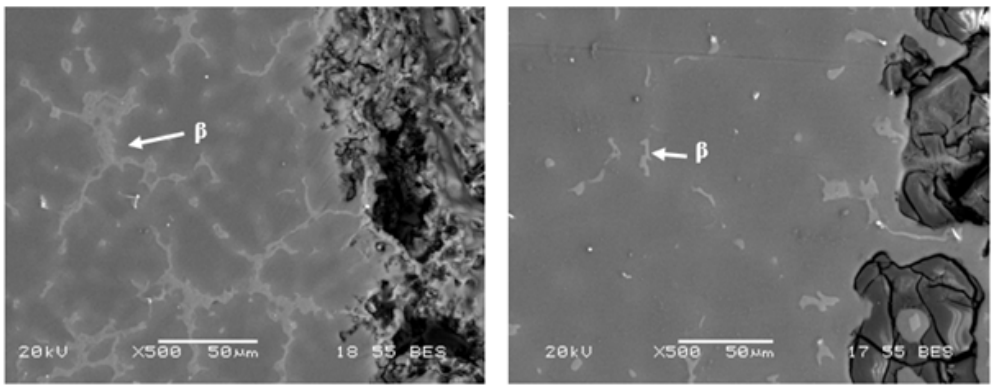


Figure 5: Cross-sectional SEM images of (a) AZ91 and (b) AZ91+0.5Pb Mg alloys after corrosion (Dark areas show corrosion products).

In our other studies [21,24,71] on the microalloying of AZ91 and AZ31alloys with Ti, it was observed that the corrosion resistances of the alloys containing Ti were significantly improved. The effects of Ti were attributed to; (1) changes in the morphology and distribution of the β phase (transformation of β phase from lamellar and partially divorced eutectic to fully divorced eutectic (Figure 2), and (2) increased amount of Al in α-solid solution. In another study [72] on the corrosion resistance of AZ91 alloys containing 0.1-0.5wt.% Ti and Cr, it was reported that the corrosion resistance increased with increasing Ti and Cr addition. Studies by Ai and Quan [55] on the effect of Ti on the corrosion properties of AZ91 Mg alloys showed that the addition of 0.1-0.5wt.% Ti improves the corrosion resistance of the cast Mg alloy in agreement with Refs [21,24,71,72]. The effect of trace amount of Ti microalloying to AZ31, AZ61 and AZ91 Mg alloy on microstructure and corrosion behavior was studied by another research group also [38,57,58]. In the first study by Choi and Kim [58], the effects of Ti addition (0.01-0.02%) on microstructure and corrosion properties of AZ61 Mg alloys were investigated and the results showed that Ti addition changed morphology and grain size. They argued that 0.01% Ti alloying significantly increased corrosion resistance, but 0.02% Ti addition reduced corrosion resistance and Ti addition had no systematic effect.

In other studies, by Choi and Kim [38,57], the effects of the addition of trace amounts of Ti to AZ91 and AZ31 alloys on the corrosion behaviors of the alloys were investigated. In the results, it was observed that the addition of Ti refined the β phase in both alloys and the corrosion resistance of the alloys. The results of the research conducted by this group show that the corrosion resistance of AZ31, AZ61 and AZ91 alloys containing Ti is much better than alloys without Ti. These results support our previous works [21,24,71].

The above studies reveal that improving the corrosion resistance of AZ series Mg alloys can be achieved by microalloying elements that promote formation of fully divorced β phase in the matrice.

Oxide film

In a dry atmosphere and at room temperature, Mg reacts rapidly to form Mg oxide (MgO) and shows good corrosion resistance in these environments due to the MgO film.

$$Mg_{(\kappa)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} \quad (1)$$

In the aqueous medium, a semi-passive $Mg(OH)_2$ oxide film forms on the surface of Mg and its alloys. When this porous and completely non-protective $Mg(OH)_2$ oxide film layer is left in environments containing Cl- ions for a long time, the oxide film deteriorates over time as stated in the following reaction (2).

$$2Mg^{+2}_{(aq)} + 4H_2O + 3OH^{-}_{(aq)} + Cl^{-}_{(aq)} \rightarrow Mg_2(OH)_3Cl.4H_2O_{(s)} \quad (2)$$

The resulting corrosion products ($Mg_2(OH)_3Cl.4H_2O$) form a protective layer on the Mg surface by preventing oxygen and other corrosion environments, resulting a decrease in the corrosion rate [73].

