# Corrosion Behavior

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THE CORROSION RESISTANCE of a magnesium or a magnesium-alloy part depends on many of the same factors that are critical to other metals. However, because of the electrochemical activity of magnesium (Table 1), the relative importance of some factors is greatly amplified. This article discusses the corrosion of magnesium in various service environments, as influenced by alloy content, heavy-metal impurities, fabricated form, microstructure, surface condition, and assembly practice. In some environments, a magnesium part can be severely damaged unless galvanic couples are avoided by proper design or surface protection. This aspect is discussed in detail in the section "Galvanic Corrosion" in this article. Protective finishing is discussed in the article "Cleaning and Finishing" in this Handbook.

**Commercially Pure Magnesium.** When a freshly prepared surface of magnesium is exposed to the atmosphere at room temperature, the first reaction is the formation of magnesium oxide. If moisture is present, the magnesium oxide is converted to magnesium hydroxide. This compound has an equilibrium pH of 10.4 and is therefore stable in the presence of most bases, but it rapidly breaks down in the presence of acids. The Pourbaix diagram shown in Fig. 1 summarizes this behavior. As seen in the figure, the whole domain of stability of magnesium is well below that of water. Therefore, magnesium dissolves as $Mg^+$ and $Mg^{2+}$ with accompanying hydrogen evolution. At pH values above 8.5 and up to 11.5, it can form a more

or less protective oxide or hydroxide layer. Above a pH of 11.5, the protective qualities of the $Mg(OH)_2$ layer dominates corrosion behavior, establishing a passivation zone.

As shown in Table 2, the corrosion potential of magnesium in aqueous solutions is usually about 1 V more positive than the standard potential of $-2.37$ V NHE (in acid solutions) or $-2.69$ V (in alkaline solutions). This means that the metal corrodes with an accompanying fairly stable film of rather low conductivity even in acid solutions. This film is so thin that it cannot be detected by any physical investigation methods. At pH > 9, a thick white film of precipitated $Mg(OH)_2$ is formed outside this inner film. The presence of oxidants such as chromate also promotes the formation of a protective layer and tends to shift potentials in the noble direction.

The films that form on magnesium are slightly soluble in water and do not provide protection over long periods. They also break down in the presence of certain ions, such as chloride, bromide, sulfate, and chlorate, or in water exposed to acid gases, such as $CO_2$. Increasing temperature also increases the corrosion rate of commercially pure magnesium. Table 3 and Fig. 2 present

corrosion data of pure magnesium in various media.

Magnesium is anodic to almost all other metals. Therefore, galvanic corrosion is a potential problem in the presence of electrolytes. There exists a quantitative relation between the corrosion of magnesium and the presence of cathodic impurities. For example, there is a "tolerance limit" for iron above which the corrosion rate in salt water increases dramatically (Fig. 3).

**Magnesium Alloys.** Unalloyed magnesium is not extensively used for structural purposes. Consequently, it is the corrosion resistance of magnesium alloys that is of primary concern. If a magnesium-alloy part is to perform satisfactorily in a particular application, it must not only be designed to meet the mechanical requirements, but environmental factors, finishing, and assembly methods must also be properly assessed. This article describes in detail the causes of past corrosion failures and the measures available to prevent such failures in future applications.

## Metallurgical Factors

The metallurgical factors that influence the corrosion behavior of any particular magnesium part are dependant on the combined effects of its chemical composition and its microstructure. While these effects are not mutually exclusive, they are discussed separately for the sake of convenience.

### Table 1 Standard reduction potentials

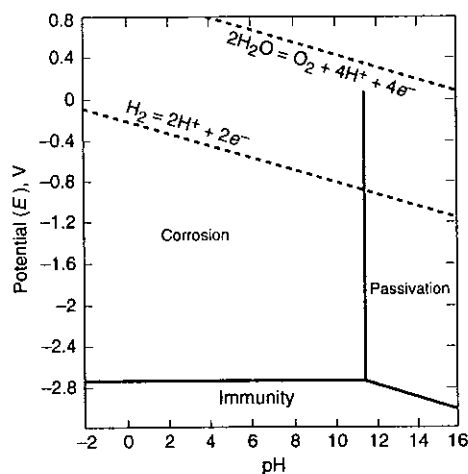| Electrode | Reaction | Potential, V |
|---|---|---|
| Li, Li$^+$ | Li$^+$ + $e^-$ → Li | −3.02 |
| K, K$^+$ | K$^+$ + $e^-$ → K | −2.92 |
| Na, Na$^+$ | Na$^+$ + $e^-$ → Na | −2.71 |
| Mg, Mg$^{2+}$ | Mg$^{2+}$ + $e^-$ → Mg | −2.37 |
| Al, Al$^{3+}$ | Al$^{3+}$ + $e^-$ → Al | −1.71 |
| Zn, Zn$^{2+}$ | 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 |



**Fig. 1** Potential-pH (Pourbaix) diagram for the system magnesium-water at 25 °C, showing the theoretical domains of corrosion, immunity, and passivation

### Table 2 Rest potential of magnesium electrodes under various aqueous solutions

| Electrolyte | $E_R$ (vs NHE) |
|---|---|
| $N$ NaCl | −1.72 |
| $N$ Na$_2$SO$_4$ | −1.75 |
| $N$ Na$_2$CrO$_4$ | −0.96 |
| $N$ HCl | −1.68 |
| $N$ HNO$_3$ | −1.49 |
| $N$ NaOH | −1.47 |
| $N$ NH$_3$ | −1.43 |
| Ca(OH)$_2$ saturated | −0.95 |
| Ba(OH)$_2$ saturated | −0.88 |

$N$, normal. Source: Ref 1

**Chemical Composition.** Figure 4 shows the effects of 14 elements on the saltwater corrosion performance of magnesium in binary alloys with increasing levels of the individual elements. Six of the elements included in Fig. 4 (aluminum, manganese, sodium, silicon, tin, and lead) plus thorium, zirconium, beryllium, cerium, praseodymium, and yttrium are known to have little if any deleterious 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 in Fig. 4 (cadmium, zinc, calcium, and silver) have 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. Although cobalt is seldom encountered at detrimental levels and cannot be introduced even through the long immersion of cobalt steels in magnesium melts, iron, nickel, and copper are common contaminants that can be readily introduced through poor molten-metal handling practices. These elements must be held

to levels under their individual solubility limits (or their activity moderated through the use of alloying elements such as manganese or zinc) to obtain good corrosion resistance.

Figure 5 illustrates the effect of increasing iron, nickel, and copper contamination on the standard American Society for Testing of Materials (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 magnesium-aluminum alloys in both low- and high-pressure cast form and the introduction of improved high-purity versions of the alloys. Table 4 lists the critical contaminant limits for magnesium die castings.

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 × 0.15%) (Ref 4).

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 a 10 ppm tolerance for nickel in the as-cast (F) temper. Therefore, alloys intended for low-pressure cast applications should be of the lowest possible nickel level. The low tolerance limits for the contaminants in AM60 alloy when compared to AZ91 alloy can be related to the absence of zinc. Zinc is thought to improve the tolerance of magnesium-aluminum alloys for all three contaminants, but it is limited to 1 to 3% because of its detrimental effects on microshrinkage porosity and its accelerating effect on corrosion above 3%.

For the rare earth, thorium, and zinc alloys containing zirconium, the normal saltwater corrosion resistance is only moderately reduced when compared to high-purity magnesium-aluminum alloys—0.5 to 0.76 mm/year (20 to 30 mils/year) as opposed to less than 0.25 mm/year (10 mils/year) in 5% salt spray—but contaminants must again be controlled. The zirconium alloying ele-
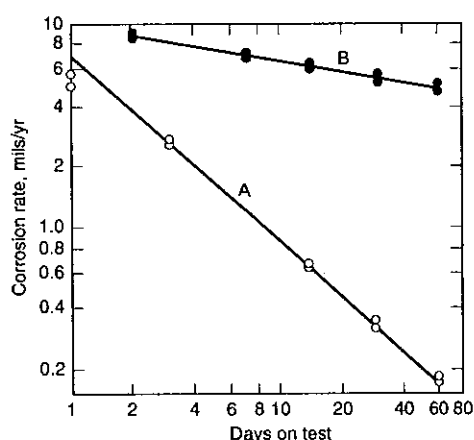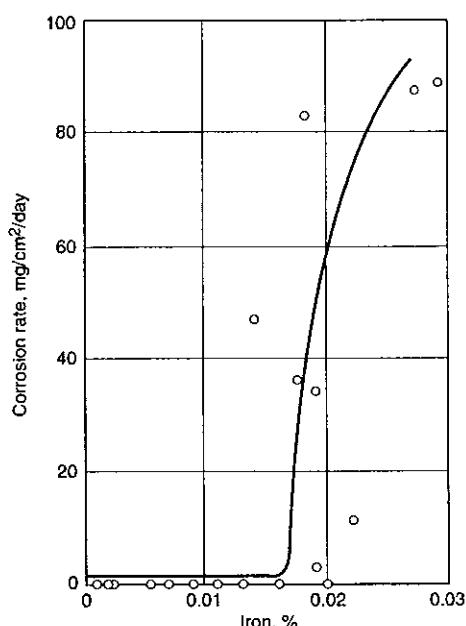
Fig. 2 Corrosion rates as a function of time for commercially pure magnesium in A, distilled water vented to air through a caustic trap; and B, distilled water exposed to atmospheric $CO_2$. Source: Ref 3

Fig. 3 Effect of iron content on the corrosion rate of commercially pure magnesium subjected to alternate immersion in 3% NaCl. Source: Ref 4
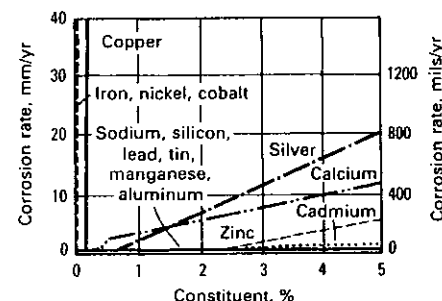
Fig. 4 Effect of alloying and contaminant metals on the corrosion rate of magnesium as determined by alternate immersion in 3% NaCl solution. Source: Ref 4

**Table 3 Corrosion rate of commercially pure magnesium in various media**

| Medium | Corrosion rate mm/yr | mils/yr |
|---|---|---|
| Humid air | $1.0 \times 10^{-5}$ | 0.0004 |
| Humid air with condensation | $1.5 \times 10^{-2}$ | 0.6 |
| Distilled water | $1.5 \times 10^{-2}$ | 0.6 |
| Distilled water exposed to acid gases | 0.03–0.3 | 1.2–12 |
| Hot deionized water (100 °C) (14 days stagnant immersion) | 16 | 640 |
| Hot deionized water inhibited with 0.25 NaF | $5.5 \times 10^{-2}$ | 2.2 |
| Seawater | 0.25 | 10 |
| 3M MgCl₂ solution | 300 | 12,000 |
| 3m NaCl (99.99% high-purity magnesium with <10 ppm Fe) | 0.3 | 12 |

Grades 9980, 9990, 9991, 9995, 9998 except for NaCl solution. Source: Compiled from Chapters 21–32 in Ref 2
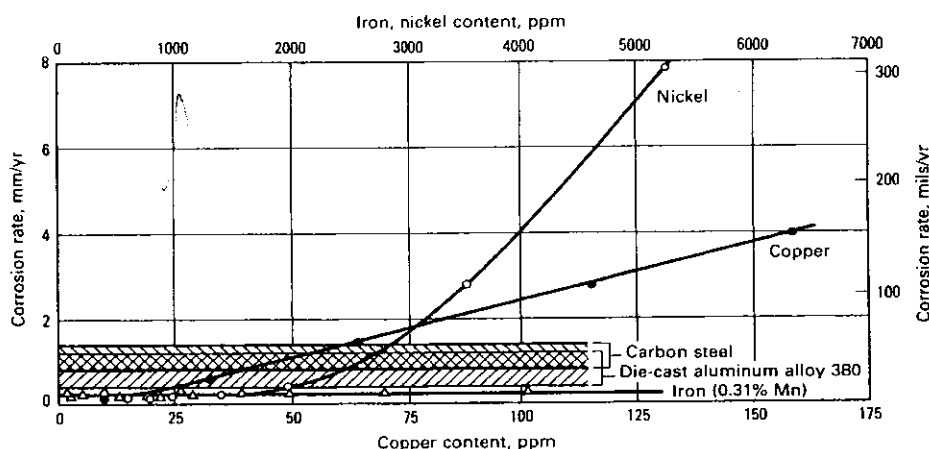
Fig. 5 Effect of nickel and copper contamination on the salt-spray-corrosion performance of die-cast AZ91 alloy. Source: Ref 5

ment is effective in this situation 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 (Fig. 4). Nevertheless, when properly finished, these alloys provide excellent service in harsh environments.

**Heat-Treating, Grain-Size, and Cold-Work Effects.** Heating or aging temperature also exerts an effect on salt-spray corrosion rate of die-cast commercial magnesium-aluminum alloys, and this is an interactive effect with contaminant levels. Figure 6 shows the adverse effect of aging temperature on salt-spray corrosion rate. Alloys having higher contents of residual elements (iron, nickel, and copper) were much more adversely affected by temperature exposure.

Using controlled-purity AZ91 alloy cast in both high- and low-pressure forms, the contaminant tolerance limits have been defined as summarized in Table 5 for the as-cast (F), the solution-treated (T4, held 16 h at 410 °C, or 775 °F, and quenched), and the solution treated and aged (T6, held 16 h at 410 °C, or 775 °F, quenched, and aged 4 h at 215 °C, or 420 °F).

Table 6 compares the average 5% salt-spray corrosion performance of sand-cast samples produced in a standard AZ91C and a high-purity

AZ91E composition. The alloys were cast with and without standard grain-refining practices used to evaluate physical and compositional effects. The cast samples were then tested in the F, T4, T6, and T5 (aged 4 h at 215 °C, or 420 °F) tempers. With 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. With the high-purity alloy, however, the T5 and T6 tempers consistently gave salt-spray corrosion rates under 0.25 mm/year (10 mils/year), whereas the as-cast and solution-treated samples exhibited an inverse response to grain size and/ or the grain-refining agents. Welds on aluminum-zinc alloys should be solution treated and aged to obtain good corrosion resistance in harsh environments and to reduce the risk of failure due to stress-corrosion cracking (SCC).

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 iron contaminants. Acid pickling to a depth of 0.01 to 0.05 mm (0.0004 to 0.002 in.) can be used to remove reactive contaminants, but unless the process is carefully controlled, reprecipitation of the contaminant is possible, particularly with steel-shot residues. Therefore, fluoride anodizing is often used when complete removal of the contaminant is essential.

**Causes of corrosion failure** typically include heavy-metal contamination, blast residues, flux inclusions, and galvanic attack.

