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AQUEOUS CORROSION OF MAGNESIUM ALLOYS

by

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AQUEOUS CORROSION OF MAGNESIUM ALLOYS

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ABSTRACT

The aqueous corrosion of magnesium alloys was investigated over the range from 53 to 150°C. Corrosion rates rose rapidly with temperature, reaching about 3 mils per day at 150°C for AZ-31 [Mg-2.5 to 3.5 w/o Al-0.7 to 1.3 w/o Zn-0.2 w/o Mn]. Additions of small amounts of copper and/or nickel to the basic AZ-31 composition reduced the corrosion rate at 150° by a factor of about two. Tin may be advantageously substituted for zinc in AZ-31.

Control of the pH in the range between 6 and 7 and maintenance of a fluoride concentration in the range between 1 and 10 ppm reduced the corrosion rate of AZ-31 and of the Argonne experimental alloys to about 0.1 mil per day at 150°C.

INTRODUCTION

The low thermal neutron capture cross section of magnesium makes it an attractive possibility for a cladding material for the fuel of a nuclear reactor. Relatively little data are available concerning the corrosion resistance of magnesium alloys in a pure water environment, such as might be found in a water-cooled reactor. Aqueous corrosion testing of these alloys reported in the literature[1,2] has been largely confined to temperatures below 100°C and to the usual type of corrosion-evaluating solutions (i.e., 3% NaCl).

Two unpublished sets of experiments pertinent to this report were performed by members of the ANL Reactor Engineering Division concurrently with the Metallurgy programs. L. E. Link in two short dynamic tests (25 ft/sec) at 60°C found that AZ-31 alloy incurred much higher weight changes when the ion exchanger was more effective in removing the corrosion products from the test solution.

N. R. Grant, using small unrefreshed test chambers, obtained average corrosion rates (during 5-day tests) fitting the curve

$$\log_{10}[\text{Corrosion Rate (mils/day)}] = 0.0375 \ T(°C) - 5.20$$

over the range from 80 to 150°C for AZ-31 alloy. There was not much change in rate between 30 and 80°C (0.004 ± 0.002 mil/day).

Two specific ANL designs of water-cooled reactors have considered the use of magnesium cladding. The first of these designs (1950-1952) involved relatively low water temperature (50-90°C) and a long, reliable service life. The experimental work described in this report for this temperature range was performed in connection with these requirements.

More recently, a research reactor producing a very high neutron flux level was conceived which would make use of magnesium cladding. Due to the extremely short fuel lifetime (~5 days), a much higher corrosion rate could be tolerated (estimated maximum of 0.001 in. per day) at the design temperature of 150°C. The major portion of this report is concerned with the preliminary exploration, alloy development and inhibitor selection necessary to meet this design corrosion rate.

EXPERIMENTAL

Commercial magnesium alloys were obtained from the Dow Chemical Co. Pure magnesium, used in the preparation of the experimental alloys, was obtained from Dominion Magnesium Ltd. (Domal). The Brooks and Perkins Co. prepared several special magnesium alloy castings. Both Howard Foundry and Dow cast commercial size ingots to ANL specifications. These were subsequently extruded into tubing by the Precision Extrusion Co. and by Magnode Products.

The developmental alloys for the high-temperature phase of the program were prepared by induction melting in an argon atmosphere and chill casting into a small, water-cooled copper mold. Sheet stock was fabricated from the castings by hot pressing and rolling.

Corrosion tests below 100°C were performed in either a refreshed Pyrex glass system under essentially stagnant conditions or in a 2-liter capacity Pyrex and stainless steel dynamic test loop previously described in detail.[3] The loop had means for maintaining gas saturation of the liquid and was modified in later tests to provide a constant replenishment of the test solution.

Preliminary corrosion tests of alloys and inhibitors at temperatures above 100°C were performed in small stainless steel autoclaves. The test conditions could not be accurately maintained because of contamination of the solution by corrosion products and the depletion of the inhibitors. More meaningful studies were run in stainless steel, constantly refreshed systems,[4] in which it was possible to control solution

composition. In the latter systems the rate of replenishing solution was low enough so that the linear velocity past the samples was essentially zero.

