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DP-1289

AEC RESEARCH AND DEVELOPMENT REPORT

CORROSION OF MAGNESIUM ALLOYS AND CERAMICS

R. S. ONDREJCIN

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

663311

DP-1289

Metals, Ceramics, and Materials
(TID-4500, UC-25)

CORROSION OF MAGNESIUM ALLOYS AND CERAMICS

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March 1972

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*CONTRACT AT(07-2)-1 WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION*

ABSTRACT

The resistance of 42 experimental magnesium alloys to corrosion by hot, refreshed deionized water was determined to select candidate materials for nuclear reactor moderator displacers. The most promising of these alloys were subsequently tested in 80-115°C water controlled at pH 5 and flowing 5 ft/sec. Four of these alloys, Mg-5Al-2Sn, Mg-1Si, Mg-5Al-0.5Ce, and Mg-3Al-0.2Ca, are more corrosion resistant than the best commercial alloy tested, AZ31B (3Al-1Zn-0.2Mn); these four alloys also meet the requirement of high scatter and low neutron absorption cross sections. Corrosion rates for all alloys without cladding were too high for reactor use. Limited studies of potential ceramic materials showed that MgAl_2O_4 should be suitable, from a corrosion standpoint, as an alternative material if aluminum-clad magnesium alloys were found unsuitable for other reasons.

CONTENTS

	<u>Page</u>
Introduction	5
Summary	6
Discussion	7
Description of Experimental Alloys	7
Corrosion in Refreshed Water	10
Experimental Technique	10
Results	12
Magnesium Alloys	12
Ceramics	15
Corrosion in Flowing Water	18
Experimental Technique	18
Results	20
Evaluation of Cladding Penetration	23
Appendix A -- Magnesium Alloys for Corrosion Evaluation	27
Appendix B -- Ceramics for Corrosion Evaluation	28
Acknowledgments	28
References	28

LIST OF FIGURES AND TABLES

<u>Figure</u>	<u>Page</u>
1 Inhomogeneity of As-Received Magnesium Alloys	8
2 Inhomogeneity Reduced by Heat Treatment	9
3 Extruded Structure of Mg-5Al-2Sn After Billet Heat Treatment	10
4 Laboratory Corrosion Test Equipment	11
5 Corrosion Evaluation of Nonhomogenized Alloys	12
6 Corrosion Evaluation of Homogenized Alloys	14
7 Effects of Exposure of Ceramics to 80°C Water	16
8 Spalling and Cracking of Ceramics in 80°C Water	17
9 Corrosion Loop Schematic	18
10 Loop Sample Holder	19
11 Types of Corrosion Observed on Magnesium Alloys	21
12 Effect of Some Alloying Elements on Magnesium Corrosion	23
13 Attack of Aluminum-Clad Magnesium in "Pinhole" Through Cladding	26

<u>Table</u>	
I Corrosion Rates Before and After Alloy Homogenization	13
II Effect of Iron on Magnesium Corrosion in Low Conductivity Water	13
III Corrosion Rates of Selected Magnesium Alloys Refreshed 80°C, Deionized Water	15
IV Typical Loop Corrosion Conditions	19
V Magnesium Alloy Corrosion Rates at 115°C	20
VI Temperature Effect on Magnesium Alloy Corrosion in Flowing Water	22
VII Alloying Elements in AZ31B and Corrosion Film	24
VIII Effect of Increasing Cathodic Area on Magnesium Corrosion	25

INTRODUCTION

The resistance of magnesium alloys to corrosion in flowing water was evaluated because of their potential for use as a moderator displacer if a Savannah River reactor were converted to resonance operation. This conversion was considered as a means to adjust the neutron spectrum to favor production of certain isotopes such as ^{252}Cf .

Excessive corrosion of the moderator displacers would greatly reduce the reliability and control of a resonance reactor. Although magnesium alloys are known to corrode rapidly in certain aqueous environments,¹ spent, magnesium-alloy-clad fuel elements have been successfully stored in water by controlling the pH at 12.² Control of pH at this high a level is not practical in Savannah River reactors because of extensive use of aluminum, the ion exchange system in use, and the potential for caustic stress cracking of sensitized stainless steel welds in the reactor tanks. A more practical method of corrosion control was the use of aluminum-clad magnesium alloys with an overall displacer composition of 90 wt % Mg - 10 wt % Al (including cladding). However, because of the potential for cladding defects allowing penetration by the moderator, a corrosion-resistant magnesium alloy was desired.

