Corrosion of Magnesium and Magnesium Alloys

Abstract:

The corrosion resistance of magnesium or magnesium parts depends on similar factors that are critical to other metals. However, because of the electrochemical activity of magnesium, the relative importance of some factors is greatly amplified.

This article will discuss the effects of heavy-metal impurities, the type of environment (rural atmosphere, marine atmosphere, elevated temperature etc), the surface condition of the part (such as as cast, treated, and painted), and the assembly practice. In some environments magnesium part can be severely damaged unless galvanic couples are avoided by proper design or surface protection...

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Unalloyed magnesium is not extensively used for structural purposes. Consequently, the corrosion resistance of magnesium alloys is of primary concern. Two major magnesium alloy systems are available to the designer.

The first includes alloys containing 2 to 10% Al, combined with minor additions of zinc and manganese. These alloys are widely available at moderate costs and their mechanical properties are good up to 95 to 120°C. Beyond this, the properties deteriorate rapidly as temperature increases.

The second group consists of magnesium alloyed with various elements (rare earth, zinc, thorium, silver etc) except aluminum, all containing a small but effective zirconium content that imparts a fine grain structure and thus improved mechanical properties. These alloys generally possess much better properties at elevated temperature, but their more costly alloying additions, combined with the specialized manufacturing technology required, result in significantly higher costs.

Chemical Composition

Six elements (aluminum, manganese, sodium, silicon, tin and lead) plus thorium, zirconium, beryllium, cerium, praseodymium and yttrium are known to have little if any effect on the basic saltwater corrosion performance of pure magnesium when present at levels exceeding their solid solubility or up to a maximum of 5%.

Four elements (cadmium, zinc, calcium and silver) have to mild-to-moderate accelerating effects on corrosion rates, whereas four others (iron, nickel, copper and cobalt) have extremely deleterious effects because of their low...
solid solubility limits and their ability to serve as active cathodic sites for the reduction of water at the sacrifice of elemental magnesium.

The effects of increasing iron, nickel and copper contamination on the standard ASTM salt spray performance of die cast AZ91 test specimens as compared to the range of performance observed for cold-rolled steel and die-cast aluminum alloy 380 samples. Such results have led to the definition of the critical contaminant limits for two magnesium-aluminum alloys in both low- and high-pressure cast form and the introduction of improved high-purity versions of the alloys.

The iron tolerance for the magnesium-aluminum alloys depends on the manganese present, a fact suggested many years ago but only recently proved. For AZ91 with a manganese content of 0.15%, this means that the iron tolerance would be 0.0048% (0.032 x 0.15%). It should also be noted that the nickel tolerance depends strongly on the cast form, which influences grain size, with the low-pressure cast alloys showing just 10-ppm tolerance for nickel in the as cast (F) temper. The zirconium as an alloying element is effective in this case because it serves as a strong grain refiner for magnesium alloys and it precipitates the iron contaminant from the alloys before casting. However, if alloys containing more than 0.5 to 0.7% Ag or more than 2.7 to 3% Zn are used, a sacrifice in corrosion resistance should be expected. Nevertheless, when properly finished, these alloys provide excellent service in harsh environments.

**Heat treating, Grain Size and Cold-Work Effects**

Using controlled purity AZ91 alloy cast in both high-and-low pressure forms, the contaminant tolerance limits have been defined as cast (F), the solution-treated (T4, held 16h at 410°C and quenched), and the solution treated and aged (T6, held 16h at 410°C, quenched and aged 4h at 215°C).

In the case of the high-iron-containing AZ91C, none of the variations tested significantly affected the poor corrosion performance resulting from an iron level 2 to 3 times the alloy tolerance.

In the case of the high-purity alloy, however, the T5 and T6 tempers consistently gave salt spray corrosion rates under 0.25 mm/yr, whereas the as-cast and solution -treated samples exhibited an inverse response to grain size and/or the grain-refining agents.

Cold working of magnesium alloys, such as stretching or bending, has no appreciable effect on corrosion rate. Shot- or grit-blasted surfaces often exhibit poor corrosion performance, not from induced cold work but from embedded contaminants.

**Environmental Factors**

**Atmospheres.** A clean, unprotected magnesium alloy surface exposed to indoor or outdoor atmospheres free from salt spray will develop a gray film that protects the metal from corrosion while causing only negligible losses in mechanical properties.

Chlorides, sulfates and foreign materials that hold moisture on the surface can promote corrosion and pitting of some alloys unless the metal is protected by properly applied coatings. The surface film that ordinarily forms on magnesium alloys exposed to the atmosphere gives limited protection from further attack. Unprotected magnesium and magnesium alloy parts are resistant to rural atmospheres and moderately resistant to industrial and mild marine atmospheres provided they do not contain joints or recesses that entrap water in association with an active galvanic couple.

Corrosion of magnesium alloys increases with relative humidity. At 9.5% humidity, neither pure magnesium nor any of its alloys exhibit evidence of surface corrosion after 18 months. At 30% humidity, only minor corrosion may occur. At 80% humidity the surface may exhibit considerable corrosion. In marine atmospheres heavily loaded with salt spray, magnesium alloys require protection for prolonged survival.

**Fresh Water.** In stagnant distilled water at room temperature, magnesium alloys rapidly form a protective film that prevents further corrosion. Small amounts of dissolved salts in water, particularly chlorides or heavy metal salts, will break down the protective film locally, which usually results in
Dissolved oxygen plays no major role in the corrosion of magnesium in either freshwater or saline solutions. The corrosion of magnesium alloys by pure water increases substantially with temperature.

**Salt Solutions.** Severe corrosion may occur in neutral solutions of salts of heavy metals, such as copper, iron and nickel. Such corrosion occurs when the heavy metal, the heavy metal basic salts or both plate out to form active cathodes on the anodic magnesium surface. Chloride solutions are corrosive because chlorides, even in small amounts, usually break down the protective film on magnesium. Fluorides form insoluble magnesium fluoride and consequently are not appreciable corrosive. Oxidizing salts, especially those containing chlorine or sulfur atoms, are more corrosive than nonoxidizing salts, but chromates, vanadates, phosphates and many others are film forming and thus retard corrosion, except at elevated temperatures.

**Acids and Alkalis.** Magnesium is rapidly attacked by all mineral acids except hydrofluoric acid (HF) and H₂CrO₄. Hydrofluoric acid does not attack magnesium to an appreciable extent, because it forms an insoluble, protective magnesium fluoride film on the magnesium, however pitting develops at low acid concentrations. Pure H₂CrO₄ attacks magnesium and its alloys at a very low rate.

**Organic compounds.** Aliphatic and aromatic hydrocarbons, ketones, ethers, glycols and higher alcohols are not corrosive to magnesium and its alloys. Ethanol causes slight attack, but anhydrous methanol causes severe attack. The rate of attack in the latter is reduced by the presence of water. Pure halogenated organic compounds do not attack magnesium at ambient temperatures. At elevated temperatures or if water is present, such compounds may cause severe corrosion, particularly those compounds having acidic final products.

**Gases.** Dry chlorine, iodine, bromine and fluorine cause little or no corrosion of magnesium at room or slightly elevated temperature. Even when it contains 0.02% H₂O, dry bromine causes no more attack at its boiling temperature (58°C) than at room temperature. The presence of a small amount of water causes pronounced attack by chlorine, some attack by iodine and bromine, and negligible attack by fluorine.

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