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CORROSION EXPERIMENTS WITH 2S ALUMINUM AT 200°C

by

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CORROSION EXPERIMENTS WITH 2S ALUMINUM AT 200°C

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ABSTRACT

Aqueous corrosion experiments using 2S aluminum at 200°C showed that:

(a) lowest corrosion rates were obtained in dilute sulfuric acid at pH near 3. This was also true at 250 and 300°C. The same amount of sulfate ion in neutral solution caused no significant reduction in corrosion;

(b) dichromate ion and dissolved oxygen increased the corrosion rate (neutral pH). Sodium silicate as a solute resulted in higher corrosion rate when the pH was lowered only to 9.4; at pH 3.5 it reduced the corrosion rate significantly;

(c) chloride ion (5 ppm) caused some pitting and increased the corrosion rate slightly;

(d) coupling to more cathodic materials such as graphite and zirconium caused no noticeable effect on the aluminum corrosion in distilled water.

INTRODUCTION

It has been shown⁽¹⁾ that annealed 2S aluminum sheet corrodes in a smooth and uniform manner up to at least 200°C. Above this temperature a new type of corrosion resulting in an accelerating corrosion rate was experienced. Therefore at this temperature the aluminum corrosion program at Argonne split into two logical branches. One objective was the elimination of the accelerating attack on aluminum at temperatures above 200°C. This has been accomplished and reported.⁽²⁾ The second objective was a study of the effect of solution additives and other system variables on the smooth corrosion rate at 200°C. The current report is devoted to experiments involving this second objective.

4 EXPERIMENTAL

Sample Material and Test Procedure

All corrosion-rate samples were cut from one sheet of 2S aluminum of analysis shown in Table I. The specimens were 3/4 in. x 3 in. x 1/16 in., with a 3/32-in. suspension hole drilled near one end.

Table I

ANALYSIS OF 2S ALUMINUM STOCK In Weight Per Cent

Spectrographic (Chem. Div.: plate 23180)			
Element	Amount	Element	Amount
Ag	0.01	Mg	0.01
Al	Large	Mn	0.01
As	0.1	Na	0.01
B	0.01	Ni	0.01
Ba	0.01	P	0.1
Be	0.01	Pb	0.01
Bi	0.01	Sb	0.01
Ca	0.01	Si	0.1
Co	0.01	Sn	0.01
Cr	0.01	Ti	0.01
Cu	0.5	Zn	0.01
Fe	0.5	Zr	0.01
Chemical (Chem. Div.: Sample C-317)			
Element		Amount	
Si		0.13 - 0.14	
Fe		0.52 - 0.52	
Cu		0.12 - 0.12	

A fresh, uniform surface was prepared by wet grinding with 400 grit Durite abrasive paper on a metallographic polishing wheel. Under microscopic examination no abrasive particles were visible in the metal surface. Samples showing inclusions were discarded. Specimens were then measured, degreased in freshly distilled ethyl alcohol and weighed on an analytical balance.

Tests were performed in two types of replenished autoclave systems. In the first type, water or fresh solution was stored at temperature in a stainless steel tank. The hot solution was allowed to flow through the thermostated test autoclave to the atmosphere through a controlled leak. Flow rates of about 2 ml/min were used. In these tests the solution composition remained reasonably constant throughout the test period; there was no significant contamination by the samples. Solutions were deaerated by boiling before sealing the autoclave systems.

The second type of flow system used a high pressure pump to force cold solution through a preheater into a thermostated test autoclave at flow rates up to 30 ml/min. The usual rate was 10 ml/min. An adjustable pressure relief valve permitted variation of the operating pressure of the system without temperature adjustment. Other advantages of this type of system are that less decomposition of the test solution occurs when stored at room temperature than when stored at operating temperature and that various gas saturations may be easily used.

The samples were suspended on racks made of synthetic sapphire rod or Teflon to provide electrical insulation of the specimens from the stainless steel autoclaves.

The solutions were made with double distilled water and Reagent Grade chemicals where required. Quality control tests of the incoming and effluent solutions were made using a pH meter, resistivity bridge and, where required, a spectrophotometer for colorimetric analysis.

