

Corrosion of Magnesium Alloys: A Review

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Received 26 Dec 2022, Accepted 25 Jan 2023, Available online 28 Jan 2023, Vol.11 (Jan/Feb 2023 issue)

Abstract

Because they have such a good ratio of strength to weight, magnesium alloys are becoming more popular for application in aircraft and transportation technologies. However, because of their corrosive properties—the primary obstacle—they are not widely used as aluminium alloys. This is due to the fact that corrosion is the primary problem. The processes of magnesium corrosion are investigated in this research, which also sets the framework for the development of novel alloys with improved corrosion characteristics.

Keywords: Magnesium alloys, Corrosion characteristics etc.

1. Introduction

Magnesium is one of the lighter metals, which enables magnesium alloys to be used in a wide number of applications that are otherwise unavailable [1]. Because of their remarkable strength-to-weight ratio, magnesium alloys are particularly well suited for lightweight applications such as those found in the aviation and transportation industries. As a direct consequence of this, the future looks bright for these light alloys. As a result of their superior resistance to corrosion, magnesium alloys, on the other hand, are not nearly as often used as aluminum alloys [2]. The principles of magnesium alloy corrosion and the underlying reasons of this phenomenon are investigated in this study. It is crucial for the development of new alloys to have a solid understanding of the processes of corrosion, since this provides the foundation for the creation of alloys with superior corrosion characteristics [3].

2. Properties and Applications of Mg alloys

Magnesium has one of the lowest densities of all metals, coming in at just 1.7 grams per cubic centimeter. Crystallographically speaking, it takes the hexagonal form, and its lattice parameters are as follows: $a = 3.20 \text{ \AA}$, $c = 5.20 \text{ \AA}$, and $c/a = 1.624$. The basal plane is the plane in which the particles are crammed together the most, and the axial ratio is just marginally higher than the value predicted by theory for incompressible spheres.

The atomic diameter is $3.20 \text{ \AA}$, which indicates that it has a size factor that is advantageous for a wide variety of solute elements like aluminum (Al), cerium (Ce), zinc (Zn), yttrium (Y), Zirconium (Zr), silver (Ag), and thorium (Th). Magnesium alloys offer excellent stiffness/weight ratios, are easy to cast, and have a high damping capability. Magnesium casting alloys outperform aluminum casting alloys in terms of strength/weight ratio [4]. Because magnesium and magnesium alloys are nonmagnetic, they have relatively high thermal and electrical conductivity, as well as superior vibration and shock absorption. Because it poses no toxicity risk, it may be moulded and manipulated using any known process. Magnesium is also extensively dispersed in the earth's crust as mineral deposits and in seawater. In reality, magnesium is the seventh element in terms of both terrestrial and cosmic abundance.

Magnesium is put to use in a wide variety of applications [5-7]. Magnesium is primarily used as castings in the aerospace and general transportation industries, but some wrought products are also used in certain applications. Magnesium is used as an alloying element in aluminum alloys and nodular cast iron. Magnesium is also used in some specific applications as a nodular cast iron. In these more sophisticated applications, elemental magnesium in its purest form is seldom put to use. Applications that do not need structural support are where magnesium alloys are most often used; nevertheless, it is anticipated that structural applications will emerge in the near future. Computer disk drives and magnetic card readers both need magnesium alloys that have been die cast in order to function [8-25].

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DOI: <https://doi.org/10.14741/ijmcr/v.11.1.10>

As an example of the standard identification for magnesium alloys, the alloy AZ91D may be used; the first two letters of the code represent the two most important alloying components in the alloy, which are: Metals may be identified by their chemical symbols, such as A-aluminum, E-rare earth, H-thorium, K-zirconium, M-manganese, Q-silver, S-silicon, and Z-zinc. As a consequence of this, an alloy consisting of aluminum and zinc is denoted by the letter AZ. The first two values below are, expressed as a percentage of total weight, the nominal concentrations of the two primary alloying elements. As a result, AZ91 is an alloy that consists of 1% zinc and 9% aluminum by weight. The letter "D" indicates that AZ91D is the fourth alloy in a sequence of alloys that each include 9% aluminum and 1% zinc in their composition. Because of their high strength-to-weight ratios, magnesium alloys are of particular interest to the aerospace and transportation industries. It is for this reason that these two industries have been a primary driving force behind the development of magnesium alloys. For instance, alloys that include thorium are used in the production of missiles and spacecraft [26-30]. Aluminum alloys are a fantastic substitute for magnesium alloys in the production of automotive components, and the use of newly developed corrosion-resistant alloys that have better ductility is becoming more widespread in the production of vehicles. Components made of die cast magnesium have been used for a variety of applications, including clutch housings, gear boxes, pedal brackets, instrument panel frames, and components of wheel hub covers. The engines produced by Volkswagen made use of magnesium alloys, and the components performed admirably [8-15].

