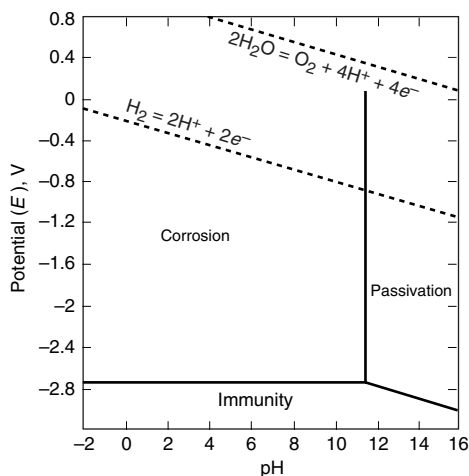# Corrosion Resistance of Magnesium Alloys

Revised by Barbara A. Shaw, Pennsylvania State University

MAGNESIUM AND MAGNESIUM ALLOYS are often thought of as rapidly corroding metals because of their active positions in both the electromotive force (EMF) series (Table 1) and the galvanic series for seawater (see Fig. 1 in the article "Evaluating Galvanic Corrosion" in this Volume). However, depending on the environment and certain design considerations, the corrosion of magnesium can be well within acceptable design limits. Knowledge of environmental factors that influence degradation, types of corrosion to which magnesium alloys are most susceptible, protection schemes, and design considerations can significantly minimize corrosion and increase use of this family of lightweight structural metals.

When unalloyed magnesium is exposed to the air at room temperature, a gray oxide forms on its surface. Moisture converts this oxide to magnesium hydroxide, which is stable in the basic range of pH values, but is not in the neutral or acid ranges as shown in the Pourbaix diagram (Fig. 1). The immunity region of the diagram is well below the region of water stability; as a result, in neutral and low pH environments magnesium dissolution is accompanied by hydrogen evolution. In basic environments, passivation is possible as a result of the formation of a $Mg(OH)_2$ layer on the metal surface. Since the films that form on unalloyed magnesium are slightly soluble in water, they do not provide long-term protection (Ref 2). When chloride, bromide, sulfate, and chlorate are present, the surface films break down. Likewise, as the CO_2 in air acidifies water, the films are not stable. Corrosion potentials for magnesium electrodes in a variety of aqueous solutions are presented in Table 2, while corrosion rate data in water and several other media are presented in Fig. 2 and Table 3.

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

The first includes alloys containing 2 to 10% Al, combined with minor additions of zinc and manganese. These alloys are widely available at moderate cost, and their room-temperature mechanical properties are maintained to 95 to 120 °C (200 to 250 °F). Beyond this, elevated temperatures adversely affect mechanical properties and the corrosion properties deteriorate rapidly with increasing temperature.

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

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

Table 2 Rest potential of magnesium electrodes under various aqueous solutions

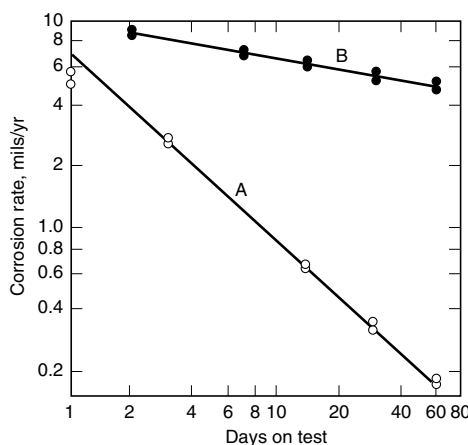| Electrolyte	E_R (vs NHE)
N NaCl	−1.72
N Na$_2$SO$_4$	−1.75
N Na$_2$CrO$_4$	−0.96
N HCl	−1.68
N HNO$_3$	−1.49
N NaOH	−1.47
N NH$_3$	−1.43
Ca(OH)$_2$ saturated	−0.95
Ba(OH)$_2$ saturated	−0.88

N, normal. Source: Ref 3

Fig. 1 Potential-pH (Pourbaix) diagram for the system of magnesium and water at 25 °C (77 °F), showing the theoretical domains of corrosion, immunity, and passivation. Source: Ref 1

Fig. 2 Corrosion rates as a function of time for commercially pure magnesium. Curve A, distilled water vented to air through a caustic trap; curve B, distilled water vented to atmospheric CO_2. Source: Ref 2

higher costs. Table 4 lists some of the compositions commonly available in both systems. Note the aluminum group alloy designations begin with "A."