*Heavy-metal contamination* often results in general pitting attack that is unassociated with fasteners or dissimilar-metal attachments. The rate of attack on unpainted surfaces is essentially unaltered by surface condition, that is, freshly sanded or machined, acid pickled, or chrome treated. The iron, nickel, or copper content will analyze in excess of the tolerance limit for one

### Table 4 Contaminant tolerances and manganese limits for magnesium die castings

| Alloy | Critical contaminant limit (max), % | | | Mn limit, % |
|---|---|---|---|---|
| | Cu | Ni | Fe | |
| AM50A | 0.010 | 0.002 | 0.004(a) | 0.26–0.6(a) |
| AM60A | 0.35 | 0.03 | ... | 0.13–0.6 |
| AM60B | 0.10 | 0.002 | 0.005(a) | 0.24–0.6(a) |
| AS41A | 0.06 | 0.03 | ... | 0.20–0.50 |
| AS41B | 0.02 | 0.002 | 0.0035 | 0.35–0.7 |
| AZ91A | 0.10 | 0.03 | 0.30(b) | 0.13–0.50 |
| AZ91B | 0.35 | 0.03 | 0.3(b) | 0.13–0.50 |
| AZ91D | 0.30 | 0.002 | 0.005(a) | 0.15–0.50(b) |

Per ASTM B 94. (a) In alloys AS41B, AM50A, AM60B, and AZ91D, if either the minimum manganese limit or the maximum iron limit is not met, then the iron/manganese ratio shall not exceed 0.010, 0.015, 0.021, and 0.032, respectively. (b) Not specified, but included in the limits for "other metals"



**Fig. 6** Effect of heating temperature on corrosion rate of die-cast AZ91D and AM60B in salt-spray test for 10 days according to ASTM B 117. Data are for test specimens that were heated for 0.5 to 36 h. Source: Ref 7

### Table 5 Contaminant tolerance limits versus temper and cast form for AZ91 alloy

High-pressure die cast, 5–10 μm average grain size; low-pressure cast, 100–200 μm average grain size

| Contaminant, % | Critical contaminant limit(a) | | | |
|---|---|---|---|---|
| | High pressure, | Low pressure | | |
| | F | F | T4 | T6 |
| Iron | 0.032 Mn | 0.032 Mn | 0.035 Mn | 0.046 Mn |
| Nickel | 0.0050 | 0.0010 | 0.001 | 0.001 |
| Copper | 0.040 | 0.040 | <0.010 | 0.040 |

(a) Tolerance limits expressed in wt% except for iron, which is expressed as the fraction of the manganese content (for example, the iron tolerance of 0.2% Mn alloy = 0.0064% Fe in F temper)
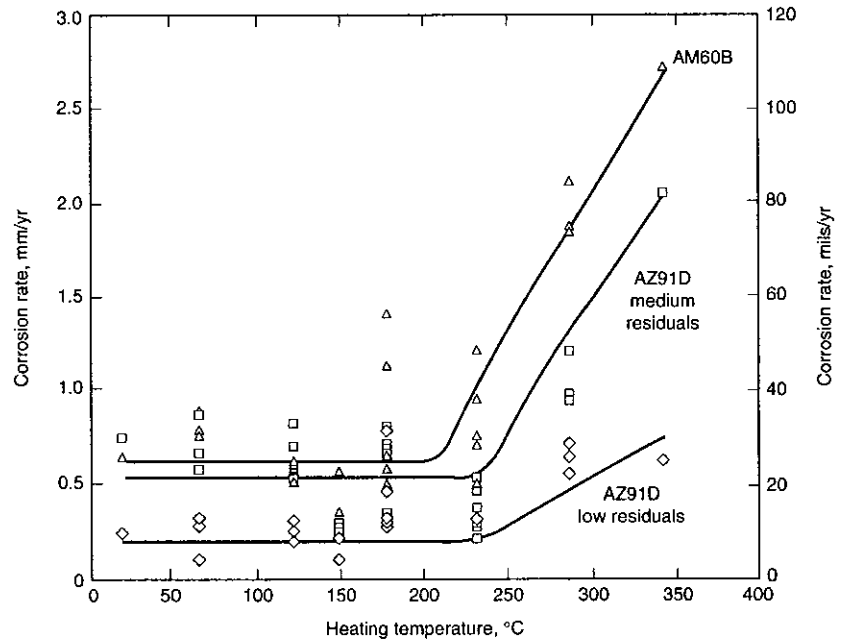
### Table 6 Typical corrosion rates versus temper and grain size for two magnesium alloys

ASTM B 117 salt-spray test

| Alloy | Grain size, μm | Mn, % | Fe(a) | Temper corrosion rate | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | F | | T4 | | T6 | | T5 | |
| | | | | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr |
| AZ91C (untreated) | 187 | 0.18 | 0.087 | 18 | 700 | 15 | 600 | 15 | 600 | ... | ... |
| AZ91C (degassed and grain refined) | 66 | 0.16 | 0.099 | 17 | 690 | 18 | 700 | 15 | 600 | ... | ... |
| AZ91E(b) (untreated) | 146 | 0.23 | 0.008 | 0.64 | 25 | 4 | 160 | 0.15 | 6 | 0.12 | 5 |
| AZ91E (degassed and grain refined) | 78 | 0.26 | 0.008 | 2.2 | 90 | 1.7 | 70 | 0.12 | 5 | 0.12 | 5 |
| AZ91E (untreated) | 160 | 0.33 | 0.004 | 0.35 | 14 | 3 | 120 | 0.22 | 9 | 0.12 | 5 |
| AZ91E (degassed and grain refined) | 73 | 0.35 | 0.004 | 0.72 | 29 | 0.82 | 33 | 0.1 | 4 | 0.1 | 4 |

(a) Iron is expressed as a fraction of analyzed manganese content. (b) AZ91E alloy pending ASTM approval. Source: Ref 8–10

or more of the elements. Figure 7 illustrates the effect of heavy-metal contamination on the ASTM salt-spray-corrosion performance of low-pressure cast AZ91.

*Blast residues* can cause general pitting attack in saline environments. Attack is normally limited to unmachined surfaces of sand castings. Sanded or acid-etched (2% sulfuric acid [$H_2SO_4$] for 15 to 30 s) samples show vastly improved performance in saltwater-immersion or salt-spray tests because of removal of the contaminant. Scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) analysis samples cleaned in chromic acid ($H_2CrO_4$) can be used to confirm and identify the presence of the contaminant, which is usually iron (from steel-shot blasting) or silica (from sand blasting). Preventive measures are discussed in the section "Protective Coating Systems" in this article.

*Flux inclusions* result in localized attack that is clustered or distributed randomly on machined surfaces of castings. Freshly machined surfaces exposed to 70 to 90% relative humidity develop active corrosion sites overnight. Scanning electron microscopy/EDX analysis of a freshly machined surface (free of fingerprints or other sources of contamination) reveal pockets of magnesium and potassium chloride, as well as possible traces of calcium, barium, and sulfur. In zirconium-bearing alloys, elemental zirconium and zirconium-iron compounds may also be associated with the deposits. Chromic-acid pickling followed by chemical treatment and surface sealing can alleviate the problem of inclusions in finished castings. The use of sulfur hexafluoride ($SF_6$) cover gases to replace fluxes for the protection of melts during casting has practically eliminated this problem in die casting.

*Galvanic attack* is usually observed as heavy localized attack on the magnesium, normally within 3.2 to 4.8 mm ($\frac{1}{8}$ to $\frac{3}{16}$ in.) of fasteners, or other parts of dissimilar metal. Proper design and assembly methods can minimize galvanic attack, as detailed in subsequent sections of this article.

## Environmental Factors

The information in this section is based on the behavior of unprotected metal. Improved resistance is obtained by using proper protection systems. The alloy composition affects corrosion behavior, as summarized above. Table 7 indicates the suitability of magnesium for exposure to a wide range of substances. Further testing, however, is recommended before final conclusions are drawn concerning specific alloys and exposure conditions.

**Atmospheres.** A clean, unprotected magnesium-alloy surface exposed to indoor or outdoor atmospheres free from salt spray will develop a gray film that offers some corrosion protection to the metal 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.

The composition of the corrosion products that form on magnesium varies from one loca-

tion to another and from indoor to outdoor exposure. X-ray diffraction analysis of corrosion products scraped from magnesium ingots after 18 months of exposure in a rural atmosphere has shown the presence of various hydrated carbonates of magnesium, including $MgCO_3 \cdot H_2O$, $MgCO_3 \cdot 5H_2O$, and $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. In an industrial atmosphere, hydrated and basic carbonates were found, together with magnesium sulfite ($MgSO_3 \cdot 6H_2O$) and magnesium sulfate ($MgSO_4 \cdot 7H_2O$).

These analyses, in addition to similar analyses after shorter periods of exposure, indicate that the primary reaction in corrosion of magnesium is the formation of magnesium hydroxide ($Mg(OH)_2$), followed by a secondary reaction with carbonic acid to convert the hydroxide to a hydrated carbonate. In atmospheres contaminated with sulfur compounds, sulfites or sulfates may also be present in the corrosion product. The sulfates may be formed by the reaction of acidic sulfur-bearing gases with $Mg(OH)_2$ or $MgCO_3$.

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, break down the protective film locally, which usually results in pitting.

Dissolved oxygen plays no major role in the corrosion of magnesium in either freshwater or saline solutions. However, agitation or any other means of destroying or preventing the formation of a protective film leads to corrosion. When magnesium is immersed in a small volume of stagnant water, its corrosion rate is negligible. When the water is constantly replenished so that the solubility limit of $Mg(OH)_2$ is never reached, the corrosion rate will increase.

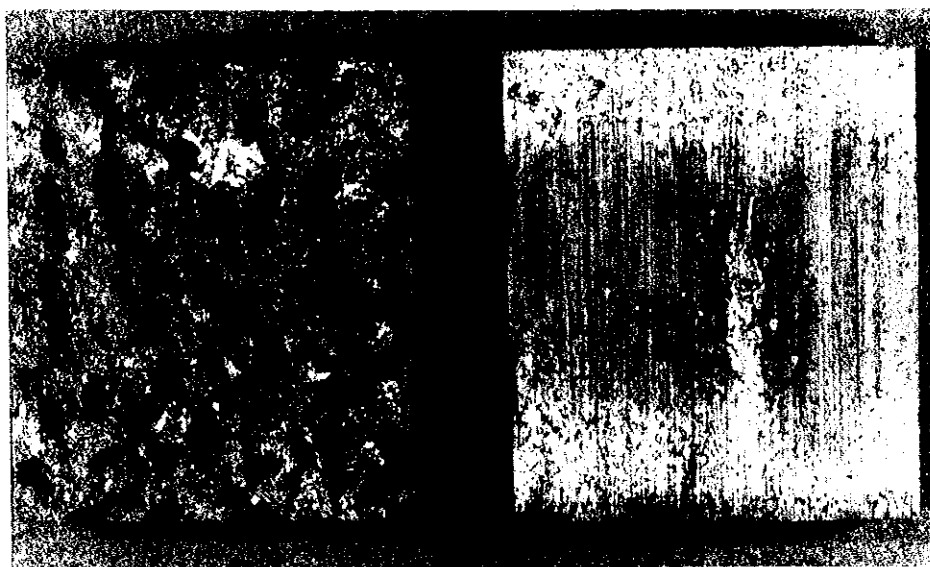The corrosion of magnesium alloys by pure water increases substantially with temperature.



**Fig. 7** Effect of heavy-metal contamination on the salt-spray (ASTM B 117) performance of sand-cast AZ91 samples in the T6 temper. The samples, containing less than 10 ppm Ni and less than 10 ppm Cu, were simultaneously exposed for 240 h. The sample at left contained 160 ppm Fe and had a corrosion rate of 15 mm/year (591 mils/year). The sample at right contained 19 ppm Fe, and the corrosion rate was 0.15 mm/year (5.9 mils/year).
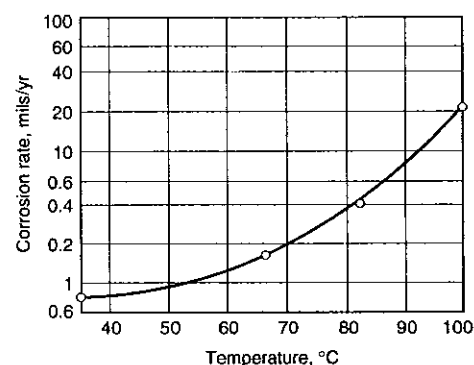


**Fig. 8** Corrosion rate of AZ61A in distilled water as a function of temperature. Source: Ref 11

## Table 7 Magnesium suitability for testing in various substances

Follow precautions in text.

