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EXPERIMENTS IN CORROSION MECHANISM:
ALUMINUM AT HIGH TEMPERATURES

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	3
INTRODUCTION	3
EXPERIMENTAL	4
Samples	4
Corrosion Testing	4
Hydrogen Analyses	6
Electrochemical Measurements	6
DATA AND RESULTS	6
Hydrogen Analyses	6
Cathodic Second Phase	8
Corrosion Resistance of the Second Phase	12
Electrochemical Experiments	13
Solid Solution Alloying Additives	14
Film Conductivity	15
Corrosion Film Study	17
Aqueous Corrosion Inhibitors	18
Superheated Steam	20
Suitable Alloys	20
Comparison with Zircaloy-2	22
High Purity Aluminum	23
DISCUSSION	24
Hydrogen Damage Hypotheses	24
Alloys	25
Corrosion Mechanism	25
REFERENCES	26

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Schematic Drawing of Superheated Steam Testing Equipment .	5
2.	Effect of Distribution of the Second Phase in Aluminum- 1.1% Fe-0.5% Ni-0.3% Si Alloy on the Corrosion Resis- tance at 350°C in Distilled Water	9
3.	Effect of Distribution of the Second Phase on the Corrosion Resistance of Aluminum-Nickel Binary Alloys - 350°C Water for 1 Day	10
4.	Effect of Distribution of the Second Phase on the Corrosion Resistance of Aluminum-Nickel-Iron Ternary Alloys - 350°C - Distilled Water - One-Day Exposure	11
5.	Cathodic Polarization Curves - 200°C Distilled Water	13
6.	Corrosion Film of Aluminum Alloy M-388 After 10 Days Exposure at 290°C (Distilled Water)	17
7.	Aluminum Alloys After 2 Weeks in Steam at 450°C, 300 psig .	22
8.	Corrosion in Superheated Steam at 400°C - 4000 psig	23

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I	Hydrogen Analyses of Corroded 1100 Aluminum	7
II	Corrosion Behavior of Intermetallic Compounds in Distilled Water	12
III	Effect of Alloying Additions on the Corrosion of an Aluminum-0.9% Nickel Alloy	15
IV	Relative Film Forming Efficiency	16
V	Effect of Phosphate Additions on M-388 Corrosion at 350°C . .	19
VI	Corrosion of Alcoa Experimental Alloys in Superheated Steam	20
VII	Corrosion in Superheated Steam	21
VIII	Aluminum Alloys	24

EXPERIMENTS IN CORROSION MECHANISM: ALUMINUM AT HIGH TEMPERATURES

J. E. Draley and W. E. Ruther

ABSTRACT

Hydrogen analyses of corroded 1100 aluminum alloy have indicated an increase in hydrogen content of the metal near the corroding surface. Analyses of M-388 aluminum high temperature alloy have not indicated any such increase.

The resistance to disintegrating attack in high temperature water is shown to improve with the amount and dispersion of the cathodic second phase present in the aluminum alloys. The relative abilities of various second phases to protect the alloy against disintegration are in the same order as their abilities to act as effective cathodes at the temperature of testing.

Attempts to reduce the corrosion rate of resistant alloys by alloying the aluminum matrix with a solid solution additive have been largely unsuccessful. One alloy, Al-1% Ni-0.1% Ti, gave a lower equilibrium rate but a higher initial intercept.

Phosphoric acid at pH 3.5 produces a sizable reduction in the equilibrium corrosion rate of M-388 alloy at 290°C.

Tests in superheated steam indicate that cathodic second phases provide corrosion resistance in this medium as they do in water. A special aluminum alloy is shown to possess superior corrosion resistance when compared with Zircaloy-2 at 400°C-4000 psig.

INTRODUCTION

Most commercial aluminum alloys corrode at an accelerating rate in water above about 200°C. Corrosion product mounds and hollow blisters are formed. A previous report by this group⁽¹⁾ presented the clues leading to the formulation of an hypothesis describing this type of attack in terms of the penetration of the corrosion-product hydrogen into the metal. The methods of eliminating this attack suggested by the hypothesis actually performed as anticipated, and resistant alloys were developed.