Samples were annealed for one-half hour at 260°C and wet ground (240-grit) prior to exposure. In a few cases, samples prepared in this fashion were corrosion tested with other samples in the as-rolled condition. There was no appreciable difference in results.

The samples were electrically insulated from the stainless steel system with synthetic sapphire rods. The corrosion products were removed at the conclusion of the test by immersing the samples in boiling 15% chromic acid for one to three minutes.

The solution resulting from the high-temperature corrosion of magnesium-aluminum alloys contained a colloidal dispersion, probably magnesium or aluminum hydroxide. When a conventional glass electrode pH meter was used to determine the pH of such solutions at room temperature, difficulty was encountered at pH values below the 10-11 range. After an initial relatively low reading, the value rapidly increased to about 10.5. Values obtained with pH indicating paper corresponded to the initial value obtained with the pH meter. pH values are given as a range to express this uncertainty.

DATA AND RESULTS

Low-Temperature Corrosion Behavior

Initial testing of magnesium alloys was performed at 53°C. The hydrogen-saturated distilled water was continuously refreshed so that the pH remained at 6.8. The results are shown in Figure 1. The corrosion was roughly linear with time (24-day test) and a rate of 8.6 mdd (milligrams/decimeter^2/day) was obtained.

Samples of AZ-31/alloy (Mg-2.7 w/o Al-1.0 w/o Zn-0.4 w/o Mn) were tested in stagnant closed Pyrex chambers at the same temperature. Very little attack occurred (35-day test duration) if the water was deoxygenated at the start with tank nitrogen. Coupling with mild steel had no visible effect on the slight corrosion observed. When oxygen was present, much

O Alloy AZ-31(2.7% Al, 1.0% Zn, 0 2-0 4% Mn)
□ Dow PE Alloy (3 2% Al, 1.0% Zn, 0.10% Mn)

FIGURE I. CORROSION OF MAGNESIUM ALLOYS IN DISTILLED WATER AT 53°C - pH 6.8

heavier corrosion occurred. The pH remained at 10.0 ± 0.02 in these tests, apparently controlled by the magnesium corrosion product.

Four experimental runs were made in the dynamic system at 90°C. Dilute alkali solution was used. The potassium hydroxide solution was made up to pH 10.0, since tests at lower temperatures had indicated this to be approximately the pH of the solution which magnesium will maintain by the corrosion process. In the first two tests, no special provision was made to maintain the pH. A small amount of solution was added as required to maintain the water level in the system. In these cases, the pH diminished rather rapidly for the first several days and then more slowly, reaching a value of the order of 8.2 at the end of the twenty-day test.

It was suspected that the drop in pH was due to air (containing CO_2) leaking into the system. The tests were repeated for alloy AZ-31 with small continuous addition of fresh solution in an effort to maintain the original pH. In these tests the solution pH dropped from 10.0 to 9.7. The flow rate was 17 ft/sec as compared with 20 ft/sec in the first two tests. One test was run with oxygen gas saturation and the other with helium gas saturation. Results of these tests are shown in Figure 2. Unlike the previously described stagnant test at 53°C, there was no significant difference between the behavior of the samples in oxygen-saturated solution and that in helium-saturated solution. Corrosion rates subsequent to the first ten days were of the order of 15 mdd at pH slightly below 8.5 and a flow rate of 20 ft/sec; 25 mdd at pH 9.7 and flow rate of 17 ft/sec.
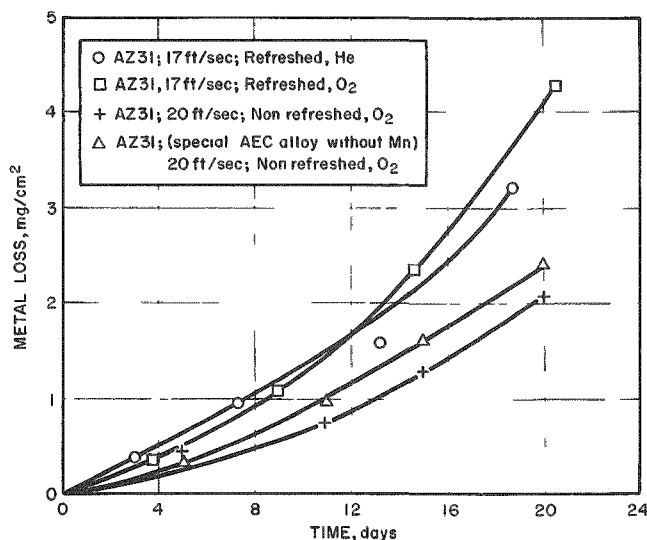
FIGURE 2. CORROSION OF MAGNESIUM ALLOYS IN DILUTE POTASSIUM HYDROXIDE SOLUTION AT 90°C