| Chemical | Concentration, % | Service test warranted | Chemical | Concentration, % | Service test warranted | Chemical | Concentration, % | Service test warranted |
|---|---|---|---|---|---|---|---|---|
| Acetaldehyde | Any | No | Ethylcellulose | 100 | Yes | Orthodichlorobenzene | 100 | Yes |
| Acetic acid | Any | No | Ethyl chloride | 100 | Yes | Orthophenylphenol | 100 | Yes |
| Acetone | Any | Yes | Ethyl salicylate | 100 | Yes | Oxygen | 100 | Yes |
| Acetylene | 100 | Yes | Ethylene (gas) | 100 | Yes | Paraphenylphenol | 100 | Yes |
| Alcohol, butyl | 100 | Yes | Ethylene dibromide | 100 | Yes | Paradichlorobenzene | 100 | Yes |
| Alcohol, ethyl | 100 | Yes | Ethylene glycol solutions | Any | Yes, may need inhibitors | Pentachlorophenol | 100 | Yes |
| Alcohol, isopropyl | 100 | Yes | | | | Perchloroethylene | 100 | Yes |
| Alcohol, methyl | 100 | No | Fats, cooking (acid-free) | 100 | Yes | Permanganates (most) | Any | Yes |
| Alcohol, propyl | 100 | Yes | Fatty acids | Any | No | Phenol | 100 | Yes |
| Ammonia (gas or liquid) | 100 | Yes | Ferric chloride | Any | No | Phenyl ethyl acetate | 100 | Yes |
| Ammonium salts (most) | Any | No | Fluorides (most) | Any | Yes | Phenylphenols | 100 | Yes |
| Ammonium hydroxide | Any | Yes | Fluosilicic acid | Any | No | Phosphates (most) | Any | Yes |
| Aniline | 100 | Yes | Formaldehyde | Any | Yes | Phosphoric acid | Any | No |
| Anthracene | 100 | Yes | Fruit juices and acids | Any | No | Polypropylene glycols | 100 | Yes |
| Arsenates (most) | Any | Yes | Fuel oil | 100 | Yes | Potassium fluoride | Any | Yes |
| Benzaldehyde | Any | No | Gasohol (10% ethanol) | 100 | Yes, if inhibited | Potassium hydroxide | Any | Yes |
| Benzene | 100 | Yes | | | | Potassium nitrite | Any | No |
| Bichromates | Any | Yes | Gasohol (10% methanol) | 100 | Yes, if inhibited | Potassium permanganate | Any | Yes |
| Boric acid | 1–5 | No | | | | Propylene glycol U.S.P. | 100 | Yes |
| Brake fluids (most)(a) | 100 | Yes | Gasoline (lead-free) | 100 | Yes, if inhibited | Propylene oxide | 100 | Yes, may need inhibitors |
| Bromides (most) | Any | No | | | | | | |
| Bromobenzene | 100 | Yes | Gasoline (leaded) | 100 | Yes, if inhibited | Pyridine (acid free) | 100 | Yes |
| Butter | 100 | No | | | | Pyrogallol | Any | No |
| Butylphenols | 100 | Yes | Gelatine | Any | Yes | Rubber and rubber cements | 100 | Yes |
| Calcium arsenate | Any | Yes | Glycerine C.P. | 100 | Yes | Seawater | 100 | No |
| Calcium carbonate | 100 | Yes | Grease (acid-free) | 100 | Yes | Sodium bromate | Any | No |
| Calcium chloride | Any | No | Heavy metal salts (most) | Any | No | Sodium bromide | Any | No |
| Calcium hydroxide | 100 | Yes | Hexamine | 3 | Yes | Sodium carbonate | Any | Yes |
| Camphor | 100 | Yes | Hydrochloric acid | Any | No | Sodium chloride | Any | No |
| Carbon bisulfide | 100 | Yes | Hydrofluoric acid | 5–60 | Yes | Sodium cyanide | Any | Yes |
| Carbon dioxide (dry) | 100 | Yes | Hydrogen peroxide | Any | No | Sodium dichromate | Any | Yes |
| Carbon monoxide | 100 | Yes | Hydrogen sulfide | 100 | Yes | Sodium fluoride | Any | Yes |
| Carbon tetrachloride | 100 | Yes | Iodides | Any | No | Sodium hydroxide | Any | Yes |
| Carbonated water | Any | No | Iodine crystals (dry) | 100 | Yes | Sodium phosphate (tribasic) | Any | Yes |
| Castor oil | 100 | Yes | Isopropyl acetate | 100 | Yes | Sodium silicate | Any | Yes |
| Cellulose | 100 | Yes | Isopropyl benzene | 100 | Yes | Sodium sulfide | 3 | Yes |
| Cement | 100 | Yes | Isopropyl bromide | Any | No | Sodium tetraborate | 3 | Yes |
| Chlorides (most) | Any | No | Kerosene | 100 | Yes | Steam | 100 | No |
| Chlorine | 100 | No | Lanolin | 100 | Yes | Stearic acid (dry) | 100 | Yes |
| Chlorobenzenes | 100 | Yes | Lard | 100 | Yes | Styrene polymer | 100 | Yes |
| Chloroform | 100 | Yes | Lead arsenate | Any | Yes | Sugar solutions (acid-free) | Any | Yes |
| Chlorophenols | Any | No | Lead oxide | Any | Yes | Sulfates (most) | Any | No |
| Chlorophenylphenol | 100 | Yes | Linseed oil | 100 | Yes | Sulfur | 100 | Yes |
| Chromates (most) | Any | Yes | Magnesium arsenate | Any | Yes | Sulfur dioxide (dry) | 100 | Yes |
| Chromic acid | Any | Yes | Magnesium carbonate | 100 | Yes | Sulfur chloride | Any | No |
| Citronella oil | 100 | Yes | Magnesium chloride | Any | No | Sulfuric acid | Any | No |
| Cod liver oil (crude) | ... | Yes | Mercury salts | Any | No | Sulfurous acid | Any | No |
| Copals | 100 | Yes | Methane (gas) | 100 | Yes | Tannic acid | 3 | No |
| Coumarin | 100 | Yes | Methyl bromide | Any | No | Tanning solutions | Any | No |
| Cresol | 100 | Yes | Methyl cellulose | 100 | Yes | Tar, crude and its fractions | 100 | Yes |
| Cyanides (most) | Any | Yes | Methyl chloride | 100 | Yes | Tartaric acid | Any | No |
| Dichlorohydrin | 100 | Yes | Methylene chloride | 100 | Yes | Tetrahydronaphthalene | 100 | Yes |
| Dichlorophenol | 100 | Yes | Methyl salicylate | 100 | Yes | Titanium tetrachloride | 100 | Yes |
| Dichromates (see bichromates) | | | Milk (fresh and sour) | 100 | No | Toluene (toluol) | 100 | Yes |
| Diethanolamine | 100 | Yes | Mineral acids | Any | No | Trichlorbenzene | 100 | Yes |
| Diethyl aniline | 100 | Yes | Monobromobenzene | 100 | Yes | Trichloroethylene | 100 | Yes |
| Diethyl benzene | 100 | Yes | Monochlorobenzene | 100 | Yes | Trichlorophenol | 100 | Yes |
| Diethylene glycol solutions | Any | Yes, may need inhibitors | Naphtha | 100 | Yes | Tung oil | 100 | Yes |
| | | | Naphthalene | 100 | Yes | Turpentine | 100 | Yes |
| | | | Nicotine sulfate | 40 | Yes | Urea | 100 | Yes |
| Diphenyl | 100 | Yes | Nitrates (all) | Any | No | Urea in aqueous solution (cold) | Any | Yes |
| Diphenylamine | 100 | Yes | Nitrous gases | 100 | No | Urea in aqueous solution (warm) | Any | No |
| Diphenylmethane | 100 | Yes | Nitric acid | Any | No | | | |
| Diphenyl oxide | 100 | Yes | Nitroglycerin | Any | No | Vinegar | Any | No |
| Dipropylene glycol | 100 | Yes | Oil, animal (acid- and chloride-free) | Any | Yes | Vinylidine chloride | 100 | Yes |
| Divinylbenzene | 100 | Yes | | | | Vinyl toluene | 100 | Yes |
| Dry cleaning fluids | 100 | Yes | Oil, mineral (chloride-free) | 100 | Yes | Water, boiling | 100 | No |
| Ethers | 100 | Yes | Oil, vegetable (chloride-free) | 100 | Yes | Water, distilled | 100 | Yes |
| Ethanolamine (mono) | 100 | Yes | Oleic acid | 100 | Yes | Water, rain | 100 | Yes |
| Ethyl acetate | 100 | Yes | Olive oil | 100 | Yes | Waxes (acid-free) | 100 | Yes |
| Ethyl benzene | 100 | Yes | Organic acids (most) | Any | No | Xylol | 100 | Yes |
| Ethyl bromide | 100 | No | Orthochlorophenol | 100 | No | | | |

(a) Anhydrous brake fluids may react destructively with magnesium at 150 °C (300 °F).

At 100 °C (212 °F), the AZ alloys corrode typically at 0.25 to 0.50 mm/year (10 to 20 mils/year) (Fig. 8). Pure magnesium and alloy ZK60A corrode excessively at 100 °C (212 °F) with rates up to 25 mm/year (1000 mils/year). At 150 °C (302 °F), all alloys corrode excessively.

**Salt Solutions.** The corrosion rates of magnesium and two wrought magnesium-aluminum alloys in various magnesium-salt solutions are given in Table 8. The corrosivities of the anions are in the order $Cl^- > Br^- > ClO_4^-$. The lower rates in 2 $M$ solutions are attributable to concentration polarization. AZ61 shows higher corrosion rates than AZ31 in all the electrolyte solutions.

Severe corrosion can occur in neutral solutions of salts of heavy metals, such as copper, iron, and nickel. Such corrosion occurs when the heavy metal plates 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 tend to passivate. Oxidizing salts, especially those containing chlorine or sulfur atoms, are more corrosive than nonoxidizing salts, but chromates, vanadates, phosphates, and 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 $H_2CrO_4$. 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. With increasing temperature, the rate of attack increases at the liquid line, but to a negligible extent elsewhere.

Pure $H_2CrO_4$ attacks magnesium and its alloys at a very low rate. However, traces of chloride ion in the acid will markedly increase this rate. A boiling solution of 20% $H_2CrO_4$ in water is widely used to remove corrosion products from magnesium alloys without attacking the base metal. Magnesium resists dilute alkalis, and 10% caustic solution is commonly used for cleaning at temperatures up to the boiling point.

**Organic Compounds.** Aliphatic and aromatic hydrocarbons, ketones, and ethers are not corrosive to magnesium and its alloys. Ethanol and higher alcohols are not corrosive at ordinary temperatures, but they may react destructively at high temperature (150 °C, or 300 °F). Anhydrous

methanol attacks magnesium alloys catastrophically at room temperature; however, the rate of attack is reduced by the presence of water. Gasoline-methanol fuel blends in which the water content equals or exceeds about 0.25 wt% of the methanol content do not attack magnesium.

Pure halogenated organic compounds do not attack magnesium at ambient temperatures. At elevated temperatures or if water is present, such compounds can cause serious corrosion, particularly those compounds having acidic hydrolysis products.

Dry fluorinated hydrocarbons, such as the freon refrigerants, do not attack magnesium alloys at room temperature, but when water is present they may stimulate significant attack. At elevated temperatures, fluorinated hydrocarbons may react violently with magnesium alloys.

Acidic foodstuffs, such as fruit juices and carbonated beverages, attack magnesium seriously. Milk causes attack, particularly when souring.

At room temperature, ethylene-glycol solutions cause minor corrosion of magnesium that is used alone or galvanically connected to steel; at elevated temperatures such as 115 °C (240 °F), the rate increases and corrosion is serious enough to preclude use of solutions of ethylene glycol and water in liquid-cooled magnesium engines. Anhydrous propylene glycol coolant is reported to be successfully used in prototype magnesium-alloy engines having modified cooling systems.

**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% $H_2O$, dry bromine causes no more attack at its boiling temperature (58 °C, or 136 °F) 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. Wet chlorine, iodine, or bromine below the dew point of any aqueous phase causes severe attack of magnesium. Dry, gaseous sulfur dioxide causes no attack at ordinary temperatures. If water vapor is present, some corrosion may occur. Wet (below dew point) sulfur dioxide gas is severely corrosive to magnesium due to the formation of sulfurous and sulfuric acids. Ammonia, wet or dry, causes no attack at ordinary temperatures. Dry gaseous sulfur dioxide ($SO_2$) or ammonia causes no attack at ordinary temperatures; some corrosion may occur if water vapor is present.

Water vapor in air or in oxygen sharply increases the rates of oxidation of magnesium and its alloys above 100 °C (212 °F), but boron trifluoride ($BF_3$), $SO_2$, and $SF_6$ are effective in reducing oxidation rates. The presence of any of the three in the ambient atmosphere is effective in suppressing high-temperature oxidation up to and including the temperature at which the alloy normally ignites.

The oxidation rate of magnesium in oxygen increases with temperature. At elevated temperature (approaching melting), the oxidation rate is a linear function of time. Cerium, lanthanum, calcium, and beryllium in the metal reduce the oxidation rate below that of pure magnesium. Beryllium additions of 5 to 10 ppm have the most striking effects, protecting some alloys at temperatures up to the melting point over extended periods of time. Structural applications of magnesium alloys at elevated temperature are usually limited by creep strength rather than by oxidation.

**Soils.** Except when used as galvanic anodes, magnesium alloys have good corrosion resistance in clay or nonsaline sandy soils, but they have poor resistance in saline sandy soils.

## Corrosion in Real and Simulated Environments

**Structural applications** of magnesium alloys usually involve environmental conditions ranging from indoor atmospheres (computer disk-drive components) to intermittent salt splash (automotive clutch housings). The amount of corrosion that can be tolerated in these applications may range from zero for disk-drive parts or critical military and aerospace components to substantial for some automotive castings, provided there is no interference with function for a specified period. Magnesium alloys of controlled high purity have demonstrated the capability of withstanding these environments in properly designed assemblies. Designers, however, must have advance information about the type and magnitude of corrosion that can occur under particular service conditions.

The best sources of such information would be previous service experience or long-term data from tests in the actual environment. When these are lacking, accelerated corrosion tests, such as alternate (intermittent) immersion in salt water or salt spray, are often used to compare the corrosion resistance of magnesium alloys to each other and to other metals. In addition, such tests are used to examine the relative merits of protective chemical treatments and coatings and the galvanic compatibilities of dissimilar metals with magnesium. The ASTM B 117 salt-spray test in particular is widely used and is firmly established as an acceptance test in many specifications. Magnesium is also subjected to various salt-water-based accelerated corrosion tests developed for special purposes. An important example is the proving ground cycle tests used by automobile manufacturers. Correlation has been estab-

**Table 8  Corrosion rates of magnesium and magnesium-aluminum alloys in various magnesium-salt solutions**

| Alloy | 1 $M$ solution, mg/cm²/day | | | 2 $M$ solution, mg/cm²/day | | |
|---|---|---|---|---|---|---|
| | $Mg(ClO_4)_2$ | $MgBr_2$ | $MgCl_2$ | $Mg(ClO_4)_2$ | $MgBr_2$ | $MgCl_2$ |
| AZ31 | 9.2 | 142 | 289 | 4.2 | 117 | 264 |
| AZ61 | 27 | 153 | 311 | 6.4 | 127 | 272 |
| Mg | 258 | 289 | 473 | 128 | 225 | 384 |

Specimens were immersed in the solutions for 5 h and the weight loss measured. Source: Ref 12
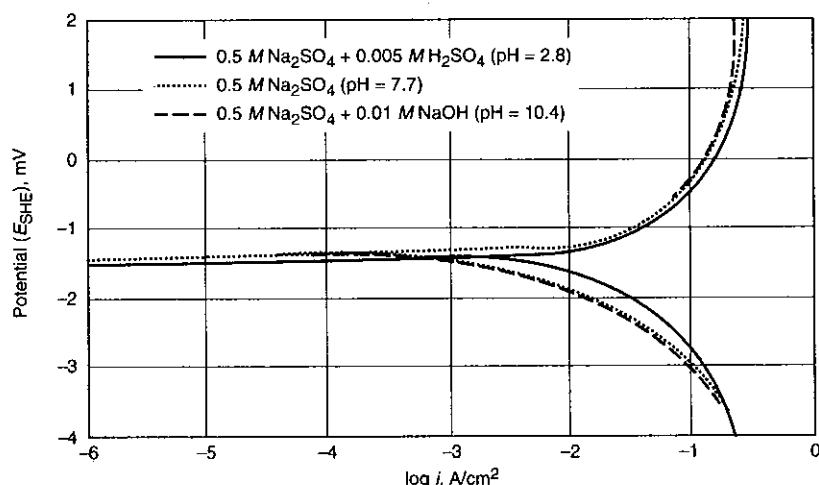
**Fig. 9** Stationary potentiodynamic polarization curves of magnesium in 0.5 $M$ Na$_2$SO$_4$ solutions having different levels of pH. Source: Ref 13
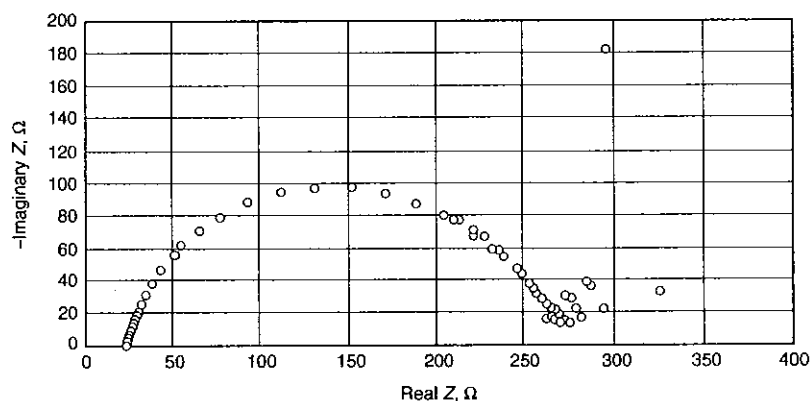


**Fig. 10** Electrochemical impedance data for cast pure magnesium (99.98% pure) in pH 9.2 sodium borate presented in the Nyquist format. Source: Ref 14
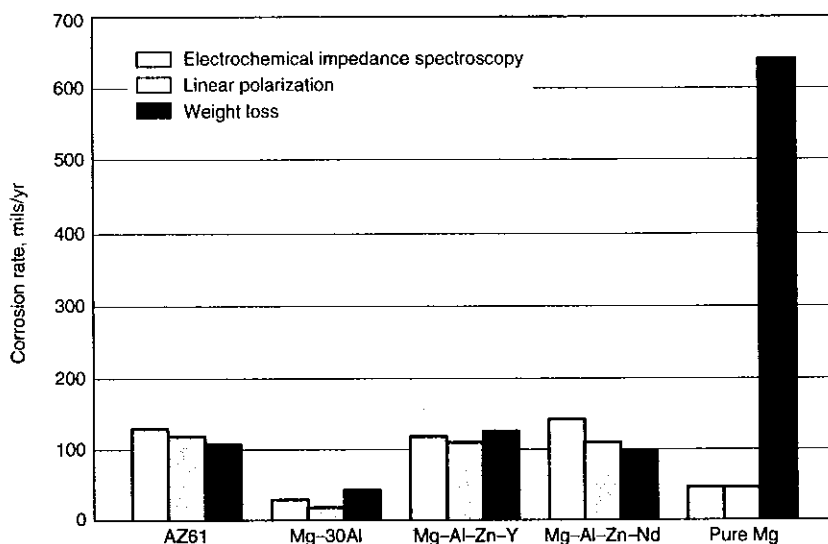


**Fig. 11** Comparison of corrosion rates of pure magnesium (99.98% pure) and magnesium alloys determined by electrochemical and gravimetric techniques. Source: Ref 14

lished between proving ground cycle performance and vehicle corrosion in long-term service.