Determination of Corrosion Rates

Temporarily assuming that none of the corrosion product was lost from the samples, and knowing the amount of aluminum metal corroded and the amount of coat left at the end of the test, the corrosion product was assumed to be $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$. The value of X was determined from the weighings. Since it was determined by X-ray diffraction techniques that the composition of the corrosion product was $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, deviations of the calculated values of X from 1 were presumed to be caused by the loss of corrosion product to the solution. Values of X at various times throughout the tests were estimated by assuming that at zero test time X equalled 1 and changed linearly until the end of the test, at which time its value was determined. Using these values of X, the amount of metal corroded to correspond to the amount of weight change of the samples at each weighing period was computed.

The samples were stripped of their corrosion coating by a two-step procedure. Eight ma/cm^2 of DC was first applied between sample and a platinum electrode in specially purified saturated solution of boric acid at room temperature (sample connected to the positive lead). After

one minute the samples were removed and the bulk oxide removed by brushing. The samples were then given a cathodic treatment in a hot solution containing 4% CrO_3 and 10% H_3PO_4 (by weight) which chemically removed the more tenaciously held oxide coating. About 8 ma/cm^2 was also used in this case.

DATA

Solution Additive

Aluminum corroding in dilute aqueous solution at 200°C rapidly acquires a uniform, moderately thick, light grey coating of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The rate of metal conversion is quite high upon initial immersion but after several days the rate of further corrosion may be considered approximately linear with time. A typical corrosion curve is shown in Figure 1. The duration of all the test was approximately 20 days. In reporting rates the slope of the linear portion of the curve in milligrams per square decimeter per day (mdd) is given. The intercept on the weight loss axis is also given. Obviously, from these pieces of information estimates of metal loss at extended times may be made.

Effect of pH: Previous work had indicated a reduction of corrosion rate of 2S aluminum as the pH was lowered to 5. A test was therefore run to determine if a further reduction in pH produced a lower rate in corrosion. The results of this series of experiments are shown in Table II.

Table II

EFFECT OF SOLUTION pH ON THE CORROSION OF ALUMINUM AT 200°C

Solution	Gas	pH	Slope, $\text{mg/dm}^2/\text{day}$	Intercept, mg/dm^2
Distilled Water	He	6.5 - 7	2.8	82
Dilute H_2SO_4	He	5.0	1.4	21
Dilute H_2SO_4	He	3.5	0.7	21

The reduction in rate is striking. Attack by the solution on the stainless steel autoclave prevented any further reduction in pH for long-term tests. However, some preliminary tests were performed in small autoclaves for short times. The results of these tests at 200°C and also 250° and 300°C are presented in Table III. The pH of minimum attack

WEIGHT CHANGE, mg/dm²
ACTUAL METAL CORRODED ← → UNCLEANNED SAMPLES

FIGURE 1

CORROSION OF 2S ALUMINUM AT 200°C, pH 7 (Dist. H₂O)

(for short times) is near 3 for the three temperatures tested. To eliminate the possibility that SO_4^- was acting as an inhibitor, the last test in the table was run. When potassium sulfate was added in quantities sufficient to have a sulfate ion concentration equal to that in pH 3 sulfuric acid, no difference in corrosion from that in distilled water was noted.

Table III

CORROSION OF 2S ALUMINUM AS A FUNCTION OF pH

Aluminum Metal Corroded, mg/cm^2

pH (H_2SO_4)	200°C; 48 hours	250°C; 20.5 hours	300°C; 6 hours
2	1.3	0.59	0.51
3	0.16	0.07	0.19
4	0.18	0.36	0.23
5	0.25	0.42	0.36
6.5	0.25	0.47	0.60*
(Distilled)			
6.3	SO_4^- Conc. = pH 3 H_2SO_4 (K_2SO_4)		0.57*

* Calculated from weight gain - Sample could not be effectively stripped due to blisters.

Dichromate and Silica Additions: At temperatures around 50°C, the corrosion rate of 2S aluminum in pure water is reduced by the additions of oxidizing agents such as dissolved oxygen or dilute dichromate. The rate has also been reduced by additions of soluble silica. Potassium dichromate and sodium metasilicate with and without pH control were therefore chosen as possible high temperature inhibitors for investigation at 200°C.

The results of these experiments are shown in Table IV. The distilled water test was included for reference.

Two features of this table are of interest. First, only a combination of low pH and silica proved beneficial, while the other additions actually increased the corrosion rate from 4 to 9 times that obtained in distilled water. Second, at the high rates obtained with neutral and alkaline solutions, the intercept is essentially zero. This is a departure from the usual aluminum behavior.

