



Improvement of Corrosion Resistance in EZ33 Magnesium Alloy via Yttrium Addition

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Received:
31 December 2024

Accepted:
28 September 2025

Publish online:
31 December 2025

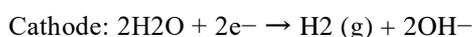
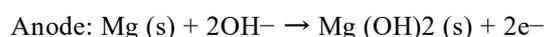
Abstract

In recent years, researchers have been investigating different alloying elements to improve the corrosion resistance of magnesium alloys. One such element is Yttrium (Y), which has shown promising results in enhancing the corrosion resistance of magnesium alloys, such as EZ33. The susceptibility of magnesium alloys to corrosion is a major challenge, as corrosion can lead to structural degradation and compromise the integrity of the material, especially in harsh environments. The influence of a single yttrium (Y) addition on the corrosion resistance of the EZ33 Mg alloy was examined in this work. The corrosion resistance was measured using the loss weight method, and the specimens' surfaces were examined using an optical microscope and a scanning electron microscope. The results showed that the corrosion rate decreased with the addition of Y, and microstructure examination illustrated that the corrosion product film formed at the alloy treated with Y was more stable than those formed at the microstructure of the base alloy. Moreover, the corrosion attacked the area where the intermetallic phases formed, which was shown via optical microscope images. Y can be an effective alloying element to enhance the durability of Mg alloys in structural or biomedical applications.

Keywords: Corrosion; Magnesium Alloys; Rare Earth.

INTRODUCTION

The application of magnesium (Mg) and its alloys in various industries has gained significant attention due to their lightweight properties and excellent mechanical strength. However, one major challenge associated with Mg alloys is their susceptibility to corrosion. Corrosion can lead to structural degradation and compromise the integrity of the material, particularly in harsh environments (Zhang et al., 2023). The standard potential of Mg is -2.37 V, which is lower than that of iron and aluminum. So, it is extremely susceptible to the formation of a Mg oxide film on its surface when exposed to air. This film is loose and porous, and it cannot protect the magnesium substrate as completely as the aluminum oxide film on Al alloys (Wu & Zhang, 2023). Mg alloys are prone to hydrogen evolution and corrosion behavior when exposed to a humid environment. Hydrogen ion reduction and cathodic hydrogen overpotential play a major role in the corrosion process of Mg alloys. The anodic and cathodic reactions in the corrosion process are as follows:



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Mg alloys suffer from more complicated transitional changes during the actual corrosion process. General corrosion, local corrosion, galvanic corrosion, and stress corrosion cracking are the primary forms of corrosion (Xu et al., 2022). To enhance the corrosion resistance of magnesium alloys, researchers have been investigating a variety of alloying elements in recent years (Çam & Günen, 2024; Tan & Ramakrishna, 2021; Wu & Zhang, 2023). Fast corrosion of Mg is caused by electrochemical nature, as a result in difference of surface area between the anodic area and the cathodic area, which leads to form electrochemical corrosion, called galvanic corrosion whereby electrochemical attacks only at the grain boundaries (Chen et al., 2022; Trivedi et al., 2016). However, in the case of Mg alloys such as EZ33, very little research has been done to measure the corrosion rate and failure mechanisms. The commercial interest in EZ33 alloy is growing due to its better mechanical properties and creep resistance compared to other Mg alloys. Also, the use of Mg alloys as high-strength materials is increasing in automotive and electronics industries (Siemionek et al., 2023; Wu & Zhang, 2023).

Previous study showed that both AJ62 and AE42 Mg alloys undergo selective corrosion, where Al and Al-rich intermetallic are preferentially corroded and the corrosion of these intermetallic phases is related to the microgalvanic effect between the intermetallic and the matrix (Li et al., 2014). Previous studies have shown that Mg alloys which containing rare earth (Mg-RE alloys) such as AE42 are highly resistance to general corrosion in comparison with other cast Mg alloys such as AZ91 (Mg-Al-Zn) (Lunder et al., 1995). One such rare earth element is Yttrium (Y), which has shown promising results in improving the corrosion resistance of Mg alloys (Li et al., 2021; Liu et al., 2017; Nouri et al., 2013). This study will delve into the effect of Yttrium addition on the corrosion resistance of EZ33 magnesium alloy, exploring its corrosion rate and effect on the specimen's surface. To achieve this aim, an immersion corrosion test was carried out using 3.5 wt. % of NaCl solution.