This report describes the results of an evaluation of corrosion resistance of forty-two experimental alloys. These alloys were designed to meet the special requirements of a moderator displacer, low absorption and high scatter cross sections for neutrons and low corrosion rates. Limited corrosion evaluation of several potential ceramic displacers is also included. The mechanical properties and irradiation test results for these same alloys will be reported in another document.

SUMMARY

Four experimental alloys, Mg-5Al-2Sn, Mg-1Si, Mg-5Al-0.5Ce, and Mg-3Al-0.2Ca, have good corrosion resistance to hot flowing water and, when clad with aluminum, might be used as moderator displacer materials to convert a Savannah River heavy water reactor from thermal to resonance operation. These experimental alloys are more corrosion resistant than the best commercial alloy tested, AZ31B (Mg-3Al-1Zn-0.2Mn), and also have the low neutron absorption and high scattering cross sections required for a moderator displacer.

Initial screening of candidate displacer materials was in refreshed deionized water at 80°C with zero flow velocity past the test specimens; the more resistant of the 45 magnesium alloys evaluated, corroded at about 12 mg/(dm²-day) at a pH of 8-9. Fifteen alloys were selected from these tests and evaluated in a corrosion loop where a side stream of water was continuously deionized, and the loop water was maintained at pH 5.0 ±0.2; the temperature was controlled at 80, 100, or 115 ±2°C and the flow at 5 ft/sec. The corrosion rates of the more-resistant samples rose from about 500 mg/(dm²-day) (1.1 mils/day penetration) at 80°C to about 700 mg/(dm²-day) (1.6 mils/day penetration) at 115°C. Pure magnesium (99.96%) corroded at about 1900 mg/(dm²-day) (4.3 mils/day) at 115°C. The lower corrosion rates observed in the experimental alloys are due to the formation of a corrosion film that is typically depleted in magnesium and enriched in the alloying elements.

Galvanically accelerated corrosion of magnesium because of contact with aluminum was not observed in low conductivity water. The corrosion rate of aluminum-clad AZ31B in a 1/16-inch-diameter "pinhole" was about the same as for an unclad AZ31B specimen under no-flow conditions. The aluminum cladding adjacent to the magnesium in the "pinhole" was attacked slightly by the basic solution formed in the pinhole because of dissolution of corrosion products; however, this effect was minor.

The ceramic MgAl₂O₄ is a possible alternative displacer material to the magnesium alloys, based on corrosion tests of several oxides. The <0.9 mg/(dm²-day) attack rate observed in the 80°C over-flow system for 95% dense MgAl₂O₄ was the lowest observed for any metal or ceramic evaluated.

DISCUSSION

DESCRIPTION OF EXPERIMENTAL ALLOYS

Magnesium alloys are used satisfactorily in some aqueous environments. Generally, water at a pH of about 12 or with a low conductivity, flow rate, and temperature does not attack magnesium.² Under these conditions, the metal is protected by a hydroxide coating, but this compound has a relatively high solubility in water at elevated temperatures (43 $\mu\text{g/ml}$ at 100°C). Anything, such as an ion exchange resin, that removes Mg^{+2} or OH^- from a solution will increase the magnesium corrosion rate because the hydroxide will dissolve more rapidly to maintain the $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{+2} + 2\text{OH}^-$ equilibrium. The hydroxide is not very adherent, and loss of the coating leads to high corrosion rates even at lower temperatures, if the flow rate is high.

Very little is known about the use of alloying additions to reduce magnesium corrosion in hot, flowing, low-conductivity water. The only agreement found in the literature¹ and among the manufacturers was that aluminum additions were helpful. Argonne National Laboratory recommended $\text{Mg}-(2.5-5.0)\text{Al}-(0.8-1.2)\text{Sn}-(0.5-1.0)\text{Cu}$ for corrosion resistance at 150°C in initially pure water.³ Because of the lack of information about the effect of alloy additions on corrosion resistance under the desired conditions, 45 different magnesium alloys, including 42 experimental ones, were purchased from the Dow Chemical Company for evaluation. The alloys were ordered in two groups; the second group was selected on the basis of the corrosion and metallographic examination of the first group.