4

This report continues to develop the hydrogen hypothesis and also presents the results of other experiments concerned with the mechanism of the attack of high temperature water and steam on aluminum alloys.

EXPERIMENTAL

Since the type of experiments required such diverse equipment, only a brief general description will be given here. Important variations will be covered in the presentation of the data and results.

Samples

Most of the aluminum alloys were made by heating the components together in a covered, high purity aluminum crucible within an electric muffle furnace. After complete dissolution the melt was cooled to the vicinity of 700°C and sparged for one minute with dried argon gas. This sparge both stirred the melt effectively and presumably helped to remove dissolved hydrogen gas. A small water-cooled copper chill casting mold was used. The average size of the melts was 200 gm.

The high purity aluminum, 0.5% Ni* and 1.0% Ni alloys were supplied by the Kaiser Aluminum Company.

A 3000-lb commercial melt of 1100 aluminum with 0.9% Ni added (M388) was purchased from the Aluminum Company of America. The corrosion of rolled sheet stock from this source was used as a reference point for comparison tests.

Samples were prepared for corrosion testing by wet grinding to 240 grit on a metallographic grinding wheel. The exposed area was measured, after which the samples were degreased in methanol and weighed.

Corrosion Testing

High temperature testing was accomplished in the stainless steel autoclaves described in a previous report.⁽¹⁾ Both refreshed and stagnant tests were performed. The aluminum samples were electrically insulated from the autoclaves by artificial sapphire rods. The solutions were made from Reagent Grade chemicals and distilled water of specific resistance $>10^6$ ohms-cm.

*Percentage compositions given in this report are by weight.

For tests in superheated steam, two types of equipment were used. At 400°C - 4000 psig, a small standard autoclave was equipped with a bleed valve and pressure gauge. This autoclave was cooled and the water replaced each week. At 450°C - 300 psig steam, a different system was used, as shown schematically in Figure 1. Water from the reservoir was forced up the central tube by its vapor pressure. The heaters on this chamber were controlled by a pressure switch to maintain 300 psig. When the liquid water entered the hotter upper chamber it flashed into steam and the pressure thus developed prevented the chamber from filling with water. A constant bleeding of the upper chamber removed the hydrogen gas produced by corrosion and provided a fresh steam supply. Several hundred degrees of superheating was used to insure dry steam. The valve in the water supply line permitted bringing the equipment to operating temperature before admitting the steam.

Figure 1
Schematic Drawing of Superheated Steam Testing Equipment

After corrosion, the samples were "defilmed" by one of two methods. Either the oxide was removed from the sample by a two-step electrolytic process previously described(1) or the metal was dissolved away from the oxide by a methanol-iodine solution at 50°C (10 gm I₂ per 100 ml of CH₃OH).(2) The choice of method depended on the time and temperature of testing, since the electrolytic method would not completely remove coatings put on at temperatures above about 300°C.

Hydrogen Analyses

Hydrogen analyses were performed by the vacuum fusion method (alundum thimble). A palladium valve insured that only the hydrogen content was measured. Toepler pumps transferred the hydrogen to a known volume where the pressure was measured by a calibrated thermocouple gauge.

Electrochemical Measurements

Cathodic polarization curves were measured using an electronic interrupter technique. A linear increase of current vs time was applied between the sample and a suitably placed working electrode. The potential of the sample was measured electronically during the one to five-millisecond interruption of the current. A corroded stainless steel reference electrode was used.

DATA AND RESULTS

Hydrogen Analysis

One of the basic ideas of the theory of the accelerating corrosion at high temperature as developed at Argonne is the penetration of the metal by some of the corrosion hydrogen, with the subsequent formation of gas pockets (blisters). The aluminum alloys which withstand high temperatures successfully are presumed to liberate the hydrogen formed during corrosion into the solution. Therefore no penetration of the metal by hydrogen should be noted.

In order to test this hypothesis, samples of 1100 aluminum and 1100 aluminum plus 0.9% Nickel (M-388) were corroded for 2 days in water at 290°C. The M-388 samples when analysed with the corrosion coating intact produced some hydrogen (presumably from the reaction of $3\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + 2\text{Al} \rightarrow 4\text{Al}_2\text{O}_3 + 3\text{H}_2$).