MATERIALS AND METHODS

The present investigation uses EZ33 magnesium alloy as a base alloy, which has a chemical composition of Mg-2wt. %Zn-1wt. %Zr-3wt. % RE (rare earth added as mish metal). Using an electrical resistance furnace with a steel crucible, the base alloy is melted using a cover-gas mixture of argon and 2 vol. % SF6. After the base alloy melts at around 730°C, yttrium (Y) is added in small pieces in contents of 0.25 wt.%, 0.50 wt.%, 0.75wt.%, 1wt.%, 1.25wt%, and 1.75wt% separately. Furthermore, to ensure dissolution of the alloying elements, the mixture is stirred for a few minutes. The molten metal is then poured into a steel mold preheated to 350°C. Three specimens are taken from each alloy for corrosion rate measurements, which are cut into plates (25 mm×15 mm×5 mm) and then ground gradually from 80 to 2000 grit finish using SiC abrasive papers, then washed with acetone and then dried. Subsequently, they are immersed into 3.5 wt. % NaCl aqueous solutions for 24, 48, 72, 96, 120, 144, 168, 192, and 216 h, at room temperature. The specimens were taken out of the test solution, washed with distilled water, and then dried. The corrosion weight loss is measured using a 1/10000 electronic balance, and the average corrosion rate is calculated using established calculations based on Faraday's law (Cramer et al., 2003):

$$CR = KW/AT\rho, \text{ (mm/year)} \quad (1)$$

Where K is a constant (8.76×10^4), T is the time of exposure (hours), A is the surface area of specimen (cm^2), W is mass loss (grams), and ρ is material density in g/cm^3 . Furthermore, an optical microscopy with a scale is used to observe corrosion effect at specimen's microstructure. Figure 1 shows experimental setup. Optical microscope (OM) and scanning electron microscope (SEM) were used to exam the surface and microstructure of the specimens after corrosion occurred.

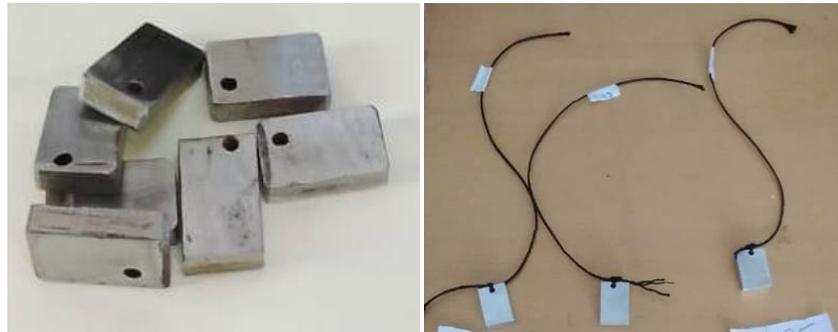


Figure: (1). Experimental specimens

RESULTS AND DISCUSSION

Figure 2 shows the surface morphologies of base alloy and base alloys treated with 1 wt. % of Y after 216 h of immersion in 3.5% NaCl solution, without remove corrosion products.