Because magnesium is such a potent reducing agent, it is used in the process of extracting reactive metals like titanium, zirconium, and uranium from their ores. Titanium may be produced from tetrachloride if magnesium is present in the reaction. Due to their high cathodic free corrosion potentials, magnesium and magnesium alloys are often used as sacrificial anodes in order to protect a wide variety of other structural materials from the effects of corrosion. The anode alloys AZ63 and M1A (Mg-1.5Mn) are typical examples; they produce higher voltages than the aluminum or zinc equivalents, respectively. Magnesium, due to its high level of reactivity, is usually used in the anode position of batteries [9-10]. Magnesium-based batteries outperform traditional zinc-based batteries in a number of areas, including the following: 1) high cell voltage; 2) high energy density per unit weight and volume, especially at high power densities; 3) low discharge temperatures; and 4) high storage temperatures. As a direct result of this, the number of magnesium alloy anode batteries that are used in several main and reserve battery types around the globe has increased [31-36]. However, the use of magnesium alloys in construction applications is restricted due to the materials' poor resistance to corrosion, limited ability for strengthening, and inadequate ductility.

3. Corrosion Behaviour

Because magnesium has poor resistance to corrosion, the element's applications are severely limited. When certain metallic impurities are present or when the magnesium alloy is exposed to corrosive electrolyte species such as Cl⁻ ions, corrosion resistance is reduced [37-39].

The oxide coating on magnesium may provide significant protection against the air corrosion that magnesium is exposed to in rural settings, industrial settings, and maritime settings in that order. Even when they are exposed to marine atmospheres, magnesium alloys have a stronger resistance to atmospheric corrosion than mild steel does. This is the case regardless of the environment in which they are used. In general, the rate of corrosion of magnesium alloys is comparable to the rate of corrosion of aluminum and mild steel. This is because magnesium and aluminum are both metals that are relatively soft. Magnesium may be more resistant than some aluminum alloys under certain circumstances; yet, when it is employed in practical applications, magnesium is resistant to corrosion in solutions containing chloride. Magnesium may be more resistant than certain aluminum alloys under certain situations. Cast alloy AZ91 demonstrates higher resistance to the corrosive effects of salt spray as compared to aluminum and steel die. The resistance of high purity alloys, such as AZ91E, against the corrosion caused by salt water is ten to one hundred times greater than the resistance of standard quality alloys. In addition, high purity alloys are on par with or even superior than die cast aluminum alloy 380 and mild steel in terms of performance.

Magnesium and magnesium alloys often experience corrosion that begins in limited parts of the material first. When it comes to defining the corrosion morphology of magnesium and magnesium alloys, both the environmental conditions and the alloys themselves play an important effect. For example, when we evaluated the impacts of corrosion under air and submerged settings, we discovered that atmospheric corrosion is broader, but submerged corrosion is more confined. This was one of the findings of our study. This was one of the discoveries that came out of our research. However, the corrosion of magnesium alloys was more homogeneous [40-41]. The corrosion of magnesium of commercial quality was transgranular. In a way that is analogous, Makar and Kruger discovered that the corrosion of pure magnesium was non-uniform, resulting in an etched appearance. This was the cause of the etched appearance. On the other hand, AZ61 was attacked in a way that was relatively even, and rapidly solidified alloys were attacked in a manner that was more consistent than ordinary alloys.

There are two primary factors that contribute to the poor corrosion resistance of magnesium alloys [5-7]. To begin, the presence of the second phases and pollutants might lead to the development of internal galvanic corrosion. The second reason is that the passive hydroxide film that develops on magnesium is not as

stable as the passive films that grow on other metals, such as aluminium and stainless steel. The pitting resistance that it offers for magnesium and magnesium alloys is very average at best.