The first group of 30 alloys had a variety of alloying elements. This group included three commercial magnesium alloys, AZ31B (3Al-1Zn-0.2Mn), AZ61 (6Al-1Zn-0.2Mn), and AZ91 (9Al-1Zn-0.2Mn), for comparison with the experimental alloys, although the manganese content of the commercial alloys precluded satisfactory neutron properties. Four Mg-Fe alloys ranging from 0.001 to 0.1 wt % were also ordered to evaluate the effect of iron on corrosion of magnesium in low conductivity water. Three Mg-Al alloys with an aluminum content (>5%) too high for use in an aluminum-clad displacer were also included to evaluate the effect of this element over a wide alloying range.

Metallographic examination of the first group of alloys showed many of them to be inhomogeneous (Figure 1). Several alloys were given homogenization treatments recommended by the Dow Chemical Company. At the end of recommended homogenization periods, all alloys showed a significant grain growth (5-10X), and although alloying elements were more homogeneous, they were still concentrated in grain boundaries (Figure 2).

FIG. 1 Inhomogeneity of As-Received Magnesium Alloys

FIG. 2 Inhomogeneity Reduced by Heat Treatment

A second series of 15 new alloys were ordered and examined metallographically. The alloying elements Al, Be, Ca, Ce, and Sn were added singly or in combination to make up the second group of alloys. Because of the inhomogeneity in the first group, some billets from both groups of alloys were heat treated before extrusion. Extrusions ratios as large as 140:1 were used to further increase uniformity and to break up billet grain boundaries. Some precipitation occurred in grains and grain boundaries, but the alloys were generally improved by the heat treatments and extrusions (Figure 3).

Transverse Section

FIG. 3 Extruded Structure of Mg-5Al-2Sn After Billet Heat Treatment

All magnesium alloy compositions ordered are listed in Appendix A.

CORROSION IN REFRESHED WATER

Experimental Technique

Evaluation was based on the amount of metal oxidized during immersion in refreshed, deionized water at 80°C. Water was added to and overflowed from a stainless steel beaker at a rate of 20 ml/min. Specimens (50x25x3.2 mm) were insulated from the beaker by nylon-coated holders to prevent galvanic corrosion (Figure 4a). The resistivity of water entering the beaker was $>1 \times 10^6$ ohm-cm; the overflow had a resistivity of $1-4 \times 10^5$ ohm-cm at pH 8-9. This pH represented 0.01-0.1 ppm of Mg as $Mg(OH)_2$ in the water. Temperature of the flowing water was controlled to $80 \pm 1^\circ C$ by flow rate and bath temperature (Figure 4b). This temperature was the highest feasible to maintain a reasonably low CO_2 concentration (solubility: 0.15 ppm at 80°C) because CO_2 accelerates magnesium corrosion.^{2,4}

Candidate alloys were eliminated on the basis of their corrosion rates. The extent of corrosion was evaluated by determining the weight of metal lost. This change in weight of the specimens was measured after the corrosion film had been stripped in boiling 15 wt % CrO_3 - 1 wt % $AgNO_3$.

a. Test Alloy in Beaker

b. Deionized water flows to hold tank, then to manifold and through adjustable stopcocks to individual beakers. Water overflows into recirculating hot water bath that maintains water temperature in the beaker.

FIG. 4 Laboratory Corrosion Test Equipment

Results

Magnesium Alloys

The initial corrosion evaluation of 45 magnesium alloys reduced the number of alloys for further testing to 15.

The corrosion rates of the first group of 30 alloys were measured in duplicate after 1, 2, 6, and 9 days exposure in the laboratory equipment. The rates for selected alloys of this group are compared to 99.96% Mg in Figure 5. The most corrosion resistant of the three commercial magnesium alloys was AZ31B (3Al-1Zn-0.2Mn). All alloys corroded at lower rates than 99.96% Mg except Mg-6Zn-0.5Zr.

FIG. 5 Corrosion Evaluation of Nonhomogenized Alloys

Homogenization treatments after extrusion did not improve corrosion resistance. Equivalent or poorer corrosion performance was consistently observed after heat treatment. Corrosion rates of several homogenized alloys based on 200 hour tests in 80°C refreshed deionized water are tabulated in Table I and compared with as-received controls. Opposite results were expected because inhomogeneity was expected to increase the rate of corrosion, at least locally. An explanation for the increase in corrosion rates may be that heat treatment concentrated the more cathodic alloying elements in the grain boundaries (Figure 3).