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The use of these common low temperature corrosion inhibitors would obviously be very unwise at 200°C unless pH adjustment was also used.

Table IV

CORROSION OF 2S ALUMINUM AT 200°C

Solution	Gas	Corrosion Rate, mg/dm ² /day	Intercept, mg/dm ²
Distilled Water	Deaerated	2.5	54
50 ppm K ₂ Cr ₂ O ₇ pH 6.1 (Adjusted with KOH)	Deaerated	9	0
50 ppm K ₂ Cr ₂ O ₇ pH 8.4 (KOH)	Deaerated	21	0
30 ppm SiO ₂ (Added as Na ₂ SiO ₃) pH 9.4 (H ₂ SO ₄)	Deaerated	10	0
30 ppm SiO ₂ pH 3.6 (H ₂ SO ₄)	Deaerated	0.2	14

Chloride Additions: The chloride ion is noted for its tendency to produce pitting and increased corrosion of aluminum in aqueous solutions at ordinary temperatures. A test was performed with a 5 ppm Cl⁻ solution (KCl) at pH 3.5 (helium saturated) to evaluate this tendency at 200°C. An average of about 1 pit for every three square centimeters was formed on specimens exposed for 19 days. The pits that formed were typically surface channels with a length to breadth ratio of 3 or more. The maximum depth of the pits was 0.6 mm. Dimensions of the largest pit was 0.6 mm wide by 2 mm long.

The corrosion rate measured for this condition was 1 mdd (intercept 18 mg/dm²) as compared with a rate of 0.7 mdd (intercept 21 mg/dm²) for the same conditions except for the chloride. The data indicate that the chloride ion promotes pitting at 200°C, although the effect is apparently somewhat less than at temperatures below 100°C.

Gas Saturation

Only two gases were tried. In both cases the solutions were saturated at room temperature and force-fed under a two-pound positive gas pressure to the high pressure pump. A corrosion rate of 2.8 mdd (intercept 82 mg/dm²)

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was measured with helium and 3.5 mdd (intercept 42 mg/dm²) with oxygen in distilled water at 200°. Since a strong oxidizing agent (potassium dichromate) gave a large increase in corrosion rate, it is not surprising that a mild agent like dissolved oxygen would cause a slight increase.

The corrosion rate previously obtained for deaerated water (2.5 mdd) is quite close to the helium saturated case. It was felt that the deaeration procedure (vigorous boiling in the large storage tank before closure) probably removed more of the dissolved air than the helium saturation method. If this were the case the results are completely consistent and indicate that, in general, oxidizing agents are undesirable in high temperature aluminum corrosion.

System Pressure

A pair of tests was run to determine if the pressure within the system had an effect on the corrosion rate. A corrosion rate of 3.6 mdd (intercept 116 mg/dm²) was measured in distilled water (O₂) for 250 psig while 3.5 mdd (intercept 42 mg/dm²) was measured for 1000 psi. These results are the same within the experimental accuracy and indicate no effect of pressure over this range.

The intercept values for both the gas comparison and the system pressure tests were not consistent with the long-term corrosion rates. Typically the intercept values in distilled water corrosion are sensitive to slight variations in conditions at the start of the experiment. In this case a change from porous alundum sample supports to artificial sapphire rods was made. The lower intercepts were obtained in tests run with the sapphire.

Galvanic Couples

A few preliminary experiments were performed to evaluate the effects, if any, resulting from electrically coupling 2S aluminum to other materials of construction in distilled water at 200°C. No rates were measured under these conditions.

A graphite - 2S couple was prepared by machining matching threads on 1 in. long x 3/8 in. diameter pieces of AGR graphite and 2S aluminum rods. The couples were assembled by screwing dissimilar pieces together. Control pieces of 2S were included in the test autoclave.

The couples were removed after 39 days of exposure. There was no galvanic attack noted on either sample. The coating on the coupled sample of 2S was slightly more uniform than on the controls but all specimens were in very good condition as shown in Figure 2.

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Figure 2

2S Aluminum-AGR Graphite after 39 Days
in Distilled Water at 200°C

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Other couples were made from sheet 2S aluminum, 63S aluminum, and Bureau of Mines zirconium held together by a machine screw made of one of the materials of the couple. There was no difference in appearance between the coupled aluminum and the control pieces after a three week test at 200°C.

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