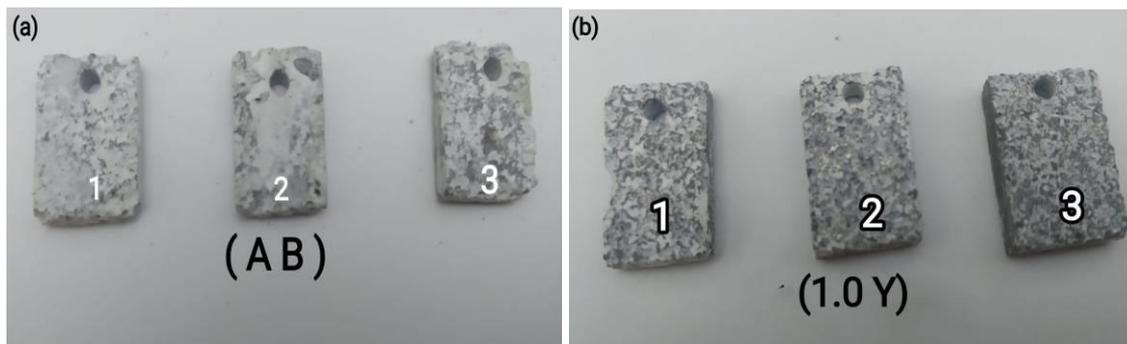


Figure: (2). Photographs of the alloys surface after 216 h immersion in 3.5% NaCl solution: (a) EZ33, (b) EZ33-1Y

As can be seen, the surfaces of the alloys extremely affected by the extension of immersion time, and the surface revealed significant pitting corrosion. General and localized corrosion, such as pitting and stress corrosion cracking, usually occurred in magnesium alloys (Jiang et al., 2023). Mg is highly reactive with oxygen and moisture. The corrosion process can involve the formation of magnesium hydroxide, which can lead to the breakdown of the alloy's structure. The presences of white deposits in the surface texture give the impression that the specimens' surface morphology has experienced of corrosion. Magnesium hydroxide and magnesium chloride, which are frequent byproducts of the corrosion of magnesium alloys in an environment containing chloride, may be the cause of the white deposits. In a sodium chloride solution, the corrosion process can be accelerated due to the presence of chloride ions, which can cause pitting corrosion. Pitting corrosion is a type of corrosion that occurs locally and causes tiny holes or pits to grow on the metal's surface (Mitchell et al., 2020). This type of corrosion can be particularly damaging because it can lead to a rapid loss of material and can weaken the structural integrity of the alloy. It has been reported that, Magnesium alloys have been shown to quickly produce a protective coating that stops additional corrosion in stagnant distilled water at room temperature. The protective film will be locally broken down by trace amounts of dissolved salts in water, especially chlorides or heavy-metal salts, which typically causes pitting. By entering the micropores and changing the $Mg(OH)_2$ into the more soluble $MgCl_2$, Cl ions in the solution hasten the disintegration of the protective layer and lead to the buildup of severe corrosion (Berezovets et al., 2021; Gray & Luan, 2002). The corrosion rates of the EZ33 magnesium alloy with various amounts of yttrium (Y) during 216 hours were deter-

mined and compared according to the experimental results presented in Figure 3, together with the related mass loss outcomes and conversion to corrosion rate in millimeters per year (mm/y) for each examined sample; the corrosion rate values for the various Y content additions are recorded. The average of the three samples examined is used to determine the average corrosion rates for each addition of Y content are also shown in Figure 3. As the corrosion rate decreases for alloys treated with Y in comparison to the base alloy, it is evident that the addition of Y enhances the corrosion resistance of EZ33 magnesium alloy. Previous studies showed that addition of Y into Mg alloys led to reduce the weight loss (meanwhile corrosion rate) of the specimens (L. Shi, 2022). Furthermore, the micro-galvanic effect between intermetallic phases formed around the α -Mg phase, where one phase acts as the cathode and the other as the anode, can be reduced by adding Y to the as-cast Mg–8Li–3Al–2Zn alloy, and Y addition also has a positive effect on preventing corrosion, which they attributed to the fact that Y addition makes the corrosion film more compact, which can prevent the base materials from being continuously attacked (M. Gu, 2016).