**Corrosion Testing.** The most commonly used techniques in testing the corrosion resistance of magnesium are weight-loss and pit-depth measurements. However, electrochemical polarization testing or impedance measurements of magnesium are also conducted to supplement weight-loss measurements. Figure 9 shows the stationary potentiodynamic polarization curve of magnesium in 0.5 $M$ sodium sulfate solutions having different levels of pH. The anodic polarization shows active dissolution of magnesium over the entire pH range tested, and the effect of pH seems minor over this range. Electrochemical impedance data for cast pure magnesium (99.98% purity) in sodium borate having a pH of 9.2 is presented in Fig. 10, which shows a single capacitance semicircle indicative that the only process occurring is charge transfer.

For most metal systems, there is usually good quantitative agreement between weight-loss and electrochemical measurements. However, for magnesium metal, especially pure magnesium, this does not seem to be true. Figure 11 gives a comparison of corrosion rates of alloys in pH 9.2 sodium borate determined from electrochemical and gravimetric techniques. For pure magnesium, the weight-loss values are roughly an order of magnitude higher than predicted by electrochemical techniques; this is called the "negative difference effect." This phenomenon is described by the increase of hydrogen evolution at anodic polarization, accompanied by an excessive metal loss. Figure 12 shows the effect of current density on the negative difference for anodic dissolution of magnesium in sulfuric acid obtained by hydrogen-evolution rate. When there is no negative difference effect, the voltage is proportional to 6.97 $I$, where $I$ is the current input. The deviation from linearity becomes more pronounced with increasing current density and decreasing acid concentration. The reasons for this effect have been exten-
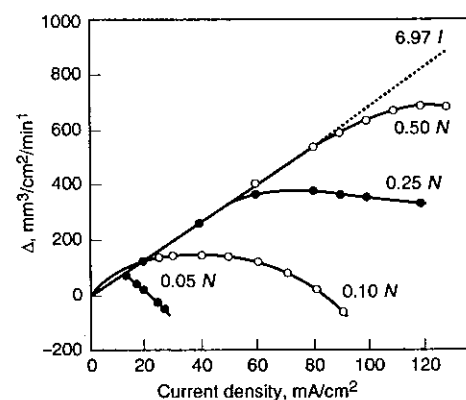


**Fig. 12** Effect of current density on the negative difference for anodic dissolution of pure magnesium in various concentrations of sulfuric acid. $\Delta$ is the difference between hydrogen-evolution rate $V_1$, from an electrode without current flowing and hydrogen-evolution rate $V_2$ from the same electrode with current flowing. When there is no negative difference effect, the voltage is proportional to 6.97 $I$, where $I$ is the current input. Source: Ref 15
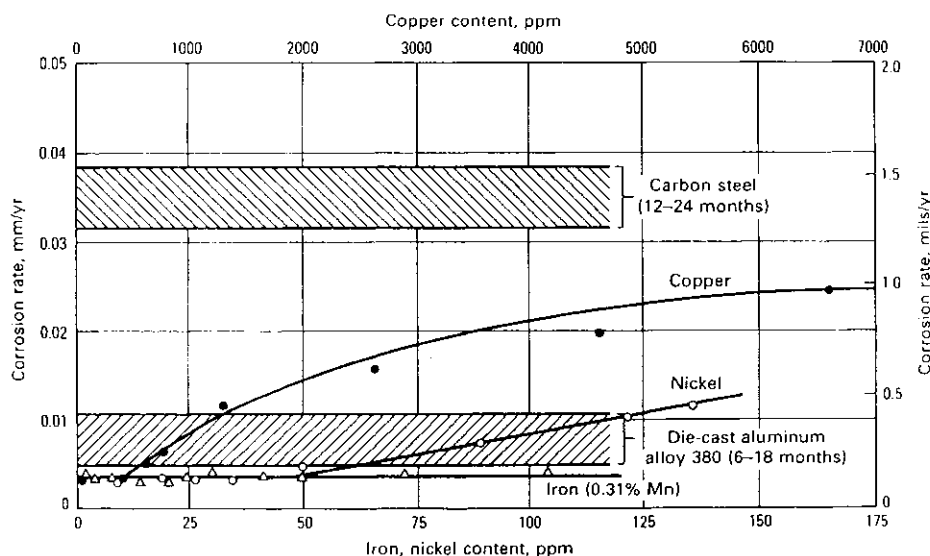
**Fig. 13** Effect of copper and nickel contamination on the atmospheric corrosion of die-cast AZ91 alloy exposed for two years on the Texas Gulf Coast

sively discussed in the literature and explained as:

- Formation of metastable monovalent magnesium ions
- Loss of metal by disintegration (chunk effect)
- Damage to protective film, exposing active metal
- Formation of magnesium hydride

**Specific Effects of Chloride Environments.** Salt-based accelerated tests can provide useful information on the performance of magnesium alloys and assemblies, both bare and coated, in saline environments. The results of such tests must be interpreted with care, however, and no attempt should be made to relate them to the behavior of magnesium in rural, urban, or industrial atmospheres in which chloride is not the controlling constituent of the environment.
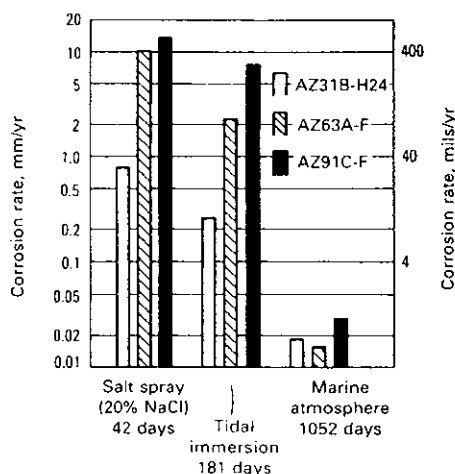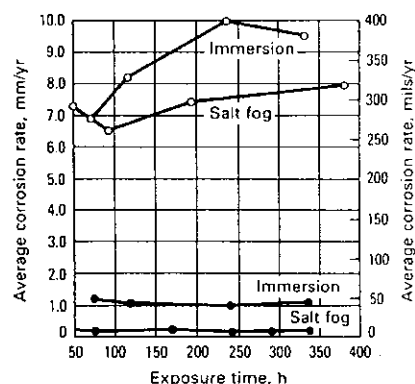


**Fig. 14** Relative performance of magnesium alloys in saltwater exposures

The corrosion of magnesium alloys in saline solutions is governed by the concentration and distribution of the critical impurities, nickel, iron, and copper, whose presence in precipitated alloy phases creates active cathodic sites of low hydrogen overvoltage. The chloride ion further stimulates corrosion through its interference with protective-film formation and through the high solubility and acidic nature of magnesium chloride that accumulates at local anodic sites. The high conductivity of the chloride electrolyte also promotes the flow of corrosion current. If an adverse galvanic couple is introduced, for example, by attaching a steel bolt to the magnesium, and if the junction is bridged



**Fig. 15** Corrosion rates of die-cast magnesium in 5% NaCl salt-spray and continuous-immersion exposures. O, AM60A; ●, AZ91D. Source: Ref 16

| | Analysis of die-cast plates, % | |
|---|---|---|
| | AM60A (O) | AZ91D (●) |
| Aluminum | 6.2 | 9.7 |
| Zinc | 0.09 | 0.74 |
| Manganese | 0.22 | 0.19 |
| Nickel | 0.003 | 0.0018 |
| Iron | 0.005 | 0.006 |
| Copper | 0.03 | 0.0067 |

by salt water, corrosion of magnesium is greatly accelerated and alloy purity provides no defense. In a salt-spray test, galvanic corrosion of magnesium in such an assembly would be excessive compared to that which would occur in a marine atmosphere or even under road-salt splash conditions.

**Corrosion Rates in Salt-Spray, Salt-Immersion, and Natural Marine Environments.** The marine-atmosphere corrosion rate of magnesium-aluminum alloys is much smaller than the salt-spray rate, but both rates are affected by the impurity content. Figures 5 and 13 show the effects of nickel, iron, and copper content on the corrosion of controlled-purity AZ91 die-casting alloy in a 10 day salt-spray (5% NaCl, ASTM B 117) test and in a two year atmospheric exposure on the Texas Gulf Coast. Although the salt-spray-corrosion scale is 200 times larger than the marine atmospheric-corrosion scale, some parallels can be drawn:

- Breakpoints relative to nickel and copper contamination are the same in both exposures (50 and 500 ppm, respectively).
- AZ91 corrosion remains low in both exposures over the iron contamination range studied (0.31% Mn alloy), confirming that the critical iron/manganese ratio (0.032 for this alloy) was not significantly exceeded.
- High-purity AZ91 alloy is shown in both exposures to have lower overall corrosion rates than carbon steel or die-cast aluminum 380.

Figure 14 shows average corrosion rates found for three unprotected magnesium alloys in salt spray (20% NaCl), tidal-immersion, and marine atmospheres. The principal alloy and impurity constituents of the specimens tested were as follows:

| Element | AZ31B-H24 sheet | AZ63-F sand cast | AZ91C-F sand cast |
|---|---|---|---|
| Aluminum | 2.6 | 5.8 | 8.8 |
| Zinc | 1.0 | 2.9 | 0.68 |
| Manganese | 0.51 | 0.25 | 0.22 |
| Silicon | 0.0017 | <0.05 | <0.05 |
| Nickel | 0.0005 | <0.001 | <0.01 |
| Iron | 0.0007 | 0.005 | 0.006 |
| Copper | 0.0019 | 0.015 | 0.013 |
| Fe/Mn | 0.0014 | 0.020 | 0.027 |

The marine atmosphere and tidal-immersion exposures were conducted at the Naval Air Station, Norfolk, VA. The atmospheric panels were suspended directly over the water, 3 m (10 ft) above mean tide level, at an angle of 45° from the horizontal and facing east-southeast. The tidal-immersion panels were mounted vertically so that they were totally immersed in the water at high tide and totally exposed to atmosphere at low tide.

The salt-spray and tidal-immersion results are in good agreement in rating the three alloys in order of actual corrosion rates. The atmospheric panels, even though directly above the water, sustained only a small fraction of the corrosion damage seen in the salt-spray and tidal tests.

No fundamental differences exist between spray and immersion tests that would lead to serious misjudgments about the relative corrosion resistance of magnesium alloys or the relative value of protective coating systems. Caution should be exercised, however, when comparing the relative performance of magnesium alloys of different families, for example, QE22 and ZE41, or when comparing magnesium with other metals. Figure 15 shows average corrosion rates over various exposure times for a standard alloy and a high-purity die-cast alloy in salt spray and in 5% NaCl continuous immersion.

There are also interactive effects of casting method and temper on corrosion rates obtained in salt-immersion tests. Table 9 shows the corrosion rate of gravity-cast AZ91 in 5 wt% NaCl solution. The alloy exhibits the highest corrosion resistance in the T6 condition, whereas treat-

ment to the T4 temper leads to the largest weight loss. The mold temperature during casting, which affects the cooling rate, does not appear to have a significant influence on the corrosion rate.

Table 10 presents the pit-initiation results for cast magnesium-aluminum alloys in salt solution. The tolerance limit for $Cl^-$ falls in the range of $2 \times 10^{-3}$ to $2 \times 10^{-2}$ M NaCl. Pure unalloyed magnesium shows exfoliation in which individual grains were preferentially attacked along certain crystallographic planes.

Marine atmospheres also produce pitting corrosion in addition to general atmospheric corrosion. The fine pitting, which is commonly seen upon exposure to marine atmosphere at the 80 ft Kure Beach site, had little effect on the strength, but it did reduce the ductility (Fig. 16).

**Influence of Galvanic Couples in Salt-Spray and Marine Atmospheres.** The combination of salt spray and dissimilar metals coupled to magnesium represents an extreme in accelerated corrosion testing. The gap between such a test and a marine-atmosphere exposure is illustrated in Fig. 17 and in Table 11. Figure 17 shows magnesium die-cast plates that were as-
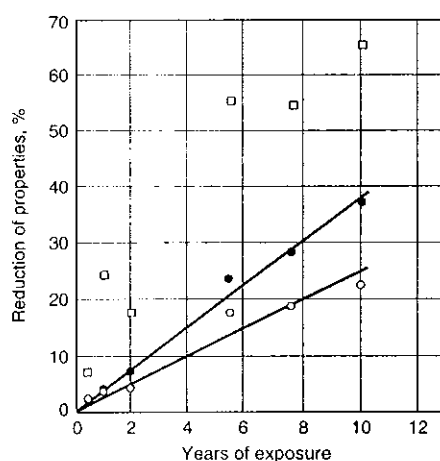
sembled with steel cap screws and nuts and exposed to salt spray (5% NaCl) for 10 days. Table 11 lists losses of tensile strength of AZ31B-H24 sheet with an original thickness of 4.8 mm (0.188 in.), coupled with various dissimilar-metal cleats and exposed for 13 months at Kure Beach, NC, at 24.4 m (80 ft) from the mean-tide point. Comparative data are shown for rural and an urban-industrial test site. Saltwater immersion of steel/magnesium couples will produce nearly complete perforation failure of 4.8 mm (0.188 in.) magnesium panels in 10 days. However, it should be noted that the panels retained 88% of their tensile strength after 13 months.