Metallurgical Factors

Chemical Composition. As the galvanic series in seawater reveals, magnesium is anodic to all other structural metals and, as a result, galvanic interactions between magnesium and other metals are a serious concern. The influence of cathodic iron impurities on the corrosion of commercially pure magnesium is presented in Fig. 3. Above the tolerance level of 170 ppm for iron in magnesium, the corrosion rate increases dramatically. Figure 4 shows the effects of iron and 13 other 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), as well as thorium, zirconium, beryllium, cerium, praseodymium, and yttrium, 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% (Ref 6). 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 must be moderated through the use of alloying elements such as manganese or zinc, to obtain good corrosion resistance. These limits are stated in Table 5 for die-cast products.

Figure 5 illustrates the effect of increasing iron, nickel, and copper contamination on the standard ASTM B 117 salt-spray performance of die-cast AZ91 test specimens as compared to the range of performance observed for cold-rolled steel and die-cast aluminum alloy 380 samples. Such results have led to the definition of the critical contaminant limits for two magnesium-aluminum alloys in both low- and high-pressure cast form and the introduction of improved high-purity versions of the alloys. Table 6 lists some of the critical contaminant limits defined to date. 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 11).

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 (Ref 8). 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% Zn because of its detrimental effects on microshrinkage porosity and its accelerating effect on corrosion above 3%.

For magnesium-rare earth, -thorium, and -zinc alloys containing zirconium, the normal saltwa-
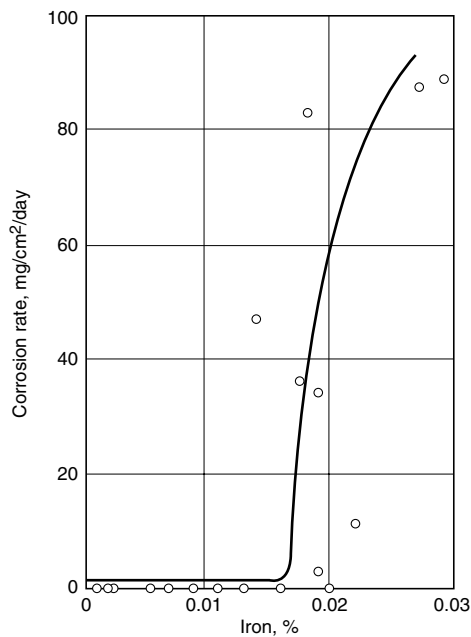
Fig. 3 Effect of iron content on the corrosion rate of commercially pure magnesium subjected to alternate immersion in 3% NaCl. Source: Ref 4
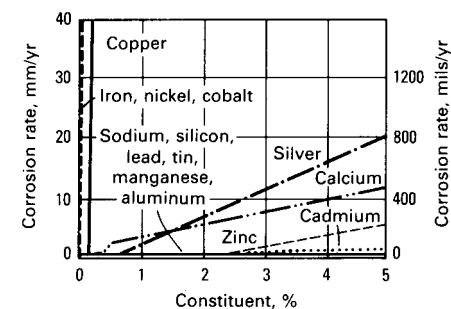
Fig. 4 Effect of alloying and contaminant metals on the corrosion rate of magnesium as determined by alternate immersion in 3% NaCl solution. Source: Ref 5