Preliminary corrosion testing at higher temperatures (see Table I) clearly indicated that none of the common commercial alloys would meet the 1-mil/day maximum rate specification previously mentioned. The high thorium content of alloy HZ-32 precluded its use as a reactor cladding material.

As shown in Table I, the reaction at 150°C is much more rapid than at lower temperatures (1 mil/day = 435 mdd). Samples which were not completely destroyed during the test were covered with plates of nonadherent, white corrosion product. Exposures for varying lengths of time at the same temperature indicated that the corrosion rate was constant for at least a 7-day period.

TABLE I

Corrosion of Commercial Magnesium Alloys in Initially Pure Water

Alloy	Composition, Wt. %									Test Time, days	Temp., °C	Average Corrosion Rate, mils/day
	Al	Zn	Mn	Ni	Si	Th	Zr	Be	Rare Earth			
Pure Mg (Domal)										2.9	120	Disintegrated
										5.0	135	Disintegrated
										1.7	150	Disintegrated
AZ-31	2.5-3.5	0.7-1.3	0.2							2.9	120	0.2
										5.0	135	1.0
										2.7	150	3.2
PE	3.2	1.0	0.1							2.9	120	0.2
										5.0	135	0.9
										2.9	150	3.5
AZ-91	8-9	0.4-1.0	0.13	0.01	0.3					1.7	150	3.1
HZ-32 (ZT1)		2.5				2.5-4.0	0.7			2.7	150	1.2
EK-41A[1]		0.3					0.4-1.0		3-5	5.0	140	Disintegrated
A-3XA[1]	2.5-3.5							trace		5.0	150	Disintegrated

[1] From data of N. Grant, Reactor Engineering Division, ANL.

Alloy Development

In an effort to improve the corrosion resistance of magnesium at 150°C, about thirty-five special alloys were made and corrosion tested. The compositions and corrosion results are summarized in Table II. In general, these alloys may be grouped into the following classes: aluminum binaries, aluminum-copper ternaries, and aluminum-copper-tin or zinc quaternaries.

The results in Table II indicated that copper was the most effective addition for producing significant improvement in the corrosion resistance of magnesium-aluminum binaries. Tin or zinc produced additional improvement. Tin was preferred for nuclear reasons: it has a lower neutron absorption cross section.

The effects on corrosion resistance of varying these three elements are shown in Tables III, IV and V. These are excerpts of data from Table II and illustrate in more convenient form the basis for choosing the optimum alloy. No special significance should be attached to variations of a few tenths of a mil per day in corrosion rates since duplicate tests frequently showed this great a difference.