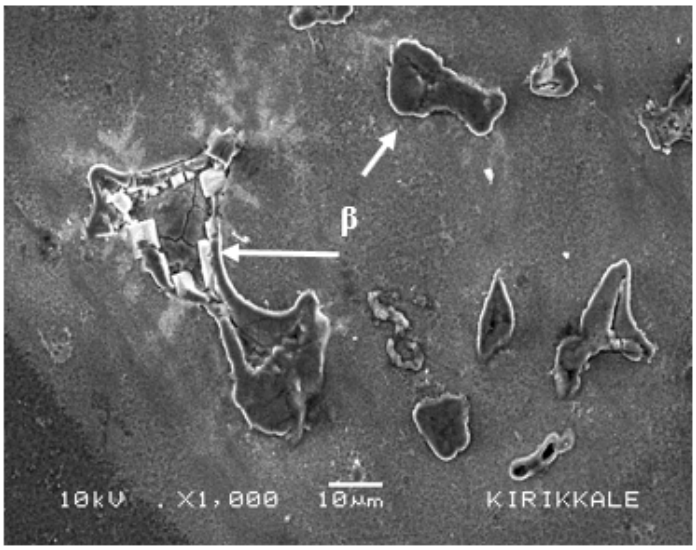


Figure 6: Surface morphology showing the disruption of continuity of the oxide film on AZ91 alloys by coarse β phase immersed in 3.5% NaCl solution for 1/4h [25].

Studies [30,36,53,73-77] have been carried out in various environments on the oxidation behavior of Mg-Al alloys.

Alloying Mg with Al changes the microstructure of matrice and the structure of the oxide film on the surface, increasing its resistance to the degrading effect of aggressive Cl- ions. Song and Atrens [36] reported that the AZ91 alloy film layer consists of three layers: the inner layer (rich in Al_2O_3), the middle layer (predominantly MgO), and the outer layer ($Mg(OH)_2$). In a more recent study, Es-

maily et al. [74] showed that the Al enrichment was evident in the inner layer of the film on the AZ91 alloy and that Al was present in the oxidized form. Both Song and Atrens [36] and Esmaily et al. [74] suggested that the positive effect of Al on the corrosion resistance of the Mg alloy was due to the protective properties of the Al-enriched layer inside the film. i.e. the formation of the Al_2O_3 layer in the interior could act as a passive film between surface of the alloy and the semi-passive film. However, in a study [25] on the corrosion behavior of AZ series Mg alloys (AZ21, AZ41, AZ61 and AZ91), it was observed that the corrosion resistance was lower in alloys with Al content above 4%. With the addition of Al, the globular shaped β phase in the AZ41 alloy has transformed into a coarser lamellar or partially divorced β eutectic net-like structure in the AZ91 alloy (Figure 4). Although AZ61 and AZ91 alloys contain more Al than AZ41 alloy, the reason for lower corrosion resistance could be based on the morphology and amount of the β phase and the interruption of the continuity of the oxide film by coarse β phase on the alloy surface. The interruption of the continuity of the oxide film on the alloy surface is shown in Figure 6, resulting from the coarsened intermetallic structure. MgO hydration occurs when exposed to water. Hydration of MgO has converted cubic MgO to hexagonal $Mg(OH)_2$, which has twice the volume of the oxide, resulting in significant degradation of the film and formation of unstable regions [53].

On the other hand, the growth rate of the oxide film formed on the β phase, such as $AlMg_x(OH)_y$, has occurred faster than that of the oxide film formed on the α-Mg [53]. Thus, volume changes between two oxide films ($Mg(OH)_2$ and $AlMgx(OH)_y$) could disrupt the interface between α-Mg and β phase. This phenomenon is shown schematically in Figure 7. The pressure created by the effect of the growth differences between the different oxide films could cause ruptures and the continuity of corrosion with long-term contact with the metal surface directly. Samaniego et al. [22] stated that in contrast to the beneficial effect of Al, Mg alloys containing a coarser β phase may corrode faster than alloys containing low Al if the protective effect of the pre-existing surface oxide film is disrupted.

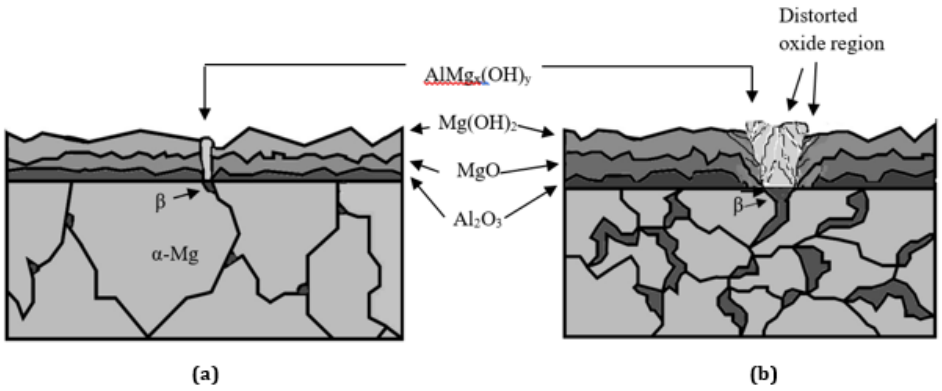


Figure 7: Schematic representation of oxide films (a) AZ21 and AZ41, (b) AZ61 and AZ91 [25].