Table 3 Corrosion rate of commercially pure magnesium in various media

Medium	Corrosion rate	
	mm/yr	mils/yr
Humid air	1.0×10^{-5}	0.0004
Humid air with condensation	1.5×10^{-2}	0.6
Distilled water	1.5×10^{-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	5.5×10^{-2}	2.2
Seawater	0.25	10
3M MgCl$_2$ solution	300	12×10^3
3M NaCl (99.99% high-purity Mg 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 4

Table 4 Typical magnesium alloy systems and nominal compositions

Alloy No.		Element(a), %							
ASTM	UNS	Al	Zn	Mn	Ag	Zr	Th	Re	Product form(b)
AM60	M10600	6	. . .	0.2	. . .	. . .	. . .	. . .	C
AZ31	M11310	3	1	0.2	. . .	. . .	. . .	. . .	W
AZ61	M11610	6	1	0.2	. . .	. . .	. . .	. . .	W
AZ63	M11630	6	3	0.2	. . .	. . .	. . .	. . .	C
AZ80	M11800	8	0.5	0.2	. . .	. . .	. . .	. . .	C, W
AZ91	M11910	9	1	0.2	. . .	. . .	. . .	. . .	C
EZ33	M12331	. . .	2.5	. . .	. . .	0.5	. . .	2.5	C
ZM21	. . .	. . .	2	1	. . .	. . .	. . .	. . .	W
HK31	M13310	. . .	0.1	. . .	. . .	0.5	3	. . .	C, W
HZ32	M13320	. . .	2	. . .	. . .	0.5	3	. . .	C
QE22	M18220	. . .	. . .	. . .	2.5	0.5	. . .	2	C
QH21	M18210	. . .	. . .	. . .	2.5	0.5	1	1	C
ZE41	M16410	. . .	4.5	. . .	. . .	0.5	. . .	1.5	C
ZE63	M16630	. . .	5.5	. . .	. . .	0.5	. . .	2.5	C
ZK40	M16400	. . .	4.0	. . .	. . .	0.5	. . .	. . .	C, W
ZK60	M16600	. . .	6.0	. . .	. . .	0.5	. . .	. . .	C, W

(a) For details, see alloying specifications. (b) C, castings; W, wrought products

Table 5 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"

Table 6 Known contaminant tolerance limits in high- and low-pressure cast forms

Alloy/form	Grain size, μm	Critical contaminant limit, %			Ref
		Fe	Ni	Cu	
Unalloyed magnesium	. . .	0.015	0.0005	0.1	5
AZ91/high pressure	5–10	0.032 Mn(a)	0.0050	0.040	8
AZ91/low pressure	100–200	0.032 Mn(a)	0.0010	0.040	8
AM60/high pressure	5–10	0.021 Mn(b)	0.0030	0.010	7
AM60/low pressure	100–200	0.021 Mn(b)	0.0010	0.010	9
AZ63/low pressure	. . .	0.003(c)	0.0040	>0.45	5
K1A/low pressure	. . .	>0.003	0.003	. . .	10

(a) Iron tolerance equals manganese content of alloy times 0.032. (b) Iron tolerance equals manganese content of alloy times 0.021. (c) Magnesium content of AZ63 reported as 0.2%

ter corrosion resistance is only moderately reduced when compared to high-purity magnesium and magnesium-aluminum alloys—0.5 to 0.76 mm/yr (20 to 30 mils/yr) as opposed to less than 0.25 mm/yr (10 mils/yr) in 5% salt spray—but contaminants again must be controlled. The zirconium alloying element is effective in this case because it serves as a strong grain refiner for magnesium alloys, and it precipitates the iron contaminant from the alloys before casting. However, if alloys containing more than 0.5 to 0.7% Ag or more than 2.7 to 3% Zn are used, a sacrifice in corrosion resistance should be expected (Fig. 4). Nevertheless, when properly finished these alloys provide excellent service in harsh environments.

