

A Review on Corrosion and Corrosion Resistance of Mg based Alloys by using Coatings

Gopal Sahu
M. Tech Student

Turbomachinery. MATS University, Raipur

Prof. Brijesh Patel
M. Tech Coordinator

Turbomachinery. MATS University, Raipur

Abstract

Magnesium (Mg) alloys are light, structural and functional engineering materials with a high strength to weight ratio which are increasingly being used in the automotive, aerospace, and electronic and energy industries. However, magnesium is chemically active with an electrochemistry differing from most conventional engineering metals. This review provided some recent progress of the research on corrosion mechanisms of magnesium and its alloys and a basis for follow on research. Galvanic corrosion, pitting corrosion, intergranular corrosion, filiform corrosion, and crevice corrosion were discussed. Additionally there is a review of coatings for magnesium alloys and an analysis of alloys and coatings. Finally it recommends an option for a future coating that may prove to be the best coating for long lasting corrosion resistant parts.

Keywords: magnesium alloy, corrosion, types of corrosion, corrosion resistance, coating

I. INTRODUCTION

Magnesium is the lightest of all structural metals, being 35% lighter than aluminum and 78% lighter than steel. As a constituent of many minerals, it represents about 2% of mineral deposits and 0.13% of seawater. The lightweight characteristics, high strength-to-weight ratio and wide availability make magnesium alloys ideal for production of weight-sensitive components such as those in aircraft, cars, light trucks, and other transportation modes. However, when all vehicles are considered, the percentage of magnesium alloys used in mass-produced vehicles is relatively low, with an average of less than 5 Kg in a typical vehicle. The main reasons for the reluctance to use magnesium in mass-produced vehicles are related to its limitations in corrosion resistance and high temperature (creep) performance. Pure magnesium readily reacts in the presence of oxygen and water producing magnesium hydroxide. Unlike other similar metals, such as aluminum, the passivation film on magnesium could become very unstable in many environments, including neutral or acid ranges of pH. Additionally, magnesium is anodic to most engineering metals, making it very prone to severe galvanic corrosion when coupled with dissimilar metals, such as steel. Over the years, there have been significant advances in alloy development and as a result, new improved magnesium alloys have become commercially available. This has been possible due to additions of aluminum, zinc, manganese, for better corrosion resistance as well as additions of zirconium, rare earths, thorium, and silver for better elevated temperature mechanical properties all, in combination with the reduction of harmful impurities such as iron, nickel, copper during the alloy making process.

In recent years, the demand for lighter, more fuel-efficient vehicles, has spurred increased interest by automakers to consider the use of magnesium in more critical components such as engine blocks, engine cradles and transmission housings (See Figure1). This has led to the formation of special interests industrial consortiums to develop solutions to the technical and economical challenges facing wide applications of magnesium and its alloys. It has also been reported [4] that costly magnesium components in aircraft often experience significant corrosion issues which often require premature removal from service affecting the readiness, safety and cost of maintenance of aircraft (see Figure 2).

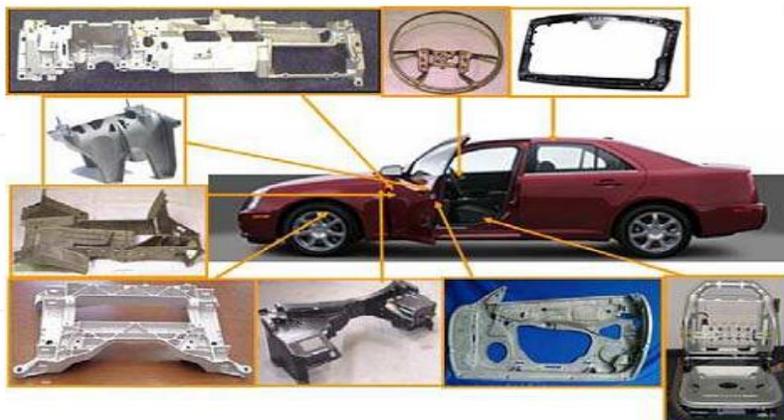


Fig. 1: Automotive applications for Magnesium alloys



Fig. 2: Corrosion damage in magnesium alloy castings used in rotor

II. TYPES OF CORROSION

A. Galvanic Corrosion:

When two dissimilar conducting materials in electrical contact with each other are exposed to an electrolyte, a current, called the galvanic current, flows from one to the other. Galvanic corrosion is that part of the corrosion that occurs at the anodic member of such a couple and is directly related to the galvanic current by Faraday's law. Magnesium alloys are susceptible to galvanic corrosion due to excessive levels of heavy metal or flux contamination, and to poor design and assembly practices. If these metals such as iron, nickel and copper, have a low hydrogen overvoltage, they can serve as efficient cathodes, consequently causing severe galvanic corrosion. Metals that combine an active corrosion potential with high hydrogen over potential such as Al, Zn, Cd and Sn, are much less damaging. The galvanic corrosion consisting of substrate and inner secondary phase is macroscopically observed as overall corrosion. The galvanic corrosion behavior and laws of AZ91D, AM50 and AM60 cast magnesium alloys coupled with A3 steel, 316L stainless steel, H62 brass and LY12 aluminum alloy.