**Corrosion in Rural, Urban, and Industrial Environments.** In contrast to wet chloride exposure, a rural atmosphere would probably cause negligible corrosion damage to the magnesium assembly referred to earlier. Some corrosion, still minor compared to that caused by salt water, would be expected in urban or industrial atmospheres containing significant acidic gas pollution, principally $SO_2$. These gases convert the insoluble hydroxide-carbonate films that form naturally on magnesium alloys into soluble bicarbonates, sulfites, and sulfates that can be washed away by rain. This increases the rate of weathering and can provide conductive electrolytic paths, allowing some galvanic corrosion to occur.

To simulate atmospheric exposure where chloride does not exert a controlling influence,
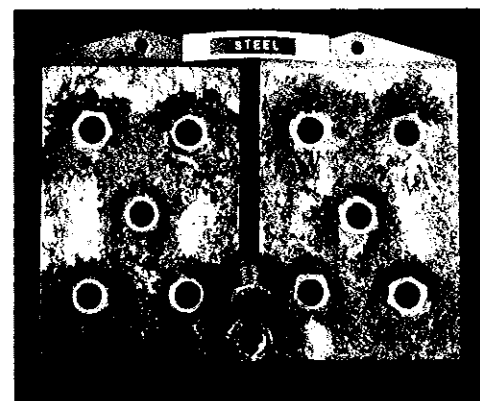
**Table 9 Corrosion rate of gravity-cast AZ91 immersed in 5 wt% NaCl solution for three days**

| Temper | Mold temperature, °C | Corrosion rate, mg/cm²/day |
|---|---|---|
| F | 400 | 1.1±0.2 |
|  | 350 | 1.4±0.1 |
|  | 250 | 2.0±0.6 |
| T4 | 400 | 3.6±1 |
|  | 350 | 1.8±0.3 |
|  | 250 | 2.7±0.1 |
| T6 | 400 | 0.5±0.1 |
|  | 350 | 0.4±0.1 |
|  | 250 | 0.4±0.1 |

Source: Ref 17

**Table 10 Pit-initiation results for wrought and cast magnesium alloys immersed in salt solutions for 24 h at room temperature**

| Alloy | Percentage of five coupons showing pitting in 0.1 M NaOH + | | |
|---|---|---|---|
|  | 0.005 M NaCl | 0.01 M NaCl | 0.02 M NaCl |
| **Wrought** | | | |
| Magnesium A8 | 100 (ex) | | |
| MA | 0 | 100 | |
| M1 | 0 | 100 | |
| AZ31 | 0 | 0 | 100 |
| AZ61 | 0 | 0 | 100 |
| AZ91 | 0 | 0 | 100 |
| **Cast** | | | |
| AM60B cold chamber | 100 | | |
| AM50 high purity | 100 | | |
| WE43 | 100 | | |
| ZE41 | 100 | | |
| ZE41A | 100 | | |
| A3A | 100 | | |
| EZ33 | 80 | 100 | |
| AZ92 | 40 (ex) | 60 (ex) | 100 (ex) |
| AZ92A | 40 | 100 | |
| AZ31 | 0 | 40 | 100 |
| AZ91E | 0 | 60 | 100 |
| AZ91D hot chamber | 0 | 80 | 100 |
| AZ91 | 0 | 80 | 100 |
| AM20 high purity | 0 | 80 | 100 |
| QE22 | 0 | 0 | 100 |
| QE22A | 0 | 0 | 100 |
| AZ91D cold chamber | 0 | 0 | 100 |

ex, exfoliation. Source: Ref 18



**Fig. 16** Loss in mechanical properties of AZ31B-H24 alloy sheet at the 80 ft marine site. Initial: 0.063 in. thick, 17.0% elongation; 37.1 ksi ultimate tensile strength. O, reduction in thickness as calculated from weight loss. ●, reduction in tensile strength. □, reduction in elongation. Source: Ref 19



**Fig. 17** Galvanic corrosion of AZ91D caused by bare steel fasteners during a 10 day exposure to 5% NaCl salt spray. Source: Ref 16

**Table 11 Loss in tensile strength of galvanically coupled AZ31 sheet versus coupled metal cleat and exposure**

| Cleat metal(a) | Loss of tensile strength, % | | |
|---|---|---|---|
|  | State College, PA (rural) | Newark, NJ (urban-industrial) | Kure Beach, NC 24.4 m (80 ft) site (marine) |
| AZ31B | (0.1 gain) | 0.7 | 0.1 |
| Aluminum alloy 6061 | (0.2 gain) | 0.8 | 1.0 |
| Aluminum alloy 5052 | 0.5 | 1.2 | 1.6 |
| AlClad alloy 7075 | 0.5 | 2.0 | 5.1 |
| AISI type 304 stainless steel | 0.9 | 3.4 | 9.0 |
| Monel | 1.1 | 4.4 | 10.7 |
| Low-carbon steel | 1.5 | 6.8 | 12.4 |
| 85–15 brass | 1.8 | 7.1 | 15.2 |

(a) Cleats bolted in register to both sides of 4.8 mm (0.188 in.) thick AZ31B-H24 sheet; tensile specimens cut so that stress is at right angle to the four corrosion bands produced. Source: Ref 20

various humidity tests have been used or proposed. Water-fog and water-immersion tests are also used, primarily to evaluate the adhesion and blister resistance of organic coatings. Table 12 lists some simulated environmental tests and their intended purposes.

**Atmospheric Corrosion in Rural, Industrial, and Marine Environments.** Magnesium-aluminum alloys, like most other metals, form protective films when exposed to the atmosphere. If $CO_2$ is present (in industrial atmos-

pheres), the film is a mixture of hydrotalcite $MgCO_3 \cdot 5Mg(OH)_2 \cdot 2Al(OH)_3 \cdot 4H_2O$ and hydromagnesite $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. Due to hydrotalcite film, the magnesium-aluminum alloys are more tarnish resistant than other magnesium alloys when exposed to the atmosphere. Magnesium-aluminum wrought alloys show slightly higher corrosion rates than cast magnesium-aluminum alloys because the aluminum levels are usually lower than cast alloys (3 to 8% instead of 6 to 9%), and the purity

of the alloys is often lower. In addition, wrought alloys are less isotropic, which may contribute to the higher corrosion rate.

Table 13 lists the average corrosion rates reported for several alloys after 2.5 to 3 years of exposure at three different atmospheric test sites: a rural site (Midland, MI), an industrial site (Madison, IL), and a severe marine site (Kure Beach, NC). It can be seen that the alloy purity level (iron content) and the type of atmosphere affect the corrosion rate. The difference in corrosion rate between sheet and extrusions, however, were found to be negligible. Alloys not containing aluminum corroded at a somewhat higher rate than those of the AZ type; the ratios were about 2 to 1 in rural, 1.65 to 1 in industrial, and 1.25 to 1 in marine/rural exposure. Table 14 shows the composition of the corrosion products on AZ31B-O alloy after four years of exposure to various atmospheres. It is deduced that aluminum ions concentrate in the film during weathering as the magnesium ions are leached away and form hydrotalcite on the top surface.

The data in Table 13 also show that of the alloys and forms tested, the combination having the best corrosion resistance in all three environments is cast AZ91C-T6 (10 ppm Fe). The alloys with the worst performance are ZE10A-0, EZ33A-T5/ZH62A-T5, and ZH62A-T5 in the rural, industrial, and marine exposures, respectively. Based on the average site corrosion rates for all alloys, the relative severity of the exposures is 1 to 2.1 to 1.7. Therefore, the industrial, $SO_2$ rich atmosphere is the most severe of the three sites.

**Effect of $SO_2$ Pollution.** Figure 18, prepared from data of the National Research Council of Canada, shows the effects of $SO_2$ pollution on the corrosion of ZK61A, AZ80A, and low-carbon steel. These effects may cause industrial atmospheres to corrode magnesium at average rates that are somewhat higher than those found in marine atmospheres (Table 13). The marine atmosphere poses a greater threat, however for two reasons:

- Greater sensitivity of the marine corrosion rate to critical impurity content
- Greatly increased susceptibility to galvanic-corrosion damage by incompatible coupling metals in a wet-chloride environment

## Table 12 Accelerated or simulated environmental corrosion tests for magnesium alloys

| Test condition | Used to evaluate |
|---|---|
| **Humidity tests** | |
| 95% relative humidity, 38 °C (100 °F) | Flux inclusions, indoor tarnishing, filiform corrosion |
| 100% relative humidity, 38 °C (100 °F), condensing (ASTM D 2247) | Paint adhesion and blistering, corrosion in rural (uncontaminated) atmospheres |
| Polluted atmosphere (DIN-50018–1960), 100% relative humidity, 40 °C (105 °F), Air + $SO_2$ + $CO_2$ for 8 h, then 16 h in air at room temperature | Corrosion and coating performance in industrial atmospheres |
| **Water tests** | |
| Water fog (ASTM D 1735), deionized water, 38 °C (100 °F) | Paint adhesion and blistering (roughly equivalent to condensing humidity) |
| Water immersion (ASTM D 870), deionized water, 38 °C (100 °F) | Paint adhesion and blistering (severe test) |
| **Salt tests** | |
| Salt spray (ASTM B 117), 5% NaCl, pH 6.5–7.2 | Corrosion of magnesium alloys, impurity effects, surface treatments and coatings on the same substrate alloy, galvanic compatibilities of other materials with magnesium. Valid for chloride environments, with careful interpretation. A severe accelerated test |
| Salt immersion, 5% NaCl, 25 °C (75 °F), pH 10.5, intermittent or continuous immersion with mild air agitation | Same as salt spray |
| Copper-accelerated acetic acid salt spray (ASTM B 368), 5% NaCl, 1 g CuCl₂·2H₂O per 3.8 L of solution, 49 °C (120 °F), pH 3.1–3.3 | Plated coatings on magnesium |
| Salt spray-$SO_2$, 5% NaCl + $SO_2$, 35 °C (95 °F), pH 2.5–3.2, naval air development center | Naval aircraft materials (simulates sea spray plus ship stack gases) |
| Automotive proving ground test, repeated cycles of salt-mud splash, partial drying, and high-humidity storage | Magnesium alloys, bare or coated, for exposed automobile and truck parts. Galvanic compatibilities. simulates severe road deicing salts exposure |

## Table 13 Corrosion rates of magnesium alloys during atmospheric exposure for 2.5 to 3 years

| Alloy and temper | Rural mm/yr | Rural mils/yr | Industrial mm/yr | Industrial mils/yr | Marine-rural mm/yr | Marine-rural mils/yr |
|---|---|---|---|---|---|---|
| **Sheet** | | | | | | |
| AZ31B-H24 (10 ppm Fe) | 0.013 | 0.52 | 0.025 | 1.0 | 0.017 | 0.69 |
| AZ31C-O (70 ppm Fe) | 0.012 | 0.46 | 0.025 | 1.0 | 0.038 | 1.5 |
| HK31A-H24 | 0.018 | 0.73 | 0.030 | 1.2 | 0.016 | 0.64 |
| HM21A-T8 | 0.020 | 0.80 | 0.032 | 1.3 | 0.022 | 0.88 |
| ZE10A-O | 0.022 | 0.88 | 0.030 | 1.2 | 0.028 | 1.1 |
| **Extrusions** | | | | | | |
| AZ31B-F | 0.013 | 0.53 | 0.025 | 1.0 | 0.019 | 0.77 |
| HM31A-F | 0.018 | 0.70 | 0.035 | 1.4 | 0.020 | 0.80 |
| ZK60A-T5 | 0.017 | 0.66 | 0.032 | 1.3 | 0.025 | 1.0 |
| **Castings** | | | | | | |
| AZ63A-T4 | 0.0086 | 0.34 | 0.022 | 0.88 | 0.019 | 0.76 |
| AZ91C-T6 (350 ppm Fe) | 0.0043 | 0.17 | 0.015 | 0.62 | 0.022 | 0.88 |
| AZ91C-T6 (10 ppm Fe) | 0.0027 | 0.11 | 0.014 | 0.57 | 0.0064 | 0.25 |
| AZ92A-T6 | 0.0094 | 0.37 | 0.020 | 0.80 | 0.025 | 1.0 |
| EZ33A-T5 | 0.020 | 0.79 | 0.040 | 1.6 | 0.028 | 1.1 |
| HK31A-T6 | 0.017 | 0.67 | 0.035 | 1.4 | 0.028 | 1.1 |
| HZ32A-T5 | 0.015 | 0.61 | 0.038 | 1.5 | 0.028 | 1.1 |
| ZH62A-T5 | 0.015 | 0.58 | 0.040 | 1.6 | 0.041 | 1.6 |
| ZK51A-T5 | 0.014 | 0.57 | 0.035 | 1.4 | 0.025 | 1.0 |
| **Site average** | **0.014** | **0.56** | **0.030** | **1.2** | **0.024** | **1.0** |

Source: Ref 21
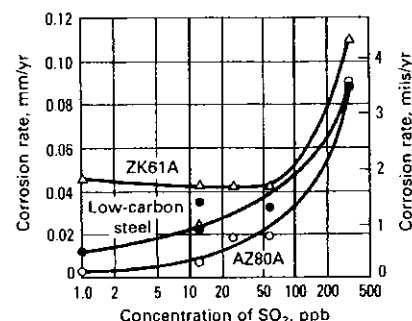
**Fig. 18** Corrosion rates versus $SO_2$ pollution levels at six exposure sites. Rainfall at the sites ranged from 533 to 965 mm/yr (21 to 38 in./yr). Source: Ref 19

These principles are demonstrated in Tables 15 and 16. Table 15 lists the corrosion rates of high- and low-iron samplings of AZ31 sheet and AZ91C-T6 castings at the three test sites represented in Table 13 plus a 20% NaCl salt-spray test for the AZ91 castings. Table 16 assesses the relative galvanic damage to AZ31B-H24 caused by various cleat metals in rural, industrial, and marine exposures.

**Indoor Atmospheres.** Before the computer age, reaction of magnesium alloys with indoor atmospheres was of concern primarily from the standpoint of appearance, not function. The widespread introduction of magnesium die castings into the computer-disk-drive environment has imposed strict new standards of surface stability on the metal because of the need to maintain a clean, particle-free atmosphere at the disk/head interface. The corrosion of magnesium alloys in indoor atmospheres increases with relative humidity. At relative humidities up to about 80%, corrosion is very minor, resulting in the formation of a nearly invisible film of amorphous $Mg(OH)_2$. As humidity increases beyond this level, heavier tarnish films develop, the principal corrosion product now being crystalline $Mg(OH)_2$. In die castings, small traces of chloride residues from cover or refining fluxes may serve as nuclei for corrosion spots in humid air.

The strict requirements of these applications are being met by a combination of the following factors:

- Constant efforts by alloy producers and die casters to provide metal that is extremely low in nonmetallic inclusions
- Use of selected conversion coatings and proprietary protective coatings for supplementary surface stabilization

Accelerated tests involving cyclic humidity and temperature variation provide useful information for these applications, both on coating performance and by detection of any nonmetallic inclusions that might be present.