TABLE I
Corrosion Rates Before and After
Alloy Homogenization

Alloy	Corrosion Rate at 80°C, mg/(dm ² -day)	
	Before	After
Mg-8Al-0.05Be	9.5	12
Mg-5Al-2Pb-0.05Be	12	14
Mg-3Al-1Zn-0.2Mn (AZ31B)	14	14
Mg-5Al-2Sn	14	17
Mg-5Al-2Sn-0.25Cu	14	20
Mg-2Sn-0.2Ca	20	20

Small concentrations of iron in magnesium alloys severely accelerate corrosion in high conductivity (sea) water. A concentration of <0.02 wt % Fe is recommended for such service.^{5,6} Four special Mg-Fe alloys were tested in 80°C refreshed, deionized water for eight days to assess the deleterious effects of iron. The average corrosion rates for these alloys (Table II) show that corrosion of magnesium in low conductivity water is essentially unaffected by iron contents up to 0.1 wt % in contrast to the results for high conductivity seawater. The range of corrosion rates in Table II is about equal to experimental error.

TABLE II
Effect of Iron on Corrosion of Magnesium
in Low Conductivity Water

Alloying Element, wt %					Corrosion Rate, mg/(dm ² -day)
Fe	Al	Mn	Ni	Others	
0.002	0.003	0.002	0.001	-	24
0.037	0.003	0.002	0.001	-	25
0.050	0.005	0.072	0.002	-	22
0.096	<0.03	<0.01	0.002	0.02 Pb	24

The second series of 15 new alloys were homogenized in billet form, then extruded at high reduction to further increase uniformity and to break up billet grain boundaries. Corrosion results for nine of the alloys are compared to 99.96% Mg in Figure 6.

FIG. 6 Corrosion Evaluation of Homogenized Alloys

The corrosion rates for the most resistant alloys in both groups of specimens are shown in Table III. The two evaluations are comparable, based on the corrosion rates of 99.96% Mg used as internal standards. The standards varied $\pm 5\%$ from the average corrosion rate at the 67% confidence level.

TABLE III

Corrosion Rates of Selected Magnesium Alloys in
Refreshed, 80°C Deionized Water^a

Alloying Element, wt. %	Weight Loss, mg/(dm ² -day)	Average Penetration, μm/day (mils/day)
8Al-0.05Be	9.5	0.50 (0.02)
8Al	10	0.55 (0.02)
5Al-0.2Ca	11	0.61 (0.02)
5Al-2Pb-0.05Be	12	0.62 (0.02)
5Al-0.05Be	12	0.63 (0.02)
5Al-0.5Ce	12	0.65 (0.03)
5Al-0.5Ce-0.3Be	12	0.65 (0.03)
5Al-0.2Ca-0.03Be	12	0.66 (0.03)
5Al-1Pb-0.03Be	13	0.62 (0.02)
10Al-0.08Be	13	0.68 (0.03)
5Al-2Sn	14	0.74 (0.03)
5Al-2Sn-0.25Cu	14	0.74 (0.03)
3Al-0.2Ca	14	0.80 (0.03)
1Si	14	0.80 (0.03)
99.96% Mg	43	2.5 (0.10)

a. Inlet water pH 7; overflow water pH 8-9

Most of these alloys were also tested in a flowing water loop with controlled flow, temperature, and pH, as described on page 18.

Ceramics

Several ceramic materials were selected to give the same neutron spectrum as Mg-10 Al. These materials were MgO at 30% theoretical density, MgAl₂O₄ at 70% TD, and Bi₂O₃ at 100% TD. Although the densities indicated were required for the reactor application, the materials were generally tested at 90-100% TD, because desired densities were not commercially available. MgAl₂O₄ was found to be the best ceramic, based on its low cost and low attack rate.