The results show that the magnesium alloys act as anode and that their corrosion rates increase when they are coupled with the above mentioned four metals. The atmospheric galvanic effect of magnesium alloys coupled with A3 steel is the largest, while that of the magnesium alloys/LY 12 aluminum alloy couple is the lowest. And there is the following ranking of the atmospheric galvanic effects of different magnesium alloys: AZ91D>AM50 >AM60.

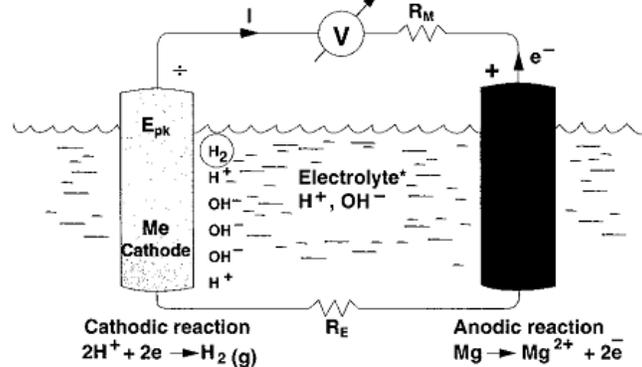


Fig. 3: Principle of galvanic corrosion

B. Pitting Corrosion:

Pitting corrosion is localized corrosion that creates small holes in the metal. It will occur at free corrosion potential of magnesium, when exposed to chloride ions in a non-oxidizing medium. For example, the as-extruded magnesium alloy AM60 was immersed in natural 3.5% NaCl solution, and the corrosion pits occurred on the surrounding of AlMn particles.

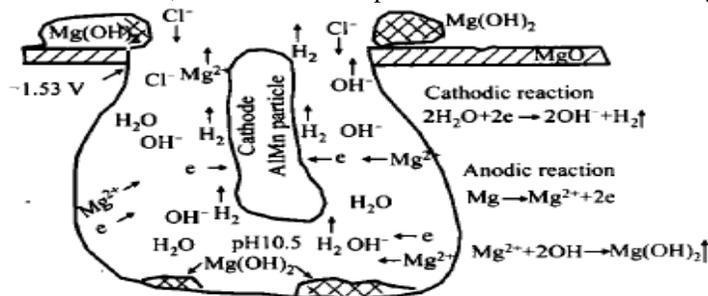


Fig. 4: Scheme of pitting corrosion mechanism for magnesium alloy AM60

- Anodic reaction: $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$
- Cathodic reaction: $2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2 \text{H}_2 \uparrow + 2 \text{OH}^-$
- Total reaction: $\text{Mg}^{2+} + 2 \text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{H}_2$

C. Intergranular Corrosion:

In Intergranular Corrosion, Localized attack at grain boundaries, with relatively little corrosion of the grains. As corrosion proceeds, the grains fall out and the metal or alloy disintegrates. Intergranular corrosion is a selective attack of a metal at or adjacent to grain boundaries. Intergranular corrosion (IGC) take places at the grain boundaries due to the precipitation of secondary phase. Recent studies, demonstrate that inter-granular corrosion can occur on magnesium alloys. For example, IGC of AE81 can be seen, because the grain bodies with a low Al concentration corrode at a faster rate than that in the Al-rich regions. Intergranular corrosion occurred after immersing aged AZ80 in 3.5% NaCl solution for 1 h (Fig.5).

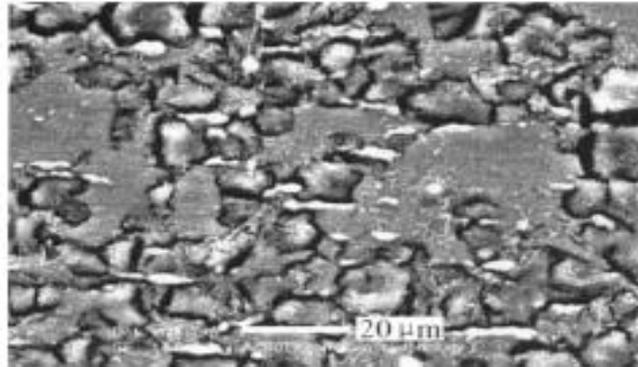


Fig. 5: Intergranular corrosion morphology of AZ80-T5 in 3.5%NaCl aqueous solution after 1 h.