**Stress-Corrosion Cracking.** Magnesium alloys containing more than about 0.5 to 2.5% Al are susceptible to stress-corrosion cracking (SCC), and the tendency increases with aluminum content. Zinc also induces SCC susceptibility in magnesium alloys, so it is not surprising that the AZ-type alloys, which are the most commonly used magnesium alloys, have the greatest susceptibility to SCC. Magnesium-zinc alloys that are not alloyed with aluminum have intermediate resistance to SCC, while magnesium alloys that contain neither aluminum or zinc are the most resistant to SCC.

The stress sources likely to promote cracking are weldments, inserts, and assembly. Welded structures of susceptible alloys require stress-relief annealing. Stress-corrosion cracking behavior of magnesium alloys is discussed in greater detail in the article "Stress-Corrosion Cracking" in this Handbook.

**Corrosion Fatigue.** Substantial reductions in fatigue strength of magnesium alloys are shown in laboratory tests using NaCl spray or drops. Such tests are useful for comparing alloys, heat treatments, and protective coatings. Effective coatings, by excluding the corrosive environment, provide the primary defense against corrosion fatigue.

## Galvanic Corrosion

Insufficient attention to galvanic corrosion has been one of the major obstacles to the growth of structural applications of magnesium alloys. Serious galvanic problems occur mainly in wet saline environments for the reasons described earlier.

Outstanding improvements in general saltwater-corrosion resistance of magnesium alloys have been achieved by reducing the internal corrosion currents through strict limitations on the critical impurities, nickel, iron, and copper, as well as on the iron-to-manganese ratio. These improvements have no significant effect on galvanic corrosion, because the electromotive force (emf) for corrosion now comes from an external source—the dissimilar metal coupled to magnesium.
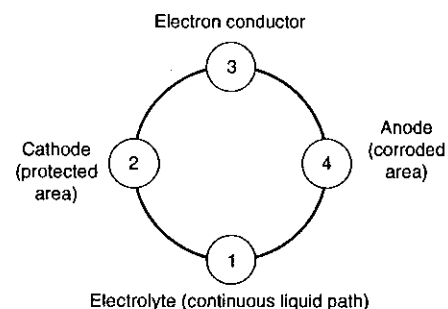
**Table 14  Composition of corrosion product on AZ31B-O alloy after four years atmospheric exposure**

| Exposure site | Corrosion rate | | Panel surface | % by x-ray diffraction | | | |
|---|---|---|---|---|---|---|---|
| | mm | mpy | | Hydromagnesite (a) | Hydrotalcite (b) | Chloride, % | Sulfate, % |
| Kure Beach, NC, | 0.014 | 0.57 | Top | 50 | 50 | 0.070 | 0.14 |
| 80 ft (marine-rural) | | | Bottom | 100 | 0 | 0.031 | 0.18 |
| Kure Beach,NC, | 0.012 | 0.50 | Top | 50 | 50 | 0.024 | 0.05 |
| 800 ft (marine-rural) | | | Bottom | 100 | 0 | 0.022 | 0.13 |
| Midland, MI, (rural) | 0.012 | 0.50 | Top | 50 | 50 | 0.006 | 0.36 |
| | | | Bottom | 100 | 0 | 0.011 | 0.57 |
| Midland, MI, (industrial) | 0.023 | 0.92 | Top | 25 | 75 | 0.016 | 1.2 |
| | | | Bottom | 75 | 25 | 0.010 | 4.5 |
| Madison, WI, (industrial) | 0.025 | 1.02 | Top | 25 | 75 | 0.016 | 1.0 |
| | | | Bottom | 75 | 25 | ... | 3.3 |

(a) $3MgCo_3 \cdot Mg(OH)_2 \cdot 3H_2O$. (b) $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$

**Table 15  Corrosion rates versus exposure and iron content for AZ31 sheet and AZ91 castings**

| Alloy(a) | Iron, ppm | Exposure and average corrosion rates | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Rural | | Industrial | | Marine | | 20% NaCl spray | |
| | | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr | mm/yr | mils/yr |
| (1) AZ31 | 70 | 0.012 | 0.5 | 0.025 | 1.0 | 0.038 | 1.5 | ... | ... |
| (2) AZ31 | 10 | 0.013 | 0.51 | 0.025 | 1.0 | 0.018 | 0.7 | ... | ... |
| Ratio of (1) to (2) | 7 | 0.9 | 0.9 | 1.0 | 1.0 | 2.2 | 2.2 | ... | ... |
| (3) AZ91 | 350 | 0.0043 | 0.17 | 0.016 | 0.6 | 0.022 | 0.87 | 95 | 3740 |
| (4) AZ91 | 10 | 0.0028 | 0.11 | 0.014 | 0.55 | 0.0064 | 0.25 | 0.71 | 27.9 |
| Ratio of (3) to (4) | 35 | 1.5 | 1.5 | 1.1 | 1.1 | 3.5 | 3.5 | 134 | 134 |

(a) (1) AZ31C sheet, (2) AZ31B-H24 sheet, (3) AZ91C-T6 cast plate (Fe/Mn = 0.15), (4) AZ91C-T6 cast plate (Fe/Mn = 0.007). Source: Ref 21

**Table 16  Severity of galvanic attack on AZ31B-H24 sheet versus coupled metal cleat and exposure**

| Cleat metal | Relative loss of tensile strength(a) | | |
|---|---|---|---|
| | Rural (State College, PA) | Urban-industrial (Newark, NJ) | Marine (Kure Beach, NC, 24.4 m, or 80 ft, site) |
| Aluminum alloy 5052 | 1.0 | 2.4 | 3.2 |
| Aluminum alloy 7075 | 1.0 | 4.0 | 10.2 |
| AISI type 304 stainless steel | 1.8 | 6.8 | 18.0 |
| Monel | 2.2 | 8.8 | 21.4 |
| Low-carbon steel | 3.0 | 13.6 | 24.8 |
| 85–15 brass | 3.6 | 14.2 | 30.4 |

(a) See data in Table 12: aluminum alloy 5052 tested at State College, PA = 1.00. Source: Ref 20



Electron conductor

Cathode (protected area)

Anode (corroded area)

Electrolyte (continuous liquid path)

**Fig. 19** The corrosion circle. 1, Electrolyte (continuous liquid path, usually water in the form of condensate, salt spray, etc.). 2, Cause (cathode—the cause of corrosion—the area through which electricity flows). 3, Electron conductor (in a structure, usually a metal-to-metal contact, e.g., rivets, bolts, spot welds, etc.). 4, Effect (anode—the surface or object that corrodes)

**Principles of Galvanic Corrosion.** The conditions necessary for galvanic corrosion to occur are shown in Fig. 19. If only one of these factors is eliminated, galvanic corrosion can be prevented.

The basic principles of corrosion are fundamental to any design involving metals; the degree to which they can be employed properly determines the amount and the kind of finishing protection required in a given environment. These basic design principles are summarized briefly in Table 17 in their order of importance.

Details of these measures are treated in the section "Protection of Assemblies" in this article. It is useful, however, to review the basic principles governing the galvanic corrosion of magnesium and the relative compatibility of dissimilar metals with magnesium.

**Relative Compatibility of Metals.** All structural metals are cathodic to (more noble than) magnesium. The degree to which the corrosion of magnesium is accelerated under a given set of exposure conditions depends partly on the relative positions of the two metals in the emf series, but more importantly it depends on how rapidly the effective potential of the couple is reduced by polarization as galvanic current flows. The principal polarization mechanism in a magnesium couple in salt water is the resistance to the formation and liberation of hydrogen gas at the cathode. Therefore, metals of low hydrogen overvoltage, such as nickel, iron, and copper, constitute efficient cathodes for magnesium and cause severe galvanic corrosion. Metals that combine active potentials with higher hydrogen overvoltages, such as aluminum, zinc, cadmium,

and tin, are much less damaging, although not fully compatible with magnesium.

Galvanic corrosion is most severe in wet chloride-bearing environments (saltwater splash, spray, or immersion), but it may also be serious in chloride-bearing atmospheres. Data were compiled in tests at Kure Beach, NC, in which sheets of dissimilar metals were fastened to panels of AZ31B and AZ61A. The dissimilar metals were divided into five groups based on observed gradations of galvanic damage to magnesium. These ratings are summarized in Table 19.

**Effects of Anode and Cathode Areas.** The relative areas of the magnesium anode and the dissimilar-metal cathode have an important effect on the corrosion damage that occurs. A large cathode coupled with a small area of magnesium results in rapid penetration of the magnesium, because the galvanic-current density at the small magnesium anode is very high, and anodic polarization in chloride solutions is very limited. This explains why painted magnesium should not be coupled with an active cathodic metal if the couple will be exposed to salt water. A small break in the coating at the junction results in a high concentration of galvanic current at that point unmitigated by any polarization. Unfavorable area effects can also be seen in the behavior of some proprietary coatings using aluminum or zinc powder. When used as a coating on a steel bolt attached to magnesium, the metallic pigment can present a very large effective surface area, which may be more detrimental than bare steel. Galvanic action is further accelerated if the metallic pigment contains such impurities as iron.

**Effects of Minor Constituents on Compatibility of Aluminum with Magnesium.** Severe galvanic corrosion is caused by the presence of metals having low hydrogen overvoltage, such as copper, nickel, and iron, in aluminum coupled to magnesium. Therefore, aluminum alloys containing small percentages of copper (7000 and 2000 series and 380 die-casting alloy) may cause serious galvanic corrosion of magnesium in saline environments. Very pure aluminum is quite compatible, acting as a polarizable cathode. However, an extremely potent cathode for magnesium is the intermetallic compound $FeAl_3$, which is present in all commercial aluminum alloys. The effect of iron is diminished by the presence of magnesium in the aluminum alloy (Fig. 20). This agrees with the relatively compatible behavior of aluminum alloy 5052, shown in Table 16.

**Cathodic Corrosion of Aluminum.** Assessment of compatibility of aluminum alloys with magnesium alloys is complicated by the fact that aluminum can be attacked by the strong alkali generated at the cathode when magnesium corrodes sacrificially in static NaCl solutions. Such attack destroys compatibility in alloys having significant iron contents, apparently by exposing fresh, active sites with low overvoltage. The aluminum alloys having substantial magnesium content (5052 and 5056) are more resistant to this effect but not completely so. The essential requirement for a fully compatible aluminum alloy, as indicated in Fig. 20, would be met by a 5052 alloy with a maximum of 200 ppm Fe or a 5056 alloy with a maximum of 1000 ppm Fe. Commercial 5052 alloy produced in the United

## Table 17 How to design corrosion out of magnesium structures

| Procedure | Method |
|---|---|
| Eliminate "sump" areas where trapped moisture is held in contact with metal. | • Design them out in the first place by careful attention to design of structure details.<br>• Provide properly located drain holes. Minimum hole size about 3.2 mm ($\frac{1}{8}$ in.) to prevent plugging. |
| Choose nonabsorbent, nonwicking materials to contact magnesium | • Determine water absorption qualities of materials to be used.<br>• Use epoxy and vinyl tapes and coatings, wax, or latex for protective barriers.<br>• Avoid, if possible, use of wood, paper, cardboard, open cell foams, and sponge rubbers. |
| Protect all faying surfaces. | • Use proper sealing materials (tapes, films, sealing compounds) on all faying surfaces.<br>• Use primers.<br>• Lengthen continuous liquid path to reduce galvanic current. |
| Use compatible metals. | • For magnesium-aluminum couples, 5000 and 6000 series alloys are most compatible.<br>• For magnesium-steel couples, plate steel with zinc, 80%Sn-20%Zn, tin, or cadmium<br>• See Table 18 for alloy preferences in bimetallic couples. |
| Select proper finishing systems. | • Choose chemical treatments, paints, plating on basis of service requirements.<br>• Service test system before setting up production run.<br>• Use past experience in similar applications as guide to choice. |

## Table 18 Choice of material for bimetallic joints in descending order of preference

**Magnesium to aluminum**

1. Aluminum alloy 5056 (wire and rivets)
2. Aluminum alloy 5052 (sheet)
3. Aluminum alloy 6061 (extrusions and sheet)
4. Aluminum alloy 6053 (extrusions and rivets)

**Magnesium to steel**

1. Zinc plate
2. 80% tin-20% zinc plate
3. Tin plate
4. Cadmium plate

## Table 19 Relative effects of various metals on galvanic corrosion of magnesium alloys AZ31B and AZ61A exposed at the 24.4 and 244 m (80 and 800 ft) stations, Kure Beach, NC

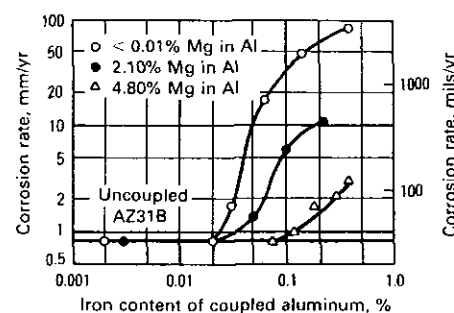| Group 1 (least effect) | Group 2 | Group 3 | Group 4 | Group 5 (greatest effect) |
|---|---|---|---|---|
| Aluminum alloy 5052 | Aluminum alloy 6063 | Alclad alloy 2024 | Zinc-plated steel | Low-carbon steel |
| Aluminum alloy 5056 | Alclad alloy 7075 | Aluminum alloy 2017 | Cadmium-plated steel | Stainless steel |
| Aluminum alloy 6061 | Aluminum alloy 3003 | Aluminum alloy 2024 | | Monel |
| | Aluminum alloy 7075 | Zinc | | Titanium |
| | | | | Lead |
| | | | | Copper |
| | | | | Brass |



**Fig. 20** Corrosion rates in 3% NaCl solution of magnesium alloy AZ31B coupled with aluminum containing varying amounts of iron and magnesium. The corrosion rate of uncoupled AZ31B is shown for comparison.
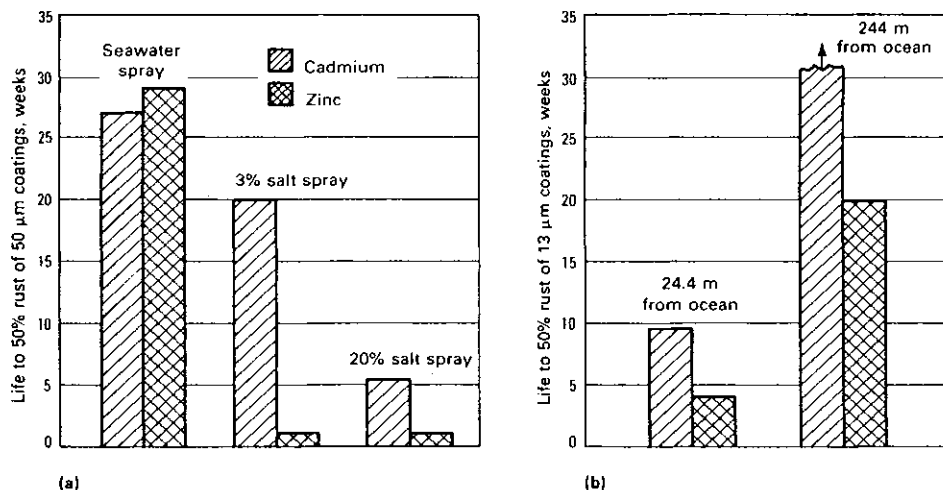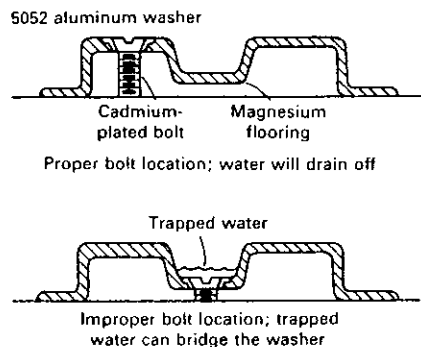
**Fig. 21** Comparison of cadmium-zinc plate on steel in salt-spray tests and marine atmospheres. (a) 200 μm coating. (b) 50 μm coating. Source: Ref 22