TABLE II

Corrosion of Developmental Magnesium Alloys in Initially Pure Water at 150°C

Alloy[1]	Composition, Wt. %										Time Test, days	Corrosion Rate, mils/day
	Al	Ce	Cu	Mn	Ni	Pb	Sn	Ti	Zn	Zr		
M1[2]										1	0.8	Completely oxidized
M2		0.5									2.7	Completely oxidized
M3	5			0.1	0.5						0.9	2.0
											4.8	1.8
M3X	5			0.1	0.5						0.9	2.2
											4.8	2.6
M4	15										0.9	3.0
											4.8	2.5
M5	5										0.9	3.7
M6	5	0.1								0.5	0.9	7.1
M7	5	0.1	0.5							0.5	0.9	1.9
											2.8	2.1
M8	5							0.2			0.9	8.2
M9	5		0.5	0.1					1		3.5	1.5
M10	5			0.1					1		0.8	3.2
M11[2]	10				0.5						0.8	4.4
M12[2]	10		0.5								0.8	1.3
M12	10		0.5								2.7	1.6
M13	5		0.5								2.7	1.8
M14	5		0.5						1		3.8	1.7
											3.8	2.0
M15	5		2	0.1					1		2.8	1.6
M16	5		0.1	0.1					1		2.8	2.3
M17	5			0.1			1				1.0	1.8
											3.8	2.1
M18	5		0.5	0.1			1				1.0	1.6
											3.8	1.6
M19	2.5		0.5				1				1.0	1.6
											4.7	2.0
M20	7.5		0.5				1				1.0	1.7
											4.7	1.7
M25	5		0.25		0.25		1				1.7	1.1
											6.8	1.3
M26[3]	3		0.6				1				2.9	1.6
M27	2.5		0.5								2.8	2.4
M28	2.5		0.5				0.5				2.8	1.9
M29	2.5		0.5				1				2.8	1.6
M30	2.5		0.5				2				1.8	2.4
												Cracked
M31	2.5		0.5		0.5		1				1.9	1.4
											3.7	2.0
											4.8	1.8
M32	2.5		0.5		0.25		1				1.9	2.0
											3.7	2.2
M33			0.5				1				2.7	2.2
M34			0.5								2.7	3.3
BP8[3]							2				2.8	3.0
BP13[4]	5			0.1							2.0	6.8

[1] Except as noted, alloys were produced at ANL and tested in the hot-rolled and annealed condition.
[2] Tested as cast and annealed.
[3] Commercially cast to ANL specifications. Hot pressed, rolled, and annealed before test.
[4] Commercially cast to ANL specifications. Tested as cast and annealed.

TABLE III

Effect of Aluminum Content on Corrosion of Some Magnesium Alloys
in Initially Pure Water at 150°C

Alloy and Composition	Test Time, days	Corrosion Rate, mils/day
M33: 0.5 Cu-1 Sn	2.7	2.2
M19: 2.5 Al-0.5 Cu-1 Sn	4.7	2.0
M18: 5.0 Al-0.5 Cu-1 Sn-0.1 Mn	3.8	1.6
M20: 7.5 Al-0.5 Cu-1 Sn	4.7	1.7

TABLE IV

Effect of Copper Content on Corrosion of Some Magnesium Alloys
in Initially Pure Water at 150°C

Alloy and Composition	Test Time, days	Corrosion Rate, mils/day
Pure Magnesium	1.7	Disintegrated
M34: 0.5 Cu	2.7	3.3
M16: 5 Al-0.1 Cu-1 Zn-0.1 Mn	2.8	2.3
M14: 5 Al-0.5 Cu-1 Zn	3.8	1.7
M15: 5 Al-2 Cu-1 Zn-0.1 Mn	2.8	1.6

TABLE V

Effect of Tin Content on Corrosion of Some Magnesium Alloys
in Initially Pure Water at 150°C

Alloy and Composition	Test Time, days	Corrosion Rate, mils/day
M27: 2.5 Al-0.5 Cu	2.8	2.4
M28: 2.5 Al-0.5 Cu-0.5 Sn	2.8	1.9
M29: 2.5 Al-0.5 Cu-1.0 Sn	2.8	1.6
M30: 2.5 Al-0.5 Cu-2.0 Sn	1.8	2.4[1]

[1] Sample cracking

Based on these results, the optimum composition for nuclear reactors appeared to be in the range

Mg- (2.5-5.0) w/o Al- (0.5-1.0) w/o Cu- (0.8-1.2) w/o Sn   .