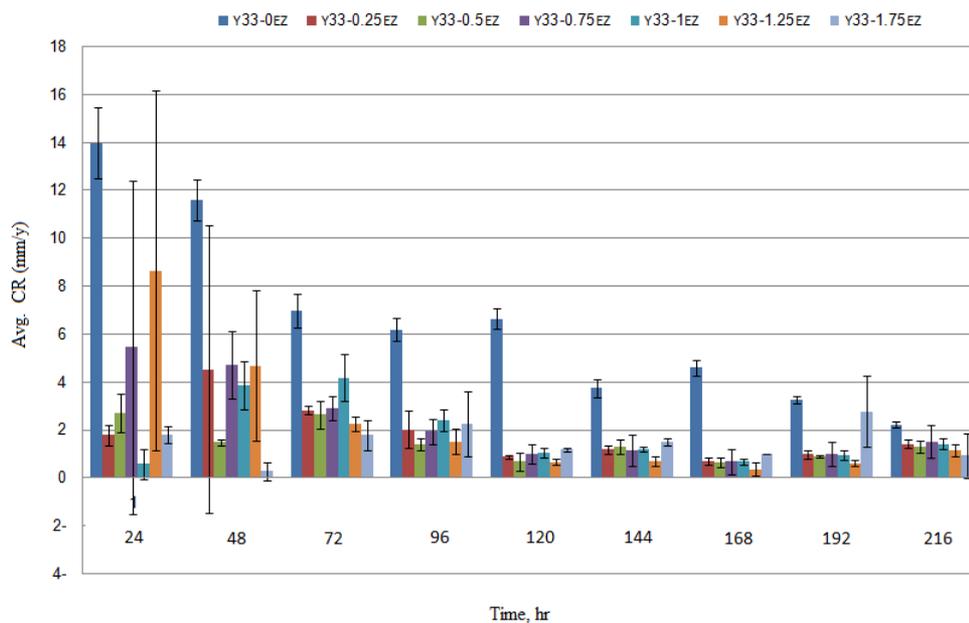


Figure: (3). Effect of Y addition on average corrosion rate of EZ33 magnesium alloy during 216 hrs.

However, the corrosion rates for EZ33-Y alloys differ; the alloy with a 0.75 wt. % Y addition has the highest corrosion rate. On the other hand, the alloy with 1.75 wt. % Y addition had the lowest corrosion rate. There is some heterogeneity in the trends and a volatility in the corrosion rates as the Y content rises from 0.25 wt. % to 1.75 wt. %. Furthermore, the corrosion rate of treated alloys fluctuated within the range of 0.259~8.654 mm/year and an average of 1.841 mm/year compared with 2.215~13.985 mm/year as a range of values and 6.574 mm/year as an average for the base alloy.

Optical microscope images for EZ33 magnesium alloy before and after corrosion attack without remove corrosion product, are shown in Figure 4 (a and b). Addition of Y into EZ33 magnesium alloy led to form intermetallic phases (Mg-Zn-Ce and Mg-Zn-Y-Ce), which crystallized along the grain boundaries as a kind of massive morphology (dark color in microstructure) beside α -Mg phase (matrix) (Ahmad et al., 2016).

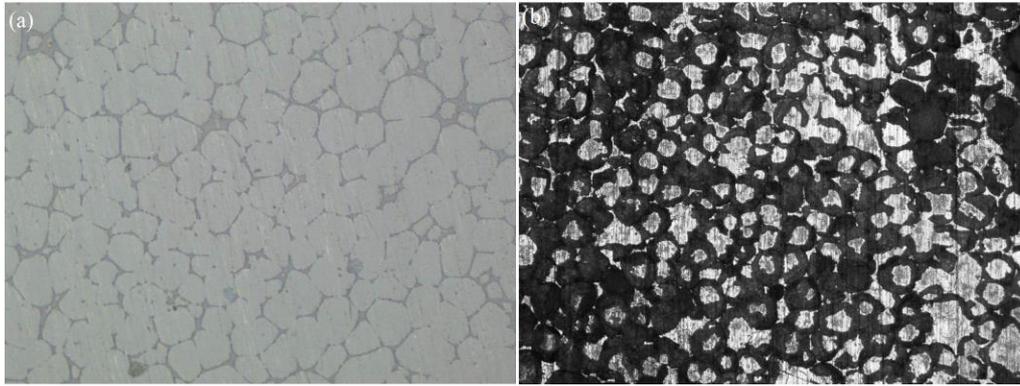


Figure: (4). The optical micrographs (a) base alloy, (b) base alloy after corrosion test, x100.