When magnesium alloys were subjected to circumstances of high humidity, their quick degradation was accelerated due to the presence of impurities such as iron, nickel, and copper, which were present in the material. They take on the function of cathodes when placed in an environment with corrosive conditions. It is very probable that they manufactured microcells by using an anodic magnesium matrix. The level of resistance that high-quality alloys have to salt water is substantially increased due to the fact that the alloys have been greatly improved (impurity concentrations are regulated to below threshold concentrations). Some of the ways that magnesium and magnesium alloys might corrode are described in the following paragraphs.

4. Galvanic Corrosion

Magnesium alloys have a much higher resistance to galvanic corrosion than other metals. Magnesium was found to have corroded in a confined region near to the cathode as a result of the existence of galvanic corrosion, which led to the detection of the corroded magnesium. Depending on the circumstances, cathodes may either be external (consisting of metals in touch) or internal (consisting of metals in contact) (impurities or second phases). When there is a large potential difference (between the anode and the cathode), a high conductivity (medium), poor polarizability of the anode and cathode, a large area ratio of the cathode to the anode, and a small distance between the anode and the cathode, the rate of galvanic corrosion is increased. Other factors that contribute to this increase include: a high conductivity (medium). Metals that have a hydrogen overvoltage that is low and an active corrosion potential are more susceptible to galvanic corrosion, while metals that have a hydrogen overvoltage that is high and an active corrosion potential are far less dangerous.

5. Intergranular Corrosion

Magnesium and magnesium alloys are resistant to the damaging effects of intercrystallite assault. The grain's interior is cathodic to the corrosion that occurs at the grain borders; therefore, the corrosion does not penetrate inwards [4, 18]. The area around the grain boundary became more corroded, and eventually the grain was undercut and lost.

6. Localized Corrosion

Because magnesium is naturally passive at its free corrosion potential, magnesium alloys are vulnerable to pitting corrosion in salt solutions that are either neutral or alkaline. This is because magnesium has a low free

corrosion potential. When the surrounding environment is not oxidizing, changes might take place in the chloride ion.

7. Corrosion Mechanisms

The corrosion processes that take place on the magnesium alloy's individual component phases are the root cause of the corrosivity of magnesium alloys. If an alloy has ingredients that are highly reactive with the environment in question, then the alloy will have a poor resistance to corrosion in that environment [42-45]. Particularly fascinating are the reactions that pure magnesium may produce. The corrosion of magnesium alloys may be understood on a fundamental level by considering these processes.

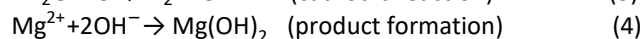
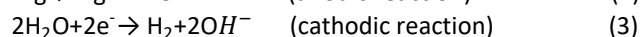
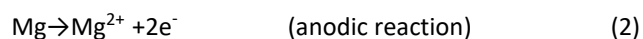
8. The Overall Corrosion Reactions

Although magnesium corrosion is not sensitive to oxygen because its dissolution in aqueous environments generally proceeds by an electrochemical reaction with water to produce magnesium hydroxide and hydrogen gas, the presence of oxygen is a significant factor in magnesium corrosion that occurs in the atmosphere. When corrosion occurs in surroundings containing water, it often includes a micro-galvanic connection between regions that are cathodic and anodic.

The overall corrosion reaction is:[4]



This overall reaction may be expressed as the sum of the following partial reactions:



In the anodic reaction (Eq. 2), which occurs in the intermediate phases, you will get the short-lived Mg^+ . The reduction process of hydrogen ions and the hydrogen overvoltage both play an important part in the corrosion of magnesium. The hydrogen evolution that occurs as a result of low overvoltage cathodes contributes significantly to the corrosion rate.

The reactivity of magnesium and the alloys of magnesium is the same when it comes to corrosion. During the anodic dissolution of Mg-Al-Zn alloys, magnesium was discovered to be the primary component that dissolved into the solution. A little amount of aluminium and zinc were also identified in the solution; however, zinc did not dissolve. Because of this, it can be concluded that the four reactions described above are still responsible for the corrosion processes that occur in magnesium alloys. In addition, it is impossible to rule out the possibility that the alloying elements, such as

aluminium and zinc, play a significant role in the reactions [46-48].