Three alloys (M-25, M-31, and M-32) were prepared in which nickel replaced part of the copper. The results were not as reproducible as would be desirable, but there were indications that nickel slightly improved the corrosion resistance of these alloys.

Alloys of the following compositions, made to order by Brooks and Perkins, were also corrosion tested at 150°C.

<u>Binaries</u>

Zn	7%,	3.5%,	1%
Sn	10%,		0.5%
Pb	20%,	5%,	1%

<u>Quaternaries</u>

5% Al + 0.1% Mn + 0.05% Be
5% Al + 0.1% Mn + 0.5% Cu

Except for the Al-Cu-Mn quaternary, these alloys failed completely after short exposures to 150°C water   This quaternary alloy corroded at the same rate as similar alloys produced at Argonne.

Beryllium binary alloys could not be prepared by this source   However, Magnox "C" (1% Al; 0.05% Be) from Magnesium Elektron Ltd., Great Britain, failed after short exposure to water at 150°C.

Some of these alloys were heat treated (420°C-1 hour - water quenched) in a manner intended to produce a supersaturated aluminum solution in the belief that the aluminum might prove more beneficial if dissolved in the magnesium. There was no appreciable effect on corrosion resistance.

<u>Coatings and Inhibitors</u>

Various chemical and electrochemical pretreatments described in Table VI were applied to AZ-31 coupons. In addition, coupons treated by the commercial HAE* process were obtained. Attempts were also made to produce surface alloys by vacuum deposition of aluminum and aluminum plus copper, followed by heat treating.

*The HAE process is an anodic treatment carried out in an alkaline bath containing KOH, Al(OH)$_3$, Na$_3$PO$_4$, KF, and K$_2$MnO$_4$.

TABLE VI

Experimental Coatings Applied to AZ-31 Magnesium Alloy

Reagents, % by weight	Temperature, °C	Time, min	Electrical data	Notes
40% KF 6.7% $(NH_4)_2HPO_4$ Bal. H_2O	25	3	5 a/dm²; 120 VDC	
65% KHF_2 35% $NaHF_2$	200	1-5	2 a/dm²; 35-40 VDC or AC	Monel Cathode
a) 20% NaOH b) 10% NaF	180 Boiling	15 60		
3% NaF	20	1-5	90-120 VDC	
32% NH_4F	25	1-5	2 a/dm²; 50-140 VDC	
30% NH_4F 25% KF	25	4	2 a/dm²; 60-80 VDC	
4% NaF $\frac{1}{2}$% NaOH $\frac{1}{2}$% $KMnO_4$	100	1-5	2 a/dm²; DC	AC superimposed on the DC

No long-lasting (more than 24 hours) beneficial effect was found for any of these pretreatments when samples were exposed to 150°C water.

AZ-31 specimens were also used to evaluate the effect of commonly used corrosion inhibitors at 150°C. Sodium salts of dichromate, borate, phosphate and fluoride were tested (100 ppm anion concentration). Only the fluoride was effective. In solutions containing initially 50 to 100 ppm F^-, better than a threefold reduction in average corrosion rate was noted for three-day exposures. Sodium, potassium, ammonium, lithium and lead fluorides were tested. All were effective inhibitors for this alloy. However, fluoride additions did not materially improve the corrosion resistance of pure magnesium. In this case, samples completely disintegrated in less than two days of exposure.