Heat Treating, Grain Size, and Cold-Work Effects. Heating influences the salt-spray corrosion rate of die-cast commercial magnesium-aluminum alloys as shown in Fig. 6, which shows that alloys with higher residual-element (iron, nickel, and copper) concentrations were more negatively impacted by temperature. Using controlled-purity AZ91 alloy cast in both high- and low-pressure forms, the contaminant-tolerance limits have been defined as summarized in Table 7 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 8 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. In the case of the high-iron-containing AZ91C, none of the variations tested significantly affected the poor corrosion performance resulting from an iron level two to three times the alloy tolerance. In the case of the high-purity alloy, however, the T5 and T6 tempers consistently gave salt-spray corrosion rates less than 0.25 mm/yr (10 mils/yr), whereas the as-cast and solution-treated samples exhibited an inverse response to grain size and/or the grain-refining agents. Welds on Mg-Al-Zn alloys should be aged or 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 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
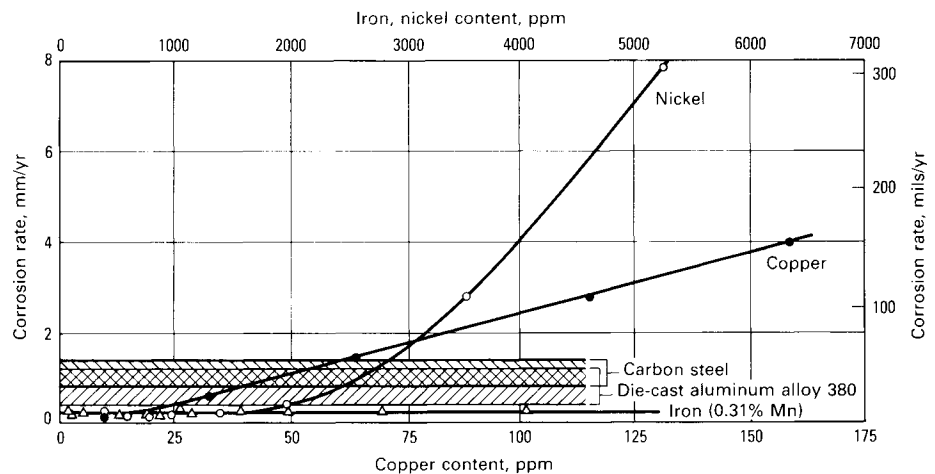
Fig. 5 Effect of nickel and copper contamination on the salt-spray corrosion performance of die-cast AZ91 alloy. Source: Ref 7

Table 7 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 8 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 (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. Source: Ref 8–10

the contaminant is possible, particularly with steel shot residues. Therefore, fluoride anodizing is often used when complete removal of the contaminant is essential (Ref 9).

Causes of Corrosion Failures in Magnesium Alloys

Causes of corrosion failures 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 will be essentially unaltered by surface condition, that is, freshly sanded, machined, or acid pickled. 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% H_2SO_4 for 15 to 30 s) samples will show vastly improved performance in saltwater immersion or salt-spray tests because of removal of the contaminant. Scanning electron microscopy and energy-dispersive x-ray 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).

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 will develop active corrosion sites overnight. Scanning electron microscopy/energy-dispersive x-ray analysis of a freshly machined surface (free of fingerprints or other sources of contamination) will 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. With the use of sulfur hexafluoride (SF_6) rapidly replacing fluxes for the protection of melts during casting, this problem should be eliminated in the future.