**Fig. 22** Schematic of the proper method of protecting faying surfaces in magnesium-to-magnesium assemblies
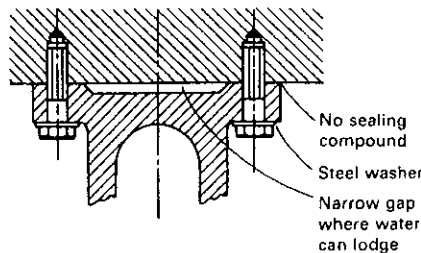
States and Canada is permitted by specification to have a maximum (iron + silicon) content of 0.45% and may typically contain 0.3% Fe. In a severe exposure such as 5% NaCl immersion, this iron content, combined with the cathodic corrosion caused by the current from the magnesium, can render the 5052 alloy incompatible with magnesium. In most real situations, however, this extreme condition would not exist, and a 5052 washer under the head of a plated steel bolt in a magnesium assembly would reduce galvanic attack of the magnesium. For maximum effect of the washer, the linear distance along the aluminum from the bolt should be about 5 mm ($^3$/$_{16}$ in.).
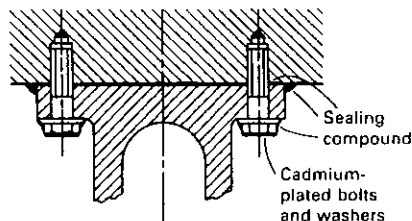
Cathodic corrosion of aluminum is much less severe in seawater than in NaCl solution, because the buffering effect of magnesium ions

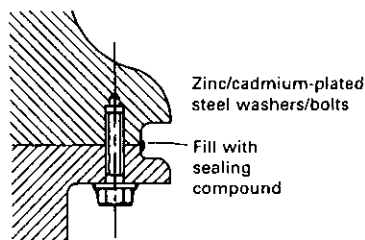reduces the equilibrium pH from 10.5 to about 8.8. The compatibility of aluminum with magnesium is accordingly better in seawater and is less sensitive to iron content.

**Cathodic Damage to Coatings.** Hydrogen evolution and strong alkalinity generated at the cathode can damage or destroy organic coatings applied to fasteners or other accessories coupled to magnesium. Alkali-resistant resins are necessary, but under severe conditions, such as salt spray or salt immersion, the coatings may be simply blown off by hydrogen, starting at small voids or pores. Because of its severity, the salt-spray test can lead to rejection of some fastener coatings that may provide useful benefits in real service environments. Salt spray should not be relied upon exclusively to evaluate these coatings.

**Compatibility of Plated Steel.** Zinc, tin-zinc, cadmium, or tin-lead plating on steel reduce galvanic attack of magnesium substantially compared to bare steel. This reflects the more compatible potentials, polarization characteristics, and/or the higher hydrogen overvoltages of the plated deposits. Supplementary chromate or other surface treatments can strongly enhance the compatibility of plated deposits. The salt-spray test is biased against bare zinc plating because zinc is rapidly removed from the steel substrate in this test medium due to general corrosion as well as cathodic attack when coupled with magnesium. This does not occur in many natural environments, and the failure of the salt-spray test to rate zinc and cadmium plating properly in marine atmospheres is well known (Fig. 21).









**Fig. 23** Design considerations for reducing galvanic corrosion. (a) Proper bolt location. (b) Poor practice. (c) Good with no gap. (d) For use when direct metal-to-metal contact is required for electrical reasons
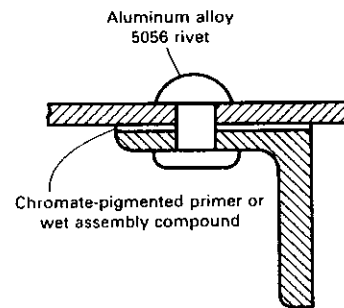
## Protection of Assemblies

A dissimilar metal in contact with magnesium will not by itself result in serious galvanic corrosion. For corrosion to occur, both surfaces must be wetted by a common electrolyte. The degree to which precautions against galvanic corrosion are taken will depend on many factors, of which the operating environment is of primary importance.

For indoor use, where condensation is not likely, no protection is necessary. Even in some sheltered outdoor environments, magnesium com-

ponents can give good service lives without special precautions against galvanic attack provided other mitigating factors are present. These factors include design elimination of water traps, good ventilation, component warmth, or the presence of an oil film.

For continuous outdoor use, during which magnesium assemblies may be wetted or subjected to salt splash or spray, precautions against galvanic attack must be taken. Although corrosive attack from any source can jeopardize the satisfactory performance of magnesium components, attack resulting from galvanic corrosion is by far most detrimental. Under corrosive conditions, use of high-purity magnesium alloys will have no significant influence in reducing the effects of galvanic corrosion.

**Magnesium-to-Magnesium Assemblies.** For all practical purposes, galvanic corrosion between magnesium alloys is negligible. However, because joining two magnesium components almost invariably involves use of dissimilar-metal fasteners and the formation of a crevice at the joint, good assembly practice dictates that in corrosive conditions some precautions should be taken (Fig. 22). Magnesium faying or mating surfaces should be assembled using wet-assembly techniques. Chromate-inhibited primers or sealing compounds are placed between the surfaces at the time of assembly. Sealing/jointing compounds that remain flexible and resist cracking

are preferred. Polymerizing-type compounds are also used for caulking operations. In bolted assemblies, the retorquing of bolts shortly after assembly will help eliminate any joint relaxation problems. For additional protection, mating surfaces should be primed before assembly and painted after assembly.

**Magnesium-to-Nonmetallic Assemblies.** Although the joining of most nonmetallic materials, such as plastics and ceramics, to magnesium will not result in any potential corrosion hazard, there are some notable exceptions. Magnesium-to-wood assemblies present an unusual problem because of the water absorbency of wood and the tendency of the assemblies to leach out natural acids. To protect magnesium from attack, the wood should first be sealed with paint or varnish, and the faying surface of the magnesium treated as described above for magnesium-to-magnesium assemblies. The joining of magnesium to carbon-fiber-reinforced plastics is another exception that, in the presence of a common electrolyte, could result in corrosion of the magnesium unless similar assembly precautions are observed.

**Magnesium-to-Dissimilar-Metal Assemblies.** Several techniques can be implemented to minimize or eliminate galvanic corrosion:

- Elimination of the common electrolyte

- Reduction of the relative area of dissimilar metal present
- Reduction of the effective potential difference between the dissimilar metal and the magnesium
- Protective coating of the dissimilar metal and the magnesium from the common electrolyte

Good design can play a vital role in reducing the threat of galvanic corrosion (Fig. 23). Elimination of a common electrolyte may be possible by the provision of a simple drain hole or shield to prevent liquid entrapment at the dissimilar-metal junction. Alternatively, the location of screws or bolts on raised bosses may also help avoid common electrolyte contact, as would use of nylon washers, spacers, or similar moisture-impermeable gaskets. The use of studs in place of bolts will reduce the area of dissimilar metal exposed by up to 50%, provided the captive ends of the studs are located in blind holes.

The degree of attack resulting from galvanic corrosion is, among other things, determined by the potential difference between the metals involved. Consequently, this should be reduced to a minimum by careful material selection or the use of selected plating or coating of metals brought into contact with magnesium.

As discussed above, the dissimilar metals that are relatively compatible with magnesium are the aluminum-magnesium (5000 series) alloys, which should be used for washers, shims, fasteners (rivets and special bolts), and structural members, where possible. Other aluminum alloys (with the possible exception of aluminum-magnesium-silicon [6000 series] aluminum alloys), steels, titanium, copper, brass, monel, and others will corrode magnesium when coupled with it under corrosive conditions, and protection may be required.

Figure 24 indicates the relative severity of galvanic corrosion of die-cast AZ91D caused by coupling with various dissimilar metals in salt spray (ASTM B 117). These ratings provide useful guidelines for selection, but they are not
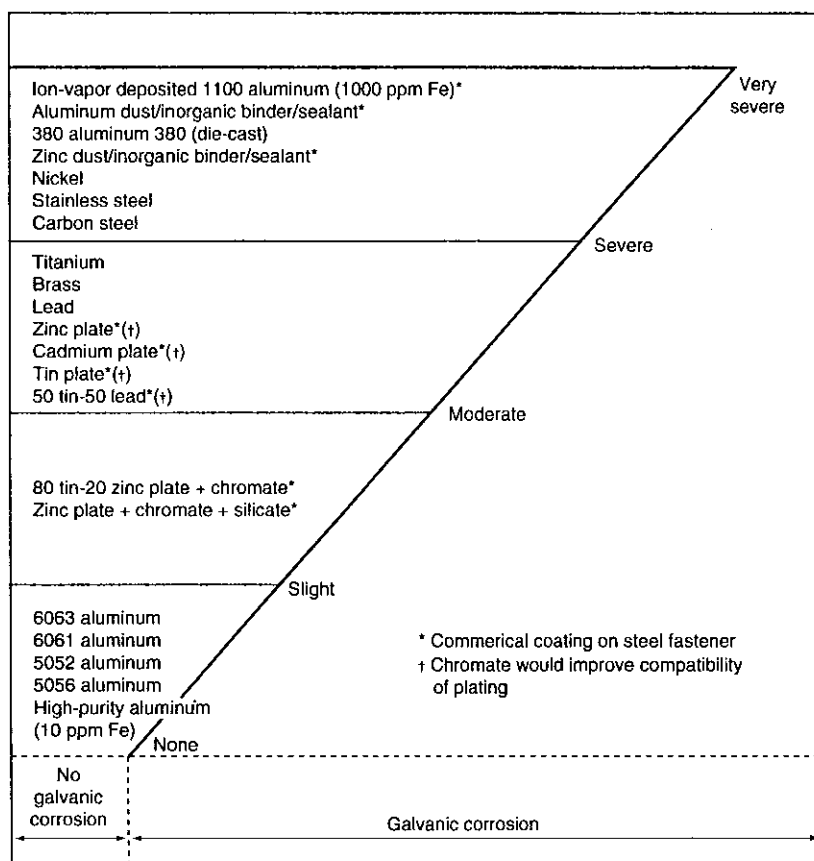


Ion-vapor deposited 1100 aluminum (1000 ppm Fe)*
Aluminum dust/inorganic binder/sealant*
380 aluminum 380 (die-cast)
Zinc dust/inorganic binder/sealant*
Nickel
Stainless steel
Carbon steel

Titanium
Brass
Lead
Zinc plate*(†)
Cadmium plate*(†)
Tin plate*(†)
50 tin-50 lead*(†)

80 tin-20 zinc plate + chromate*
Zinc plate + chromate + silicate*

6063 aluminum
6061 aluminum
5052 aluminum
5056 aluminum
High-purity aluminum
(10 ppm Fe)

No galvanic corrosion

Very severe
Severe
Moderate
Slight
None
Galvanic corrosion

* Commerical coating on steel fastener
† Chromate would improve compatibility of plating

**Fig. 24** Relative galvanic corrosion produce by dissimilar fasteners attached to AZ91D magnesium alloy (ASTM B 117 salt-spray test). Source: Ref 23, 24



Caulking  Magnesium  Caulking
Insert                              Insert

Preferable        Sometimes necessary

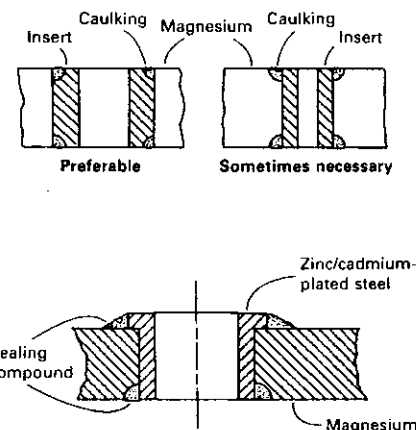Zinc/cadmium-plated steel
Sealing compound
Magnesium

**Fig. 25** Examples of good practice for bushing installations

quantified because of the major influence of design factors and the difference between actual environmental conditions and the severe salt-spray test.

Use of wet-assembly techniques, as discussed previously, will eliminate galvanic corrosion in crevices. Caulking the metal junctions will increase the electrical resistance of the galvanic couple by lengthening the electrolytic path and thus reduce the degree of attack should it occur (Fig. 25). Vinyl tapes have also been used to separate magnesium from dissimilar metals or a common electrolyte and thus prevent galvanic attack (Fig. 26). Finally, painting the magnesium and, more importantly, the dissimilar metal after assembly will effectively insulate the two materials externally from any common electrolyte.

**Fastener Selection.** The design of bolted connections and selection of fastener materials are critical decisions for magnesium assemblies

exposed to salt water. In rare instances, the problem can be completely avoided by the use of nonmetallic fasteners or insulating washers (Fig. 27). Where strength is adequate and possibility of seizure is not a concern, fasteners made of compatible aluminum alloys (5000 series, or 6000 series) can limit galvanic corrosion. In the great majority of situations, mechanical requirements and cost factors dictate the use of steel fasteners having plated or other protective coatings. However, many proprietary coatings based on zinc or aluminum powders in organic or inorganic binders prove to be completely incompatible with magnesium in salt exposure. Phosphate coatings on steel bolts do not significantly reduce galvanic corrosion of magnesium.

A recent study compared several commercial fastener coatings with two types of heavy-duty polymer encapsulation for ability to reduce galvanic attack of die-cast AZ91D test plates in salt spray (Fig. 28). The most effective coating was

nylon 11 electrostatically applied to the head surfaces of a socket-head bolt to a thickness of 0.20 to 0.25 mm (8 to 10 mils). This coating has performed satisfactorily on clamping bolts joining two halves of die-cast-magnesium 4 WD transfer cases in light-truck applications. A high level of protection was also demonstrated in this study by the molded plastic caps shown in Fig. 29. Both the plastic caps and the nylon 11 coating provide a substantial barrier to the flow of galvanic current through the electrolyte.