Analysis of the solution in the autoclave before and after testing showed that the fluoride ion was consumed at a rate of about 0.3 mg F^-/cm^2 of Mg/day. (The rate of fluoride depletion by stainless steel was less than 1/100th as fast.) In order to test at constant fluoride conditions, a constantly refreshed autoclave was used. Figure 3 indicates the type of corrosion curves obtained. All of the experiments are summarized in Table VII. These tests were two weeks in duration and the rates refer to the straight-line portion of the curve. There were slight induction periods at the three higher concentrations. The appearance of typical specimens is shown in Figure 4.
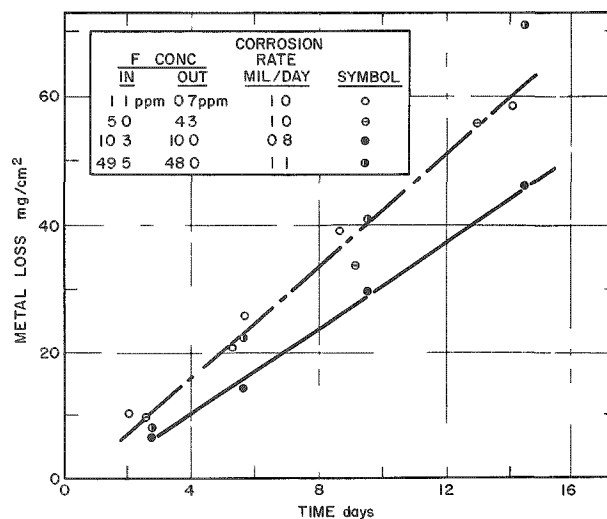
FIGURE 3 CORROSION OF AZ31 MAGNESIUM
ALLOY IN FLUORIDE SOLUTIONS

TABLE VII

Effect of Fluoride Concentration on Corrosion of Magnesium Alloy AZ-31 at 150°C[1]

Fluoride Conc , ppm[2]	Test Time, days	Corrosion Rate, mils/day	Fluoride Conc , ppm[2]	Test Time, days	Corrosion Rate, mils/day
0[3]	5	3 3	10	14	0 8
0 1	14	2 4	48	14	1 1
0 7	14	1 0	8 + 4-5 ml O$_2$/l	7	1 7
4	14	1 0			

[1]Tested in refreshed system
[2]As NaF
[3]Closed autoclave test result included for comparison

22484   1X

    3   6   10   14

Days

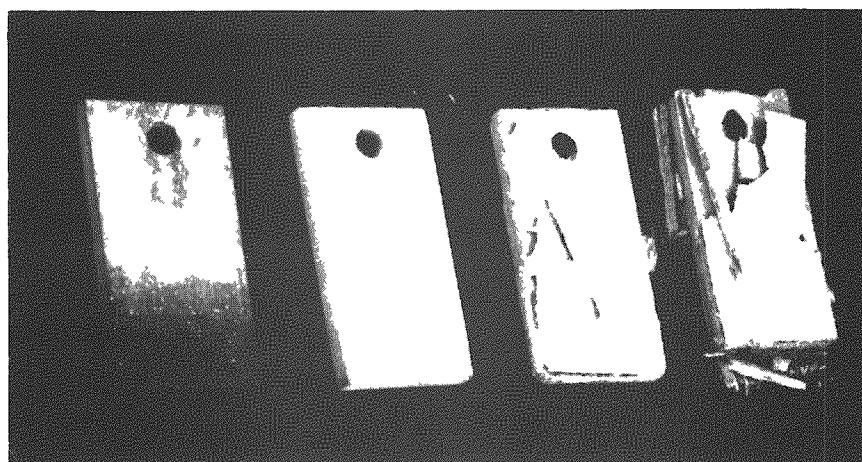Figure 4

Appearance of AZ-31 Magnesium Alloy Corroded in 10 ppm Fluoride (NaF) Solution at 150°C

It is evident that fluoride is somewhat effective at a concentration as low as 0.1 ppm. Between 1 and 50 ppm there is little effect of concentration on corrosion rate. An improvement in corrosion rate by a factor of between 3 and 4 was noted for these solutions as compared with water.

Tests were normally run with helium gas saturating the refreshing solution. In a single test, oxygen saturation of a solution containing 10 ppm F^- led to an increase in the corrosion rate by a factor of about 2. In the refreshed system, as in the closed autoclaves, if no attempt at pH control was made, the pH of the system was about 10.5.