It is clear that corrosion has evidently transpired in the matrix next to the intermetallic phases at the grain boundary, where the corrosion residues are concentrated in intermetallic phases as dark-colored (heavily stained) next to the grain boundaries, which is where that phases are concentrated, meanwhile, the matrix (at α -Mg phase) is focused in the pale tint, indicated to that the corrosion has less of an impact in this area. The same results were noticed as the ZE41 magnesium alloy was examined (Neil et al., 2009). In addition, it was found that the secondary intermetallic phases of Mg-Zn-RE alloys formed around α -Mg matrix were dissolved when immersed in NaCl solution, due to that phases acted as cathode, contrary α -Mg phase matrix acted as anode (Li et al., 2023; Wu & Zhang, 2023).

The results extracted from SEM images for EZ33 alloy and EZ33-0.25 Y alloy (Fig.5) showed formation of cracks at the corrosion product film for base alloy Figure 5a, called mud cracks according to Neil, W., et al (Neil et al., 2009). The formation of these cracks may have occurred during the drying process of the samples during the 9-day test, which involved cleaning and draying them prior to each weight measurement in this study, or within SEM exam as Neil, W., et al reported. However, deep corrosion may result from the soaking solution infiltrating through these fissures and reaching the sample matrix. Otherwise, there were no visible cracks in the EZ33-0.25 Y microstructure, indicating that the corrosion product film is more cohesive than the base alloy.

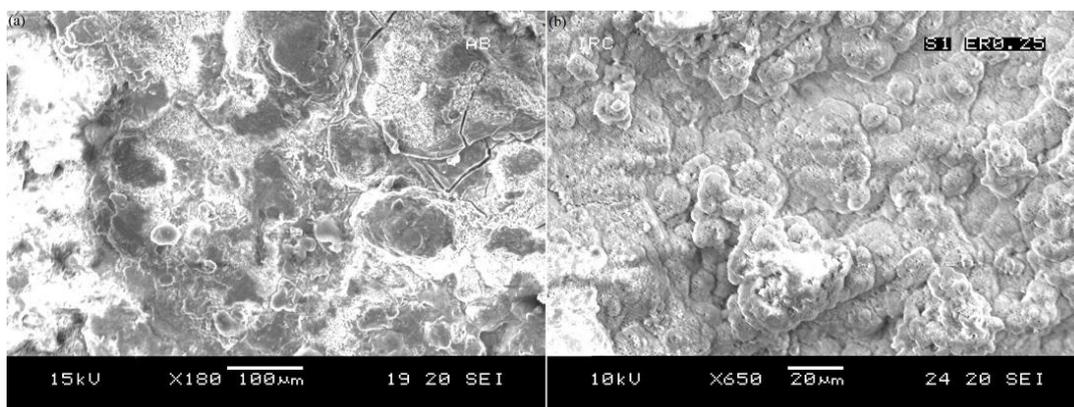


Figure: (3). SEM images of (a) base alloy, and (b) base alloy treated with 0.25 wt. % of Y.

CONCLUSION

The impact of Y addition on the corrosion resistance of EZ33 magnesium alloy was examined, and the following points can be summarized:

- Weight loss measurements of the specimens after the corrosion test showed that the base alloy improved with the addition of yttrium, as the corrosion rate increment.
- The average of alloys corrosion rates were around 6.57, 1.79, 1.44, 2.24, 1.80, 2.27, and 1.48 mm/year for EZ33, EZ33-0.25 Y, EZ33-0.5 Y, EZ33-0.75 Y, EZ33-1 Y EZ33-1.25 Y and EZ33-1.75 Y alloys respectively.
- Corrosion induces deep attack at the grain boundaries where the intermetallic phases formed, as demonstrated by optical and SEM pictures. Therefore, it can be inferred that the microstructure's key characteristics contribute to the EZ33-Y alloy's corrosion.

ACKNOWLEDGEMENT

The authors express their gratitude to the specialists at the Libyan Advanced Technology Center's metallurgical lab and the Industrial Research Center in Tajura.

Duality of interest: The authors declare that they have no duality of interest associated with this manuscript.

Author contributions: Contribution is equal between authors.

Funding: No specific funding was received for this work.

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