9. Thermodynamics

As is well known, the standard potential of magnesium has the lowest value of any of the engineering metals, as seen in Figure 1. At a temperature of 25 degrees Celsius, the magnesium standard electrode potential (Mg^{2+}/Mg) has a value of -2.37 Vnhe for magnesium divalent ions when bare magnesium metal is in contact with a solution containing magnesium.

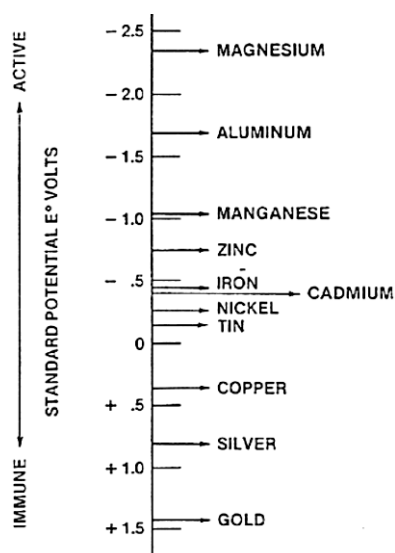


Fig. 1. Electromotive force series [1-3].

Within a solution of dilute chloride, the corrosion potential of magnesium is measured to be -1.7 Vnhe. The gap between the theoretical standard potential and the actual corrosion potential is caused by the development of magnesium hydroxide, also known as $Mg(OH)_2$, or magnesium oxide, also known as MgO . These films could have trace amounts of chlorides. When the pH is higher, namely more than nine, a precipitate layer of $Mg(OH)_2$ forms on top of the inner film.

When magnesium produces a coating of magnesium hydroxide, a certain degree of protection is supplied for higher pH ranges. This protection may be thought of as a barrier. The Pourbaix diagram provides the thermodynamics that regulate the creation of this film, and Figure 4 displays these thermodynamics. Assuming that the protective coating on magnesium is $Mg(OH)_2$ (which is most likely accurate but has not been verified yet), the Pourbaix diagram offers the thermodynamics that regulate the creation of this film. Figure 1 depicts the potential-pH diagram that was produced by Perrault using thermodynamic data that was inaccessible to Pourbaix. This diagram was used in the development of Perrault's work. According to Perrault, the thermodynamic data for the MgH_2 and the Mg^+ should have been included in the Pourbaix diagram. Following this, Perrault got to the

realization that it was impossible for a state of thermodynamic equilibrium to coexist between a magnesium electrode and a contact with an aqueous solution [49-50]. He came to this result after conducting an experiment.

A bigger quantity of reaction is taking place on the surface of magnesium, and the state of the magnesium's surface regulates the reaction that is taking place on the magnesium's surface. The cathodic evolution of hydrogen is the phase in the transformation of magnesium that determines the pace at which it occurs in acidic solutions containing both HCl and H_2SO_4 . They are able to create a surface that is free of film, and the values that were achieved via testing were constant. This is because Mg^+ was involved in the process of magnesium dissolving, which allowed for the consistency. Magnesium first became Mg^+ and then underwent a chemical reaction with H_2O , which resulted in the production of hydrogen and Mg^{2+} . This process, however, can only take place on the surface of magnesium that is not covered by a film. There is no entanglement of magnesium+ in the reaction chain when magnesium is present as a surface coating. An example of this would be magnesium present at a concentration of one part per million in sodium hydroxide.

Conclusion

The rate of corrosion, as indicated by the weight loss of magnesium in a concentrated chloride solution, was found to be 0.3 mm per year, according to a literature review. Improving the protective instinct of the passivation coating has proven to be the only method that has been successful in producing a magnesium alloy with a corrosion rate that is significantly lower than the inherent corrosion rate that is measured by the weight loss of magnesium, which is 0.3 mm/y. This has been the only technique that has proven to be effective. The corrosion rates for magnesium alloys that are calculated using electrochemical methods are often several orders of magnitude lower than the consistent corrosion rates that are approximated by the amount of weight lost. The study does not support recent claims that innovative Mg alloys have a higher corrosion resistance than Mg-based alloys that were reported in the past. These claims have been made recently.

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