It is possible that fluoride was effective is slowing the corrosion reaction primarily due to the low solubility of the magnesium fluoride formed. To test this hypothesis, preliminary tests were performed with solutions containing iodide, iodide plus fluoride, and chloride plus fluoride. As both $MgCl_2$ and MgI_2 are soluble, neither one should provide an insoluble film. In addition, it has been reported that chloride peptizes the corrosion product, making it less adherent.[5]

The results of these experiments are summarized in Table VIII. Iodide slowed the corrosion reaction, although it was not as effective as fluoride. Small amounts of iodide or chloride did not impair the effectiveness of fluoride.

TABLE VIII

Corrosion of Magnesium and Magnesium Alloys in
Aqueous Halide Solutions at 150°C[1]

Material	Initial Conditions[2]	Test Time, days	Corrosion Rate, mils/day
High-purity Mg	120 ppm I^-	2.6	Completely oxidized
AZ-31	0	5	3.3
AZ-31 Tube	120 ppm I^-	2.6	4.0
AZ-31 Plate	10 ppm I^-	2.7	1.7
AZ-31 Plate	120 ppm F^- +10 ppm I^-	2.7	0.6
AZ-31 Plate	120 ppm F^- + 5 ppm Cl^-	1.9	0.6
AZ-31 Plate	120 ppm F^- +10 ppm Cl^-	1.9	0.6
AZ-31 Plate	120 ppm F^- +10 ppm Cl^-	2.7	0.5

[1] Samples tested in closed autoclave (non-refreshed).
[2] Halide additions as sodium salts.

Effect of pH

The pH of solutions in which magnesium alloys corrode at 150°C reaches and remains about 10.5 (measured at room temperature with a glass electrode pH meter), or within the optimum range for lower temperatures.[6]

However, the alloy studies could be interpreted in terms of an important contribution of aluminum to the protective film formation. With this interpretation as a working hypothesis, it seemed reasonable to expect reduced corrosion rates at a lower pH, favoring the formation of a resistant aluminum oxide incorporated in the magnesium oxide coating. Accordingly, the effect of pH with and without other additives was studied at 150°C.

The effect of pH is summarized in Table IX.

TABLE IX

Effect of pH on Aqueous Corrosion of Magnesium Alloys at 150°C

Alloy	Test Conditions			Test Time, days	Corrosion Rate, mils/day
	pH	F^-, ppm	Cl^-, ppm		
AZ-31	4(H_2SO_4)	0	0	6	2.0
	4	10	0	8	2.3
	5-6(H_2SO_4)	0	0	5	2.7
	5-6	10	0	7	3.3
	6-7(HF)	0.3	0	8	0.8
	6-7	10	0	4	0.4
	6-7	10	5	9	0.4
	10.5[1]	0	0	5	3.3
	10.5	10	0	14	0.8
	12[1](KOH)	0	0	2	2.1
	12[1]	120		2	2.6
	13[1](KOH)	0	0	2	2.3
	13[1]	120	0	2	2.4
Argonne M14 (Commercially Fabricated Tubing)	6-7(HF)	10	0	5	0.1-0.3[2]
Argonne M26 (Commercially Fabricated Tubing)	6-7(HF)	10	0	10	0.1-0.3[2]
	6-7	10	5	5	1.0
Pretreated AZ-31[3]	6-7(H_2SO_4)	0	0	4	1.0
	6-7(HF)	0.3	0	4	0.1

[1] Closed autoclaves; solution not refreshed during test.
[2] Corrosion rate given as range - poor reproducibility of results due to poor quality of tubing.
[3] Pretreated 4 days, 150°C, pH 6-7(HF) + 10 ppm F^-; corrosion coating not removed.

Examination of the data indicated the following:

1)   The optimum condition for minimum corrosion was pH of 6-7 with a fluoride content of about 10 ppm. Under these conditions commercial alloy.AZ-31 and the recommended Argonne-developed alloy were approximately equally resistant.

2)   In the absence of fluoride, controlling the pH at values both lower and higher than the pH 10.5 equilibrium value resulted in corrosion rates lower than the rate at the equilibrium value. At pH values of approximately 4 and 5, fluoride accelerated corrosion. At pH values above the equilibrium value, fluoride exerted little if any effect.

3)   The presence of chloride under otherwise optimum conditions slightly increased the corrosion rate.