The corrosion coating was removed on other samples by anodic treatment in boric acid and cathodic treatment in chromic-phosphoric acid. These samples analyzed >0.1 ppm hydrogen, indicating no penetration of the metal.

The 1100 aluminum samples showed microscopic blister attack and behaved quite differently. An analysis gave about the same amount of hydrogen as M-388 after corrosion with the coating intact. However, when this coating was removed by the treatment described above, the hydrogen content was still 7.3 ppm (stock, uncorroded: 0.6 ppm). To further investigate the hydrogen penetration a series of samples were given the same corrosion treatment and then various amounts of metal were etched away with a dilute HNO_3 -HF mixture. The results are shown in Table I.

Table I

HYDROGEN ANALYSES OF CORRODED 1100 ALUMINUM*

Treatment	Average Metal Etched Away	Hydrogen Content (Whole Sample)	Estimate of Hydrogen in Increments of Etched Metal
As corroded	-	12.1 ppm	-
As stripped	-	7.3	-
Etched (dilute HNO_3 -HF)	0.016 mm	3.0	280 ppm
Etched (dilute HNO_3 -HF)	0.041	1.8	59
Etched (dilute HNO_3 -HF)	0.071	1.1	24
Etched (dilute HNO_3 -HF)	0.120	1.0	5
Etched (dilute HNO_3 -HF)	0.22	0.8	3
Blank (no corrosion)	-	0.6	-

*Corroded 2 days at 290°C in distilled water.

The figures in column 4 are inaccurate due to the use of different samples (probably having slightly different hydrogen penetrations) for calculation. Estimates were made by subtracting the micrograms of hydrogen from one sample to the next and then dividing by the difference in etched metal. In spite of the probable inaccuracy, the trend is very evident. The hydrogen from corrosion is apparently held within a few tenths of a millimeter from the surface, producing high local concentrations of hydrogen. Since the solid solubility of hydrogen in aluminum is very small, this supports the concept of gas pockets or blisters.

An alternative hypothesis to explain the presence of hydrogen, as due to trapped or combined water in retained oxide, must also be examined. The weight change produced by defilming the visible oxide was very close

to 3.5 mg/cm² for each of the samples for which this was measured. From the first two entries in Table I, the hydrogen supplied by this visible oxide was:

$$12.7 \text{ ppm} - 7.3 \text{ ppm} = 4.8 \text{ ppm}$$

(based on the whole sample $\approx 1.5 \text{ gm}$).

It is now assumed that there must have been an additional amount of trapped oxide to explain the remainder of the hydrogen. This would be approximately

$$\frac{(7.3 \text{ ppm} - 0.6 \text{ ppm})}{4.8 \text{ ppm}} \times 3.5 \text{ mg/cm}^2 = 4.9 \text{ mg/cm}^2 ,$$

or nearly $1\frac{1}{2}$ times the visible amount.

Further, no oxide at all was visible on microscopic examination after the first etching and brushing, since the acid opened the blisters quite effectively. Yet there were 3.0 ppm - 0.6 ppm = 2.4 ppm of hydrogen still present.

The only way to explain the experimental results by this hypothesis is to assume that only the final bits of boehmite are quantitatively converted to hydrogen and aluminum oxide. The amount of boehmite required to supply 2.4 ppm hydrogen under these conditions is only 0.2 mg total. It is unlikely, but possible, that this amount remained after etching and brushing, since it would be difficult to detect microscopically.

In view of the restrictive assumption made in this oxide hypothesis and the occasional hollow blisters found in corroded aluminum alloys, the hydrogen explanation is favored.

Cathodic Second Phase

An alloy, chill cast and rolled with the chemical composition of aluminum-1.1% Fe-0.5% Ni-0.3% Si, was found to exhibit different corrosion behavior on the opposite sides of the same 1/8" thick sample when tested in 350°C distilled water. Since an analysis indicated no chemical difference, the corroded sample, after removing the oxide, was examined metallographically (modified Keller's Etch). The difference between the two sides was very apparent, as shown in Figure 2. The side having the finer dispersion of the second phase corroded in a smooth and uniform fashion with an adherent oxide coating. The coarse dispersion side showed serious roughness and lack of uniformity upon corrosion.