The ceramics were tested under the same conditions as used for the metal alloys: 80°C refreshed, overflowing, deionized water. Structural damage or rapid deterioration of the ceramic were the criteria used to eliminate candidates. The density and purity of all ceramics evaluated are listed in Appendix B. MgAl_2O_4 was virtually unattacked (Figure 7). Although Bi_2O_3 was expected to be about equivalent to MgAl_2O_4 , grain spallation occurred; after 240 hours the surface voids originally present had increased in size 2 to 5 times. MgO at 98% theoretical density was similar to Bi_2O_3 , in that weight loss due to spallation of small crystals accompanied exposure. The MgO at 100% theoretical density appeared similar to the 98% theoretical density material until 170 hours exposure, when spalling became severe. The spalling and cracking in MgO specimens was probably due to stresses arising from hydration to $\text{Mg}(\text{OH})_2$, which has about half the density of MgO .

FIG. 7 Effects of Exposure of Ceramics to 80°C Water

MgO either lost or gained weight depending on its initial density (Figure 7). The higher density specimens tended to spall and lose weight. Additionally, the purest MgO (99.96%) hydrated, spalled, and lost weight faster than less pure specimens (98.2 to 99.6%) of about the same density because the impurities decreased

the rate of hydration. Low density MgO also hydrated rapidly, and because of the greater porosity, hydration occurred throughout the structure, not only on the surface as for the high density material. The low density specimens thus swelled and cracked with only a small amount of spalling. Examples of the effects of water on the ceramics are shown in Figure 8. No effects of surface attack were observed on the MgAl_2O_4 .

FIG. 8 Spalling and Cracking of Ceramics in 80°C Water

CORROSION IN FLOWING WATER

Experimental Technique

To mock up the in-service conditions of a nuclear reactor, a special corrosion loop was fabricated (Figure 9). This loop allowed control of test conditions to simulate expected attack by water in the temperature range of 80 to 110°C at a pH controlled to about 5. The pH of the deionized water was adjusted by nitric acid addition that had to be balanced against deionizer removal and neutralization of corrosion products. Temperature ($\pm 2^\circ\text{C}$), pH, and water resistivity were controlled and continuously recorded.

FIG. 9 Corrosion Loop Schematic

Test specimens were supported in a "Teflon"* holder to prevent galvanic acceleration of corrosion. Each holder (Figure 10) included a specimen of 99.96% Mg to be used as a control for comparison. A stainless steel flow guide, upstream of the samples, assured a uniform flow over each sample at 5 ft/sec.

FIG. 10 Loop Sample Holder

Duplicates of 15 alloys were evaluated in two tests; the conditions are shown in Table IV. Resistivity of the water in the 7-day test was lower than that for the 4-day test because the samples used in this evaluation (21 vs 18) produced more $Mg(OH)_2$, which is soluble at pH 5. Resistivity of pure water acidified to pH 5 with HNO_3 is $\sim 3 \times 10^5$ ohm-cm.

TABLE IV

Typical Loop Corrosion Conditions

Test Number	I	II
Duration, days	7.29	4.63
pH, ^a test	5.0 ± 0.2	5.0 ± 0.2
pH range, startup	4.6 - 7.3	4.6 - 6.1
Temperature, °C	115 ± 2	115 ± 2
Flow, ft/sec	5.0 ± 0.3	5.0 ± 0.3
Resistivity, ^a ohm-cm $\times 10^{-4}$	5.0 - 8.3	5.9 - 10

a. Values for pH and resistivity were outside the indicated values for about the seven hours required to reach stable operating conditions at the beginning of each test. Most of this time was spent adjusting acid flow to neutralize $Mg(OH)_2$ as formed and adding an excess to lower the pH to 5 and make up the amount of acid removed by the deionizer.

* DuPont trademark for fluorocarbon resin

Results

Loop corrosion evaluation of 15 magnesium alloys chosen after the initial laboratory evaluation showed that 5Al-2Sn, 1Si, 5Al-0.5Ce, and 3Al-0.2Ca were the best suited alloys for displacer use based on corrosion and composition requirements. These alloys are all more corrosion resistant than the commercial alloy AZ31B (Mg-3Al-1Zn-0.2Mn) under the conditions of evaluation. However, in pH 5 water, magnesium alloys corroded rapidly, and all alloys must be clad to prevent attack.

Results for the more resistant alloys at 115°C are shown in Table V and compared to 99.96% Mg. The most corrosion-resistant alloys reacted about 1/4 as rapidly as the pure magnesium standards, which lost 40-60% of their weight during the test period. The corrosion rate of the six standards varied $\pm 3.0\%$ from the average at the 95% confidence level, thus indicating that control of the corrosion conditions was quite good. Variation in corrosion rates for duplicate samples was $<5\%$.