DISCUSSION

Since the experimental work was performed in support of specific reactor designs, tests were not operated under conditions to allow evaluation of the effect of temperature on corrosion rate. Qualitatively, it has been shown here that the rate of corrosion in water increases rapidly with temperature, going from the order of 10 mdd at 53°C to 1400 mdd at 150°C. Grant obtained a low corrosion rate (~1 mdd) in a nonrefreshed test at 50°C, but at 150°C his value agrees with ours. It is possible that the discrepancy near 50°C is a result of the reduction in corrosion rate due to the accumulation of corrosion product in his nonrefreshed test. As previously mentioned, Link noted this type of behavior in dynamic tests at 60°C.

The corrosion behavior is correlated with the accumulation of corrosion product rather than correlated with pH, since: (a) conflicting estimates were obtained by the glass electrode pH meter and indicator paper; and (b) there was an increase in dynamic corrosion in the second set of tests at 90°C (pH maintained by KOH) when the solution was constantly replaced, even though the measured pH was higher

Very limited data suggest that oxygen increases corrosion. This was particularly pronounced in the stagnant test at 53°C. Dynamic tests at 90°C showed little effect of oxygen saturation.

Pure magnesium demonstrated the poorest corrosion resistance of the alloys tested at temperatures above 100°C. In this respect its behavior is similar to that of pure aluminum. The roles of the three beneficial alloying elements are not understood. It is thought that aluminum and tin (or zinc) serve to increase corrosion resistance as a result of the properties of the corrosion products. With these elements present, the cathodic alloying element is beneficial in pure water at elevated temperatures. It

should be emphasized that the copper addition was desirable for the specific case of relatively pure water at elevated temperature. In making this alloying addition it is assumed that the resistance of the cathodic corrosion process is deliberately reduced to obtain a more than proportional increase in the resistance of the anodic corrosion process. This redistribution of resistances is possible only for certain corrosion media. The bulk of the data reported[1] for various solutions at lower temperatures indicate that copper would be undesirable in alloys designed for resistance to the more common corrosion-evaluating solutions.

Copper is apparently a more effective alloying agent than nickel. In view of the experience with aluminum,[4] this was somewhat surprising. However, it has been reported[2] that nickel is confined to the grain boundaries while copper in concentrations greater than 0.1% is distributed throughout the magnesium alloys. The improved distribution of the copper cathodic second phase would be expected to increase the corrosion resistance.

No effort was made to evaluate coatings or inhibitors at temperatures other than 150°C. At this temperature no promising coating was found. Of the common inhibitors, only fluoride was useful. The reported low solubility of the fluoride corrosion product is apparently not the key to the mechanism of inhibition since other halides, producing soluble fluorides, were also shown to be somewhat effective in reducing the rate of corrosion. Optimum fluoride inhibition in systems without deliberate pH control reduced the corrosion rate of AZ-31 alloy by a factor of about three.

The control of pH in the range of pH 6-7 with fluoride inhibition produced a striking reduction in corrosion rate. As previously mentioned, it is believed that the neutral pH, favoring the production of a more corrosion-resistant aluminum oxide, significantly improves the corrosion film properties at 150°C of magnesium alloys containing aluminum.

CONCLUSIONS

As has been discussed, the corrosion rates of magnesium alloys increased rapidly with increase in temperature. The results of these studies therefore did not indicate the possibility of using magnesium in high-temperature aqueous systems, except for highly specialized ones such as the high-flux research reactor in which high corrosion rates are tolerable because of an unusually short core life.

It has been demonstrated that, by appropriate methods, it is possible to reduce by a factor of about 30 the corrosion rate of selected magnesium alloys in static aqueous environments at 150°C. Some aspects of these findings are in apparent contradiction to previous ideas. If inhibiting agents and improved alloys are correspondingly effective at lower temperatures

and with rapid flow, the performance of low-temperature research reactors could be materially improved by the substitution of magnesium for aluminum. Certain nonnuclear uses might also prove feasible.

ACKNOWLEDGEMENT

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