Opposite sides of the same 1/8" thick sample.

Figure 2

Effect of Distribution of the Second Phase in
Aluminum-1.1% Fe-0.5% Ni-0.3% Si Alloy on the
Corrosion Resistance at 350°C in Distilled Water

The systematic investigation of the influence of dispersion of the second phase on corrosion behavior was started with the binary aluminum-nickel alloys. Alloys of 0.5% and 1.0% nickel were prepared with three types of casting to achieve different dispersions. The same well-sparged and stirred crucible of alloy was used for all three types of casting. The molten metal ($\sim 700^{\circ}\text{C}$) was poured into a water-cooled chill mold, a heated graphite mold (350°C) and the remainder allowed to crucible cool in air. The metal in the chill mold solidified almost instantly, within about 10 seconds in the graphite and within two minutes in the crucible.

One of two adjacent pieces of the as-cast material was then corrosion tested in 350°C water for one day. The other piece was examined metallographically (electropolish plus modified Keller's Etch). The results of the corrosion tests are compared with the dispersion of the nickel-aluminum eutectic in Figure 3. In both alloys the very large grained

Figure 3

Effect of Distribution of the Second Phase on the
Corrosion Resistance of Aluminum-Nickel Binary
Alloys - 350°C Water for 1 Day.

material disintegrated. At approximately the same grain size, the 1% alloy with the broader eutectic network was superior to the 0.5% alloy. Two factors appear to be involved. Both good dispersion and adequate cathodic area are required for good corrosion resistance.

The experiments were continued with the aluminum-nickel-iron ternaries, since they had exhibited superior corrosion resistance. Examination of the as-cast micrographs of a borderline resistant alloy and a good alloy (350°C water) indicates a slight improvement in quantity and dispersion of the second phase, as shown in Figure 4 for the resistant alloy.

Figure 4

Effect of Amount and Distribution of the Second Phase
on the Corrosion Resistance of Aluminum-Nickel-Iron
Ternary Alloys - 350°C - Distilled Water -
One-Day Exposure

A previous publication⁽³⁾ presented an explanation in terms of the geometry of the second phase. As is shown in Figure 3, nickel compound alone produces only a somewhat favorable geometry, but with the random deposits of iron-nickel-aluminum eutectic (Figure 4) the distances between second phase cathodic sites are reduced considerably.

Corrosion Resistance of the Second Phase

The presence of a strongly cathodic second phase is common to aluminum alloys which exhibit good high temperature aqueous corrosion resistance. However, all of the cathodic phases do not possess the same ability to protect. For some the presence of other metals in the alloy greatly enhances the protective quality. A possible explanation for the superior performance of the aluminum-nickel-iron ternary alloys has been previously given in terms of the dispersion of the second phase. There was also the possibility that the intermetallic compound NiAl_3 was rapidly corroded by the water, thus preventing it from remaining on the surface long enough to provide complete protection to the aluminum grains. The presence of iron would produce the FeNiAl_9 compound, which might be much more resistant. To check this point, the intermetallic compounds FeAl_3 , NiAl_3 , FeNiAl_9 , and CuAl_2 were prepared and corroded in 290°C distilled water.

The results are given in Table II. The rate of penetration is calculated on the following assumptions: (1) all the corrosion product is retained; (2) products of corrosion are FeO , NiO , CuO , and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Attempts to remove the corrosion coating for a more accurate estimate were failures. Additional uncertainty arises because the samples (especially the NiAl_3) had hairline cracks due to the method of preparation. The penetration rate of the NiAl_3 was not sufficiently different from the rate for FeNiAl_9 to permit the explanation of the superior corrosion resistance of the ternary alloys on that basis. This result is further substantiated by the observation of uncorroded specks of second-phase compound in the corrosion film formed on these and similar alloys indicating that their in-situ corrosion rates are smaller than those of the matrix material.