In the category of electroplated coatings, zinc is fundamentally the most compatible with magnesium due to its position in the emf series and its polarization characteristics. Zinc-plating technology is highly developed, and zinc plating is economical. Specialized plating processes have been developed in which the zinc deposit is chemically augmented or alloyed with tin, nickel, or cobalt to improve the life of the coating in salt-spray environments, where unmodified zinc tends to corrode rapidly. Four commercial modified zinc-alloy plates were included in the study:

- Zinc plate + chromate + silicate (JS500)
- 80 tin-20 zinc plate + chromate
- Zinc-7 to 13 nickel plate (Zincrolyte CLZ-Ni)
- Zinc-0.2 to 0.9 cobalt plate + supplements (Zincrolyte CLZ-Co)

The first two of these coatings reduced the magnesium corrosion by more than 90%. Predictably, the zinc-nickel and zinc-cobalt alloy deposits were much less effective, a consequence of the adverse cathodic activity of nickel and cobalt.
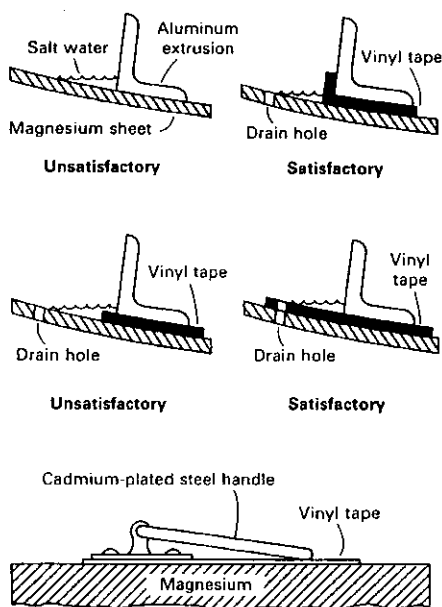


**Fig. 26** Use of insulating tapes to avoid galvanic corrosion



**Fig. 27** Use of nylon washers to separate a magnesium automobile grill from a steel hood and hold-down screw and avoid galvanic corrosion
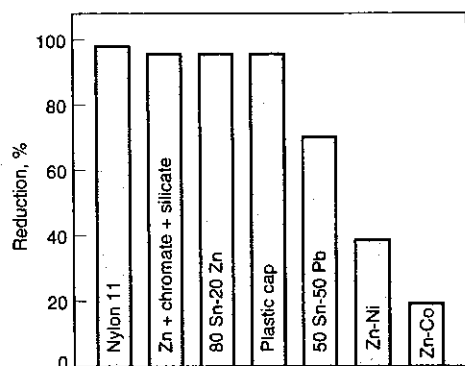


**Fig. 28** Reduction of galvanic corrosion between magnesium-alloy AM60B die-cast test plates and various coated steel fasteners, compared to bare steel fasteners. Tested for 200 h in continuous salt spray. Source: Ref 24
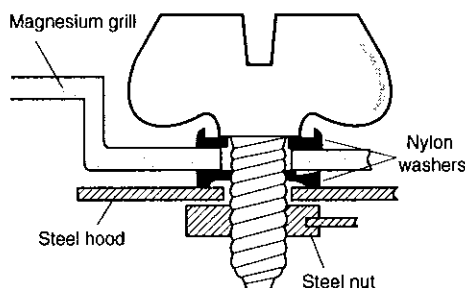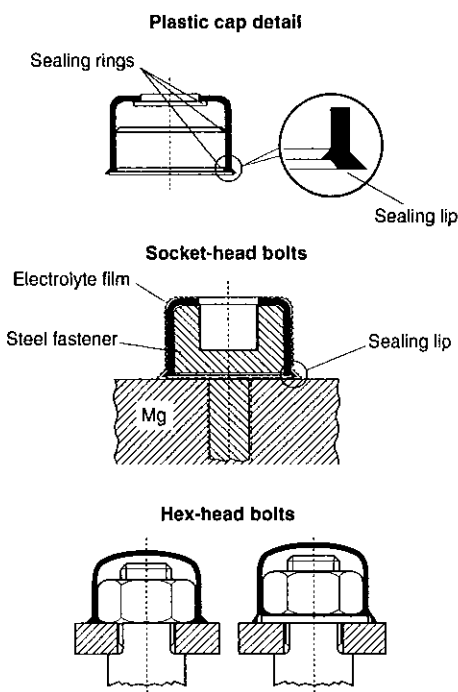


**Fig. 29** Use of molded plastic caps on socket-head and hex-head bolts to avoid galvanic corrosion. Source: Ref 24
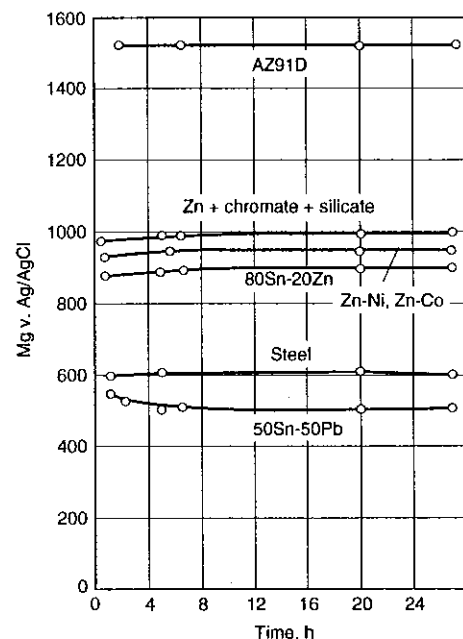


**Fig. 30** Open-circuit potentials of plated steel and bare steel fasteners and die-cast AZ91D magnesium alloy against a Ag/AgCl reference electrode in 5% NaCl saturated with Mg(OH)$_2$. Source: Ref 24

**Table 20** Salt-spray galvanic corrosion of pressure die-cast AZ91B effect of washer, washer material, and surface treatment

| Mg(b) | Assembly(a) Bolt | Washer | Corroded area around bolthead/washer, mm | Maximum penetration mm | mils |
|---|---|---|---|---|---|
| A | M12, black phosphate | None | 1030 | 2.3 | 92 |
| B | M12, black phosphate | None | 1030 | 2.8 | 112 |
| A | M12, one mil Zn-plate(c) | None | 250 | 1.7 | 68 |
| A | M12, one mil Zn-plate(c) | Steel 1 mil Zn-plate(c) | 150 | 1.1 | 44 |
| A | M12, one mil Zn-plate(c) | Al (6082) | 40 | 0.6 | 24 |
| B | M12, one mil Zn-plate(c) | None | 330 | 1.6 | 64 |
| B | M12, one mil Zn-plate(c) | Steel as above | 100 | 1.0 | 40 |
| B | M12, one mil Zn-plate(c) | Al (6082) | 20 | 1.3 | 52 |
| C | M12, one mil Zn-plate(c) | None | 320 | 2.1 | 84 |
| C | M12, one mil Zn-plate(c) | Steel as above | 130 | 1.9 | 76 |
| C | M12, one mil Zn-plate(c) | Al (6082) | 20 | 0.7 | 28 |

(a) Magnesium alloys test panels with two bolts in each. (b) Treatment: A, none; B, yellow chromate; C, anodized HAE 15–20 μm. (c) Yellow chromate post treatment

**Table 21** Effects of 5052 aluminum alloy washers with plated steel bolts in salt spray and salt-water-immersion tests

| Fastener unit | Relative weight losses of AZ91D 10 days salt spray | 16 h immersion in 5% NaCl |
|---|---|---|
| Nylon | 1.0 (0.28 g) | 1.0 (0.07 g) |
| Cadmium plated, 5052 washer(a) | 5.85 | 48.7 |
| Tin plated, 5052 washer(a) | 8.84 | 37.7 |
| Zinc plated, 5052 washer(a) | 15.82 | 39.9 |
| Bare steel, 5052 washer(a) | 6.81 | 326.0 |
| Cadmium plated | 14.0 | 26.7 |
| Tin plated | 11.8 | 17.6 |
| Zinc plated | 18.5 | 14.9 |
| Bare steel | 31.3 | 377.0 |

| Washer benefit factor(b) Bolt material | Salt spray | 5% NaCl immersion |
|---|---|---|
| Zinc plated | 1.17 (0.28) | 0.37 (1.09) |
| Tin plated | 1.33 (0.32) | 0.47 (1.09) |
| Cadmium plated | 2.39 (0.25) | 0.55 (1.11) |
| Steel | 4.60 (0.18) | 1.16 (0.14) |

(a) 1¼ in. outside diameter washer (d = 317 mils). (b) (Magnesium corrosion without washer)/(Magnesium corrosion with washer). Numbers in parentheses: weight loss of five 5052 washers. Source: Ref 23

Also included in this study were steel bolts commercially plated with a deposit of 50 tin-50 lead. This coating reduced the galvanic attack of magnesium by about 70%, despite the fact that its open-circuit potential was about 100 mV more noble than that of steel. Figure 30 illustrates the important principle that it is the polarized potential that governs galvanic corrosion rather than the position of the dissimilar metal on the equilibrium emf series.

**Washers.** Properly selected and sized washers or spacers can contribute substantially to control of galvanic corrosion at magnesium/dissimilar-metal junctions. Insulating plastics are effective where their limited mechanical properties do not cause loss of clamping force. Aluminum 5052 or other compatible aluminum alloy is a preferred material for washers and spacers. A 5052 aluminum washer interposed between cast-iron engine blocks and AZ91D magnesium clutch housings has successfully prevented galvanic attack of the magnesium under conditions of road-salt splash.

Table 20 shows the effect of washer, washer material, and surface treatment on salt-spray galvanic corrosion of high-pressure die-cast AZ91B. The improved protection by zinc plating of the fastener as compared to simple black phosphate treatment is shown. The surface condition of the magnesium alloy, from untreated through chromating and anodizing, has little effect on the galvanic-corrosion behavior.

Washers and spacers are used to increase the length of the electrolyte path that separates the dissimilar metals. Effect of spacer thickness on the galvanic corrosion (salt spray) of AZ91 coupled to cast-iron disks through plastic spacers is shown in Fig. 31. The galvanic effect caused by

contact with the cast-iron disks disappears when the plastic spacer thickness exceeds 175 thousandths of an inch. Figure 32 shows the effect of aluminum-washer size on the galvanic corrosion (salt spray) of AZ91D fastened with cadmium-plated bolts. The galvanic effect due to the cadmium plate disappears when the excess diameter plus the washer thickness reaches 150 to 200 thousandths of an inch
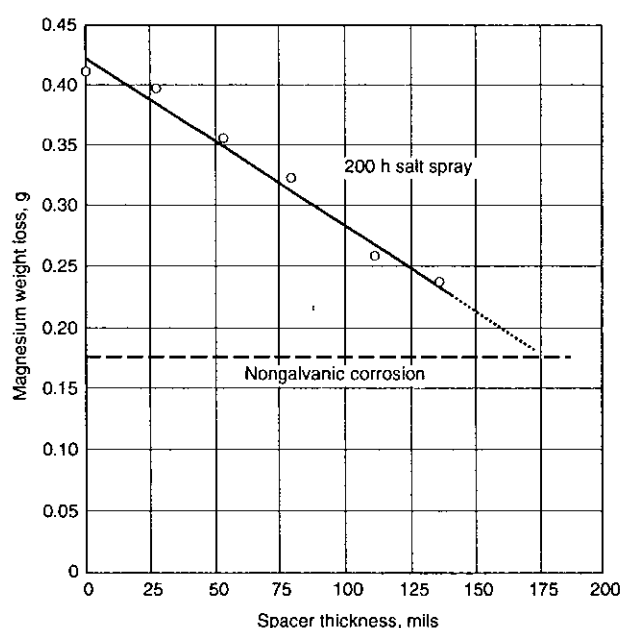


**Fig. 31** Effect of spacer thickness on the galvanic corrosion of AZ91 magnesium coupled to cast-iron disks through plastic spacers (200 h salt spray). Source: Ref 23
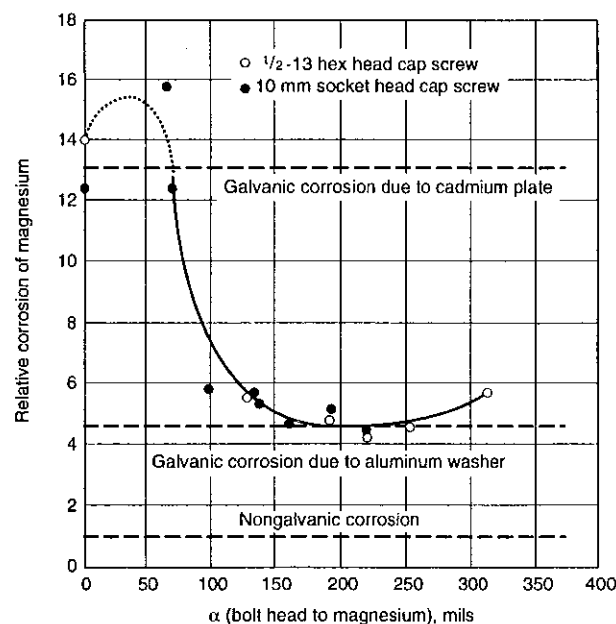


**Fig. 32** Effects of aluminum-alloy washer size on the galvanic corrosion of AZ91 magnesium fastened with cadmium-plated bolts. α is a linear distance measured from the cadmium-plated bolt head to the magnesium surface via washer surface. 10 days salt-spray exposure. ASTM standard B 117. Source: Ref 23

**Table 22  Corrosion rates of magnesium and aluminum in galvanic couples 24 h immersion in 5% NaCl**

| Couple(a) | Average corrosion rate, mm/yr | |
|---|---|---|
| | AZ91D | Aluminum |
| AZ91D, high-purity aluminum(b) | 1.8 | 0.8 |
| A91D, Al 5052 | 20.0 | 13.0 |
| A91D, Al 1100 | 31.0 | 59.0 |
| A91D, Al 380 | 73.0 | 61.0 |

(a) Exposed surface area 3 × 14 cm (both), 0.6 cm space between them. (b) Less than 10 ppm Fe. Source: Ref 23

(approximately $\frac{3}{16}$ in.). For conservative design, the spatial separation provided by the washer or spacer should be at least 5 mm (200 mil).

It is important to note that even though the use of 5052 aluminum washers decreases the galvanic effect of AZ91D connected by cadmium-, tin-, or zinc-plated steel and bare steel in salt-spray conditions, a different behavior is observed when immersed in salt solution. Table 21 shows the effects of 5052 aluminum washers with plated steel bolts in salt-spray and saltwater immersion tests. The results of 5 wt% NaCl immersion tests indicate that the washer was actually detrimental. It is reported that the ineffectiveness of the washers with plated bolts was associated with a high rate of cathodic attack on the aluminum compared to that which occurred in salt spray. Similarly, severe corrosion of AZ91D was observed (Table 22) in salt immersion when coupled with other aluminum-alloy contacts (5052, 1100, and 380), with proportionately severe cathodic corrosion of the aluminum. Magnesium assemblies are not deliberately subjected to saltwater immersion, but a situation approaching this could occur with unfavorable designs that allow accumulation of pools of salt water at dissimilar junctions.

## Protective Coating Systems

A full range of cleaning and finishing treatments are available for the protection of magnesium-alloy parts in the various service environments in which these parts are used. For a review of these treatments and their application and performance, see the article "Cleaning and Finishing" in this Handbook.

## ACKNOWLEDGMENTS

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