D. Filiform Corrosion:

This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating. •Filiform corrosion is caused by active galvanic cells across the metal surface. Filiform corrosion often occurs on the metals surface such as steel, Al alloys and Mg alloys. It is typically associated with metal surfaces having an applied protective coating. It does not occur on bare pure Mg. the filiform corrosion of magnesium is driven by oxygen concentration between the head and tail as shown in fig.6.

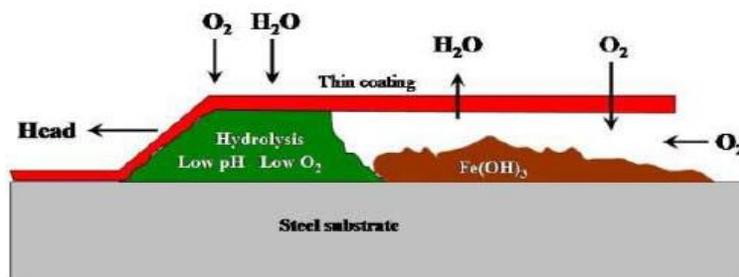


Fig. 6: Filiform Corrosion

E. Crevice Corrosion:

Crevice corrosion is the localized attack on a metal surface at, or immediately adjacent to, the gap or crevice between two joining surface. It is corrosion of metals in the metal-to-metal joint or metal-to-Non-metallic material. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. The major factors influencing crevice corrosion are : Crevice type, Crevice geometry, materials and environment (pH, Temp, halide ions & oxygen) and The formation of Mg hydroxide should influence the properties of the interface between the Mg and the solution in the crevice.



Fig. 7: Crevice corrosion

III. CORROSION RESISTANCE OF MAGNESIUM ALLOYS

Magnesium and Magnesium alloy are often thought of as rapidly corroding metals because of their active positions in both the electromotive force (EMF) series (Table 1) However, depending on the environment and certain design considerations, the corrosion of magnesium can be well within acceptable design limits. Knowledge of environmental factors that influence degradation, types of corrosion to which magnesium alloys are most susceptible, protection schemes, and design considerations can significantly minimize corrosion and increase use of this family of lightweight structural metals.

When unalloyed magnesium is exposed to the air at room temperature, a gray oxide forms on its surface. Moisture converts this oxide to magnesium hydroxide, which is stable in the basic range of pH values, but is not in the neutral or acid ranges as shown in the Pourbaix diagram (Fig. 8). The immunity region of the diagram is well below the region of water stability; as a result, in neutral and low pH environments magnesium dissolution is accompanied by hydrogen evolution. In basic environments, passivation is possible as a result of the formation of a Mg(OH)₂ layer on the metal surface. Since the films that form on unalloyed magnesium are slightly soluble in water, they do not provide long-term protection.

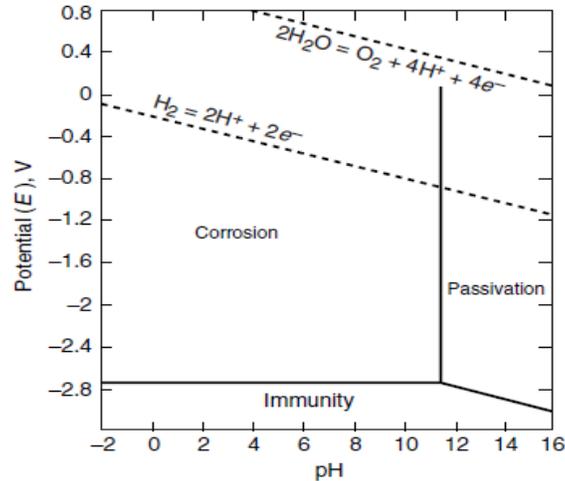


Fig. 8: Potential-pH (Pourbaix) diagram for the system of magnesium and water at 25 °C

Table 1: Standard reduction Potentials

Electrode	Reaction	Potential, V
Li, Li ⁺	Li ⁺ + e ⁻ → Li	-3.02
K, K ⁺	K ⁺ + e ⁻ → K	-2.92
Na, Na ⁺	Na ⁺ + e ⁻ → Na	-2.71
Mg, Mg ²⁺	Mg ²⁺ + e ⁻ → Mg	-2.37
Al, Al ³⁺	Al ³⁺ + e ⁻ → Al	-1.71
Zn, Zn ²⁺	Zn ²⁺ + e ⁻ → Zn	-0.76
Fe, Fe ²⁺	Fe ²⁺ + e ⁻ → Fe	-0.44
Cd, Cd ²⁺	Cd ²⁺ + e ⁻ → Cd	-0.40
Ni, Ni ²⁺	Ni ²⁺ + e ⁻ → Ni	-0.24
Sn, Sn ²⁺	Sn ²⁺ + e ⁻ → Sn	-0.14
Cu, Cu ²⁺	Cu ²⁺ + e ⁻ → Cu	0.34
Ag, Ag ⁺	Ag ⁺ + e ⁻ → Ag	0.80