TABLE V
Magnesium Alloy Corrosion Rates at 115°C

Concentration of Alloy Elements, wt %	Weight Loss, mg/(dm ² -day)	Average Penetration, μm/day (mils/day)
5Al-2Sn	570	30 (1.2)
5Al-2Sn-0.25Cu	590	31 (1.2)
1Si	700	40 (1.6)
3Al-0.2Ca	720	41 (1.6)
5Al-0.5Ce	740	41 (1.6)
5Al-1Pb-0.03Be	800	41 (1.6)
5Al-0.5Ce-0.03Be	810	44 (1.7)
3Al-1Zn-0.2Mn (AZ31B) ^α	810	44 (1.7)
5Al-0.03Be	840	44 (1.7)
5Al-0.2Ca	870	48 (1.9)
8Al ^α	920	51 (2.0)
99.96 Mg	1880	108 (4.3)

α. Unsatisfactory for moderator displacers because of nuclear properties.

The alloys can be classified into three different groups based on corrosion resistance (Table V). The two most resistant alloys had penetration rates of about 30 $\mu\text{m/day}$ (1.2 mils/day), seven intermediate alloys corroded at about 44 $\mu\text{m/day}$ (1.7 mils/day), and the remaining alloys at rates about 50 $\mu\text{m/day}$ (2.0 mils/day) or faster. For moderator displacers, the simplest alloys and the ones with the least amount of aluminum are the logical choices because of easy composition control and because of the nuclear properties of aluminum.

Two of the magnesium alloys (8Al and 5Al-0.5Ce) were evaluated in both the extruded and annealed conditions to assess the importance of internal stresses in corrosion. As expected, the extruded specimens corroded more rapidly than the annealed structures; however, the differences in the rates were small, 4% for the 8Al and 9% for the 5Al-0.5Ce.

Several types of corrosion were observed on the various specimens (Figure 11). Exfoliation, the formation and sloughing off of thin layers of corrosion product, occurred on 99.96% Mg. This type of attack is generally indicative of rapidly corroding material. Pitting that was wide and shallow was observed on only one alloy, the commercial corrosion-resistant AZ31B (3Al-1Zn-0.2Mn). A uniform attack with a resulting grey surface occurred on 5Al-2Sn; addition of 0.25 wt % copper to this alloy caused the corrosion appearance to change to a less uniform attack, but had no effect on the corrosion rate. The remainder of the alloys corroded with a slight surface roughening, which was neither a uniform attack nor a pitting form of corrosion.

FIG. 11 Types of Corrosion Observed on Magnesium Alloys

Several of the more resistant alloys were evaluated at 80, 100, and 115°C to obtain data on the temperature dependence of corrosion. The 5Al-2Sn alloy continued to corrode least (Table VI).

TABLE VI
Temperature Effect on
Magnesium Alloy Corrosion in Flowing Water^a

Magnesium Alloy	Penetration Rate, $\mu\text{m/day}$ (mils/day)		
	80°C	100°C	115°C
5Al-2Sn	24 (0.9)	34 (1.3)	30 (1.2)
1Si	25 (1.0)	36 (1.4)	40 (1.6)
5Al-0.5Ce	28 (1.1)	36 (1.4)	41 (1.6)
3Al-0.2Ca	30 (1.2)	40 (1.6)	41 (1.6)
5Al-0.2Ca	34 (1.3)	46 (1.8)	48 (1.9)
8Al	34 (1.3)	54 (2.1)	51 (2.0)
99.96 Mg	32 (1.3)	48 (1.9)	109 (4.3)

^a. Flow rate was 5 ft/sec and pH 5.0 $\pm$ 0.2

The corrosion rates of the alloys at 80°C are measured at pH 5, rather than 8-9, and a flow of 5 ft/sec, rather than ∞ . These conditions resulted in much more rapid penetration than observed previously in "static" tests (compare Table III with Table VI).