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 an interface with other parts of dissimilar metal. Proper design and assembly methods, especially in the area of joints, can minimize galvanic attack.
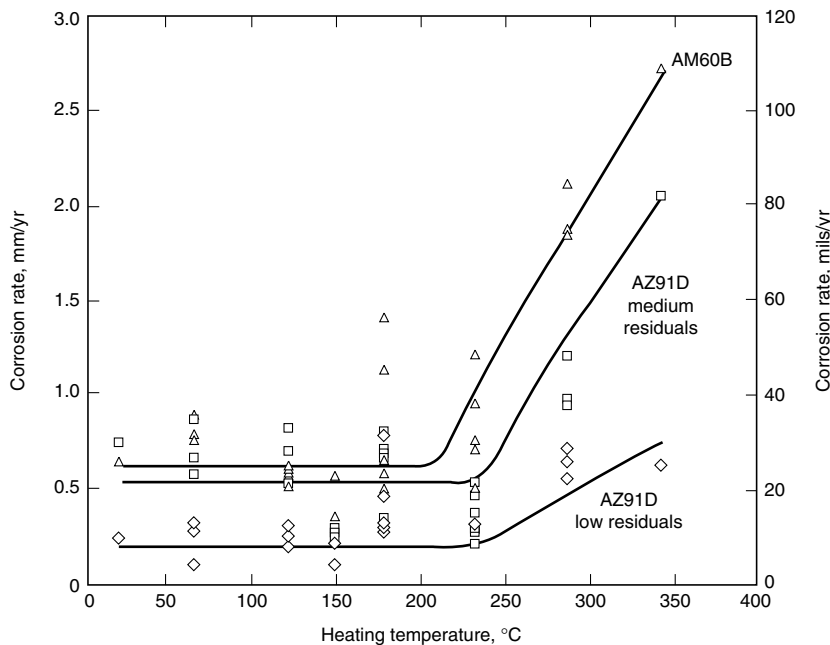
Fig. 6 Effect of heating temperature on corrosion rate of die-cast AZ91D and AM60B in salt-spray test for 10 days using ASTM B 117 method. Data are for test specimens that were heated from 0.5 to 36 h. Source: Ref 12
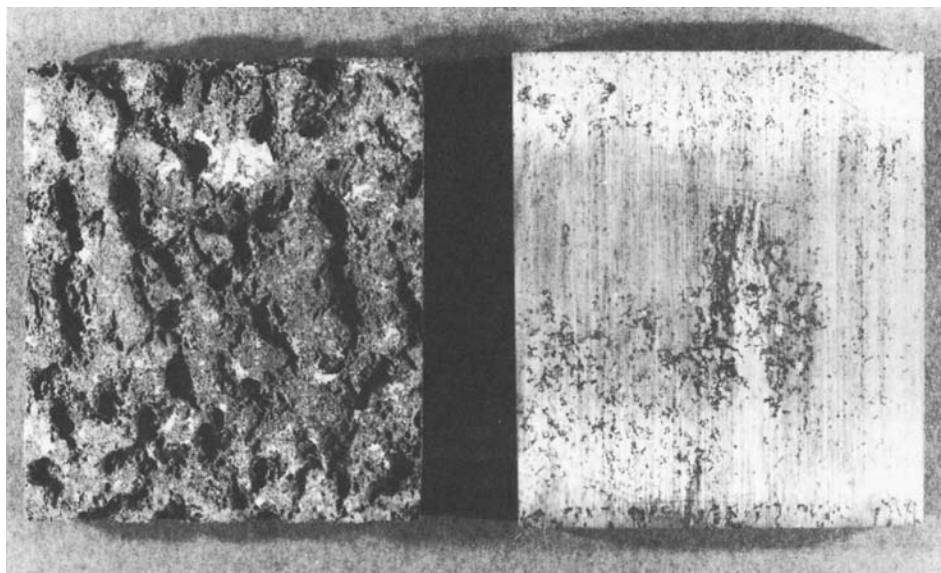
Fig. 7 Effect of heavy-metal contamination on the salt-spray performance of sand-cast AZ91 samples in the T6 temper, as determined by ASTM B 117 method. The samples, containing less than 10 ppm Ni and less than 100 ppm Cu, were simultaneously exposed for 240 h. The sample at left contained 160 ppm Fe and had a corrosion rate of 15 mm/yr (591 mils/yr). The sample at right contained 19 ppm Fe, and the corrosion rate was 0.15 mm/yr (5.9 mils/yr).

ACKNOWLEDGMENT

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