IV. COATING TECHNOLOGIES

There are a number of technologies available for coating magnesium and its alloys. These include chemical conversion phosphate treatments electrochemical plating, conversion coatings, anodizing, hydride coatings, organic coatings, vapor-phase processes and cold spray. Each of these will be described in detail their advantages and disadvantages in table 2. For many applications a single coating process is successful enough to protect the magnesium alloy from corrosion, but for aerospace applications a combination of coatings is often required. A new coating technique that is still in development is cold spray using aluminum particles which is proving to be very successful for protection of magnesium parts. This new coating technique may be the best new coating for magnesium alloys that is environmentally friendly and long lasting.

Table – 2:
Advantages and Disadvantages of type of Coating

Coating Type	Advantages	Disadvantages
Chemical Conversion	Most effective and mature process and provides good corrosion resistance.	Cr ⁶⁺ in chromate bath is a highly toxic carcinogen facing restrictions with use.
Phosphate Treatments	Similar to chemical conversion in protection, but it is chromate Free	Coarse grains can cause cracks; heavy metal ions in solution can cause environmental pollution.
Anodizing	Can improve paint adhesion to metals,	Coatings are brittle and prone to cracking or shedding after collision.
Plating (electro and electroless)	Can improve corrosion resistance depending on what material is plated on surface.	Plating films have a weak adhesion to magnesium alloys. Issues with galvanic corrosion depending on type of metal used.
Sol-Gel	Can achieve better layering than electroless plating. Some testing has proved very successful using TiO ₂	Potential issues with galvanic corrosion depending on material used.
TAGNITE	Chromate free, better abrasion resistance, wet paint adhesion, impact resistance and fatigue properties.	Has not been proven as a complete protection. Useful more in touch up conditions where fine tolerances are required.
Paint	Provides a final protective coating when used in combination of other coating techniques.	Only provides additional protection when built up correctly with other coatings. Does not provide protection when chipped or cracked.
Cold Spray	Adheres well with fewer issues than plasma spray. Testing has proved improved corrosion resistance when high purity aluminum is used as sprayed material.	Still a new technology, not widely tested. Concerns with galvanic corrosion depending on coating material used.

V. CONCLUSION

Magnesium is a critically important metal in design of aerospace and automotive parts because of its desirable mechanical properties. The low density, good heat dissipation, good damping and good electro-magnetic shield all make it a top choice for design of aerospace and automotive parts. However, the varying operational environments require a material that is more corrosion resistant. Therefore, magnesium is alloyed with other materials to provide the best material for aerospace and automotive parts.

This paper provided a review of the different types of corrosion, their causes and effect on the Mg alloy. In addition to choosing an alloy that has the best properties for a specific application and can improve the life of a magnesium part, coatings are also critical to extending the life. Numerous different coatings and their advantages and disadvantages are explored in this paper. All provide good corrosion resistance, which are documented in Table 2.

REFERENCE

- [1] Levy M. Et al “Assessment of Some Corrosion Protection Schemes for Magnesium Alloy ZE41A-75”, Tri-service corrosion Conference, Atlantic City, 1989
- [2] Zheng, W., Osborne, R., Derushie, C., and Lo, J. (2005), “Corrosion Protection of Structural Magnesium Alloys”, paper 2005-01-0732 read to the SAE World Congress.
- [3] H.P. Godard, W.P. Jepson, M.R. Bothwell, and R.L. Lane, Ed., The Corrosion of Light Metals, John Wiley & Sons, 1967.
- [4] Harvey P. Hack (Ed.), Galvanic Corrosion, STP 978, ASTM, 1988.
- [5] Kelvii Wei Guo, (2010), A Review of Magnesium/Magnesium Alloys Corrosion and its Protection, City University of Hong Kong.
- [6] MAKER G L, KRUGER J. Corrosion of magnesium. International Material Review, 1993, 38: 138-153.
- [7] ELIEZER D, UZAN P, AGHION E. Effect of second phases on the corrosion behavior of magnesium alloys [J]. Material Science Forum, 2003, 419-422: 857-866.
- [8] GHALI E, DIETZEL W, KAINER K U. General and localized corrosion of magnesium alloys: a critical review. Journal of Materials Engineering and Performance (JMEPEG), 2004.
- [9] LUNDER, LEIN J.E, HESJEVIK S M, AWE T KR, NISANCIOGLU U. Corrosion morphologies on magnesium alloy A291. Werkstoffe und Korrosion, 1994.45: 331-340.
- [10] DEXTER S C. Metals Handbook (Vol.13) [M]. 9th Ed. OH: ASM International, 1987. 106.