The relative effects of increasing temperature on the corrosion penetration rate of several alloys and 99.96% Mg are compared in Figure 12. The rate for magnesium increases much more rapidly with temperature, in the range evaluated, than that for the alloys; thus the alloying additions become increasingly important with increasing temperature. A difference in corrosion mechanism between the alloys and 99.96% Mg is shown by an Arrhenius plot of the data (Figure 12) and can be explained on the basis of the type of attack. Exfoliation would tend to produce a larger surface area for attack by hot water, and therefore to give a corrosion rate increase not seen in typical surface attack of the other alloys.

FIG. 12 Effect of Some Alloying Elements on Magnesium Corrosion

The data in Table VI and Figure 12 are conservative for corrosion of magnesium alloys. The rates are high and pseudo-zero order (i.e., constant rate, no concentration effect) over the periods of time studied because of the solubility of the corrosion products at pH 5 and the removal of the ions by ion exchange purification. In practice, however, if the cladding of the alloy were penetrated by a "pinhole", the flow of water would be restricted, and the pH would increase inside the defect and lower the corrosion rate. In this situation, the corrosion reaction would be expected to approach a first order, rather than zero order reaction, and the corrosion rates would be much lower than observed in this study.

EVALUATION OF CLADDING PENETRATION

To assure that no unacceptable effects occur in the event of penetration of the aluminum cladding and exposure of the magnesium alloys to the moderator, three questions must be answered: (1) What is the composition of the film formed over the magnesium during corrosion? (2) Is corrosion galvanically accelerated because of the small anodic magnesium area adjacent to the large

area of cladding? (3) Is the aluminum cladding adjacent to penetration attacked by the basic solution, which is formed by $\text{Mg}(\text{OH})_2$ dissolution when the hole is small enough to restrict moderator flow in the penetrated area?

$\text{Mg}(\text{OH})_2$, the hydroxide formed on pure magnesium during corrosion in water, is soluble (43 $\mu\text{g}/\text{ml}$) in water at 100°C. Thus, magnesium depletion should occur during corrosion, and the hydroxide formed on alloys would be anticipated to be low in magnesium and high in alloying elements. To evaluate this possible effect, AZ31B (Mg-3Al-1Zn-0.2Mn) was exposed to refreshed 100°C water for 25 days. Comparisons of the analyses of the elements in the alloy and hydroxide film are shown in Table VII.

TABLE VII
Alloying Elements in AZ31B and Corrosion Film

	<u>Element-to-Magnesium Weight Ratio</u>			
	<u>Al-Mg</u>	<u>Zn-Mg</u>	<u>Mn-Mg</u>	<u>Fe-Mg</u>
Metal	0.032	0.0096	0.0043	0.0006
Hydroxide	0.183	0.0153	0.0067	0.0019

A significant enrichment in the hydroxide film, up to a factor of 6 for aluminum, is observed for each of the alloy elements. This enrichment is caused by the solubility of the $\text{Mg}(\text{OH})_2$, which decreased the magnesium content of the hydroxide film. The metal contains 96% Mg; therefore, the hydroxide film should contain 39% Mg if no losses occurred. The film actually contained 32% Mg.

Galvanic corrosion occurs when two dissimilar metals are electrically connected and immersed in an aqueous solution. The more anodic metal begins to oxidize, and the cathodic metal generally discharges H^+ to release H_2 . As the size of the anode is decreased or the cathode increased, corrosion can be accelerated by the relative increase in current density at the anodic area unless there is some interference to charge transfer. To evaluate possible corrosion acceleration due to galvanic effects, flat specimens of AZ31B (Mg-3Al-1Zn-0.2Mn) were clad on both sides with 1100 Al. Specimens with different cathodic/anodic ratios were fabricated and exposed to refreshed, high resistivity (5×10^6 ohm-cm) water at 100°C. The corrosion rates or depths of penetration after various exposures are shown in Table VIII.

TABLE VIII

Effect of Increasing Cathodic Area on
Magnesium Corrosion

Cathode/Anode Ratio	Average Penetration, μm (mils)		
	After 5 days	After 9 days	After 12 days
0 (no Al)	56 (2.2) ^a	71 (2.8) ^a	68 (2.7) ^a
8	30 (1.2)	50 (2.0)	87 (3.4) ^a
23	30 (1.2)	50 (2.0)	85 (3.4) ^a
78	31 (1.2)	48 (1.9)	74 (2.9) ^a

a. Corrosion product covers magnesium alloy

Galvanically accelerated corrosion was not observed although the absolute corrosion rate was high. Corrosion product buildup accompanied exposure although water circulated freely over the surface. Additionally, the corrosion current and thus the corrosion rates may have been minimized by the low conductivity water and may have been further reduced by the corrosion product build-up.