Solidification rate

Under faster solidification conditions, networking structure of *β* phase has suppressed and transformed into a finer, more separated and isolated phases in AZ91 alloy as shown in Figure 8; [24].

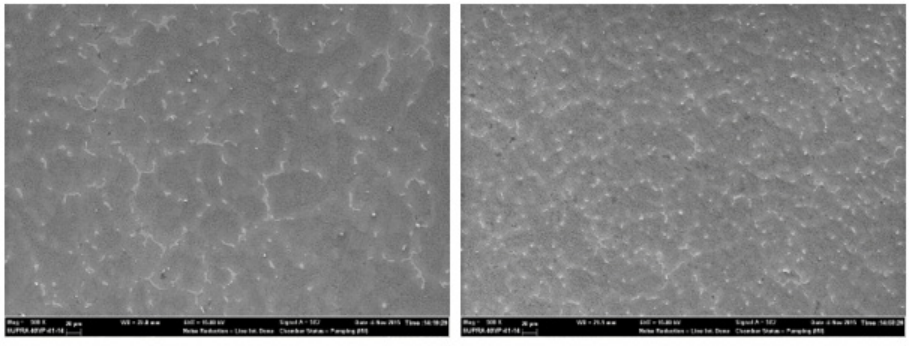


Figure 8: Microstructure of AZ91 alloy solidified at (a) 1.4 °C/sec (b) 8 °C/sec [24].

In some studies [17,26,27,34,35,42,44] given above sections on the corrosion behavior of the AZ series Mg alloys, it is inevitable that compositions and solidification conditions of the samples could differ since the samples were probably obtained from different suppli-

ers. For example, AZ31 and AZ61 alloys were compared with AZ91 alloy and discussions were made considering the Al content of the alloys ignoring the production route of the samples [17,27]. In the studies [17,27], AZ91 alloy was in the billet form whereas AZ31 alloy was in the rolled plate form. As mentioned above alloying elements [5,18,21,24,28-32,42-65], solidification rate [20,24,32,48] and production methods [33] significantly alter the microstructure which in turn affect the corrosion resistance of the alloy. The effect of solidification rate on AZ91 Mg alloys on corrosion has reported by Tanverdi [32]. As the solidification rate increased, the grain size of the AZ91 alloy has decreased, the amount of Al differed in the grain and grain boundaries, which segregated more at the grain boundaries. Therefore, the corrosion resistance of AZ91 alloy increased with increasing solidification rate [75-77].

Celik [78], Candan et al. [24] reported that the higher solidification rate could improve the corrosion resistance since it causes the grain size of the alloy to become finer. In a study [33], cast AZ91D Mg alloy has presented better corrosion resistance than its ingot form. Since AZ91D alloy is used in the pressure die casting processes, samples solidify much faster than its ingot form that probably promoted the formation of fully eutectic β phase supporting the argument. Celik [78], Candan et al. [24] have investigated the effect of solidification rate on microstructure and corrosion properties of AZ91 Mg alloys microalloyed with 0.5wt.% Pb or Ti. The results showed that the corrosion resistance of the alloy increased as the solidification rate increased. The higher corrosion resistance of the AZ91 alloy containing Pb or Ti has attributed to the smaller size of the β-phase network structure in the microstructure with the increase in solidification rate, as well as the suppression of β-phase formation by Pb and Ti.

Conclusion

In this review, the effects of microalloying elements and solidification rate on the β-phase structure on the corrosion of AZ series Mg alloys were examined by comparing the literature data with our previous and ongoing studies. At the same time, the corrosion properties of the alloys, the β phase structure and the oxide film-β phase relationship formed on the surface were also evaluated.

1) The review reveals that improving the corrosion behavior of AZ series Mg alloys could be achieved with modification of the β-phase by microalloying. Especially, Ti microalloying seems to be more promising.

2) The corrosion resistance of AZ series Mg alloys could be improved by increasing the solidification rate that resulted in a finer grain structure and formation of fully divorced β phase.

3) Volume changes between two different oxide films, $(Mg(OH)_2$ and $AlMg_x(OH)_y)$, formed on the surface of the alloys during corrosion could disrupt the interface between α-Mg and β-phase. The pressure created by the effect of the growth differences between the different oxide films could cause ruptures and the progression of corrosion with long-term contact to the metal surface.

4) Conflicting evaluations on the corrosion of AZ series Mg alloys may result from the production methods of the alloys used and the differences in the β phase morphology accordingly.

5) The β phase could play a role as an inhibitor or an enhancer of corrosion, depending on its structure and morphology. If the β phase network structure in the microstructure is in the form of fully divorced and narrow meshed net-like structure, the progression of corrosion may be blocked vice versa it may promote corrosion by micro galvanic coupling when it is in the lamellar morphology.

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