Poor circulation of water, a condition that would be expected in the event of a small hole in the cladding, did not affect corrosion of magnesium, although the aluminum cladding was attacked because of the pH change that accompanied corrosion. AZ31B specimens clad with 1100 Al were exposed to water at 100°C with "pinholes" 1/16 in. in diameter drilled through one side of the cladding, through the magnesium, and into the other side of the aluminum cladding. The pH inside the hole would be expected to increase toward the equilibrium value of 10.2 at 100°C. A high pH would be expected to decrease the corrosion rate of magnesium and cause the attack of aluminum. Figure 13 shows the result after 40 days exposure at 100°C. No corrosion product was observed in the hole. This is attributed to the dissolution of the surface film and apparently resulted in a high pH in the "pinhole."

The corrosion rate of the magnesium alloy in the hole was only slightly greater than the rate on bare specimens and again indicated that a high cathode/anode ratio does not greatly affect corrosion rates of magnesium in low conductivity water. The magnesium alloy corroded at $\sim 1 \mu\text{m/day}$ (0.04 mil/day) in the clad pinholed specimens and $0.8 \mu\text{m/day}$ (0.03 mil/day) in unclad specimens. The aluminum at the Mg-Al interface was attacked about twice as rapidly as the adjacent magnesium. This rapid corrosion of aluminum is attributed to the high local pH.

- a. Note corrosion of Mg and attack of Al cladding at Mg-Al interfaces in hole.

- b. Looking down into the hole, the Al cladding is attacked as shown by the partial obliteration of tool marks (concentric circles)

FIG. 13 Attack of Aluminum-Clad Magnesium in "Pinhole" Through Cladding

APPENDIX A

Magnesium Alloys for Corrosion Evaluation wt % Alloying Element

Al	Be	Ca	Ce	Cu	Fe	Mn	Pb	Si	Sn	Zn	Zr
10 ^a	0.1										
8 ^a											
8 ^a	0.05										
5	0.03										
5		0.2									
5			0.5								
5	0.03	0.2									
5	0.03		0.5								
5	0.03						1.0				
5									2.0		
5		0.2							2.0		
5			0.2						2.0		
5 ^b				0.2					2.0		
5	0.03	0.1	0.1						2.0		
5	0.05						2.0				
5							10.0				
5	0.05						10.0				
3		0.2									
3	0.03										
0.7		0.2									
0.2		0.5									
<0.03					0.1	<0.01	0.02				
0.005					0.05	0.07					
0.003					0.04	0.002					
0.003					0.002	0.002					
0.002					0.001	0.001					
	0.05	0.2									
		0.2									
			0.5				10				0.5
								1.0			
	0.03								5.0		
		0.2							5.0		
			0.5						5.0		
	0.03	0.2							5.0		
									3.0		0.01
		0.2							2.0		
											0.5
		0.2									0.5
	0.05										0.5
			0.5								0.5
										6	0.5
3 ^c						0.2				1	
6 ^c						0.2				3	
9 ^c						0.2				0.7	

a. Neutron properties unsatisfactory; used to determine effect of Al on corrosion.

b. Corrosion-resistant alloy, recommended by Argonne National Laboratory.

c. Commercial alloys AZ31B, AZ61, and AZ91, respectively. Physics properties unsatisfactory; used for comparison to experimental alloys.

APPENDIX B

Ceramics for Corrosion Evaluation

<u>Ceramic</u>	<u>Theoretical Density, %</u>	<u>Purity, wt %</u>
Bi ₂ O ₃	92	99.9
MgAl ₂ O ₄	95	99
MgO	75	98
MgO	98	99.6
MgO	99	99.96
MgO	100	98.2

ACKNOWLEDGMENTS

The author wishes to thank E. F. Sturcken for his assistance in procuring magnesium alloys from Dow Chemical Company and W. E. Ruther for supplying a number of alloy samples that had been evaluated at Argonne National Laboratory. M. E. Epting made most of the experimental measurements, and J. W. Lane was responsible for loop operation.

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