Table II

CORROSION BEHAVIOR OF INTERMETALLIC COMPOUNDS IN DISTILLED WATER AT 290°C

Compound	Estimated Rate of Attack During Period 1-14 Days	
	Wt. Gain, $\text{mg}/\text{cm}^2\text{-day}$	Penetration, inch/year
FeAl_3	14	0.007
NiAl_3	83	0.038
FeNiAl_9	71	0.032
CuAl_2	40	0.019

Electrochemical Measurements

Open circuit solution potentials and cathodic polarization curves were measured for the second phase present. Since the phase diagrams show eutectics for the systems of interest in the high aluminum region, the second phase would normally have the eutectic compositions. All except the copper eutectic alloy were rolled into 1/8" thick sheet before testing. The copper alloy was too brittle to roll and was used in the as-cast condition.

As a first stage in the experiment, the alloys were corrosion tested for one week at 200°C in distilled water. It was assumed that further changes in the oxide film would be relatively slow. One alloy at a time was then suspended in the special autoclave permitting electrical access to the specimen.⁽¹⁾ The experimental curves are presented in Figure 5.

Figure 5
Cathodic Polarization Curves-200°C Distilled Water

The slope of the curve is inversely related to the ability of the sample to perform as an effective cathode. The open circuit potential might not be as reliable since it is measured with respect to the stainless steel. Roughly, however, only the nickel alloy caused a significant shift in solution potential in the cathodic direction, such as might be expected from the addition of an actively cathodic phase without alteration of the basic anode reaction.

Previous corrosion tests with alloys containing these elements indicate that roughly the same order (as the inverse slopes in Figure 5) describes the relative ability to prevent blister attack on aluminum. Nickel is the best, and silicon the worst, of these additive elements.

Additional polarization curves were run at 290°C in degassed distilled water with the intermetallic compounds themselves after a one-day period to establish a film. The slopes of the curves were not significantly different for any of the compounds (ca. 2 mv per $\mu\text{a}/\text{cm}^2$). However, the open circuit potential (measured against corroded 347 stainless steel) was -0.08 volt for the NiAl_3 alloy and near -0.37 volt for the others. This phase would thus be expected to be much the most efficient cathode.

The good correlation between the electrochemical measurements of the second-phase compounds and eutectics and resistance to the "accelerating blister" type of attack for alloys containing that second phase provides additional support for the "hydrogen blister" hypothesis of high temperature corrosion mechanism.

Solid Solution Alloying Additives

In a previous report⁽¹⁾ it was shown that the weight gain curves for 1/2, 1, 1½, and 2% nickel in 2S aluminum when corroded in 315°C distilled water had the same slope ($\sim$ corrosion rate) within the experimental error. This suggested that the cathodic corrosion reaction (liberation of hydrogen) was not the rate-controlling step in the corrosion since changing the amount of cathodic area by a factor of the order of 4 did not influence the corrosion rate. Temporarily ignoring other possibilities, attention was focussed on the anodic reaction (oxidation of aluminum).

In the field of gaseous oxidation it is well established that the oxidation rate of many metals is sensitive to relatively small additions of certain other alloying metals. The alloying metals are usually of different ionic charge but of equivalent ionic size to the base metal. It is considered that these metal ions substitute for the base metal ion in the ionic structure of the oxide, modifying its diffusion characteristics.

Tables of ionic size and ionic charge were used to select the alloying additions for aluminum. About 0.1 atomic per cent was the intended amount to be added to a base of 0.9% nickel-aluminum. The results are shown in Table III. Silicon analyses are also shown, since previous work has indicated the need for low silicon content. (A "Laboratory grade" of aluminum crucible had been substituted for the usual high purity aluminum for this series.) The figures shown in the column on corrosion behavior were obtained by testing samples for 3 days and 2 weeks. The difference in metal loss/decimeter² divided by the time (14 days - 3 days = 11 days) for these

two samples was the average corrosion rate for this 11-day period. The 3-day time was chosen because a large part of the initial rapid corrosion is over by this time.

Table III

EFFECT OF ALLOYING ADDITIONS ON THE CORROSION
OF AN ALUMINUM-0.9% NICKEL ALLOY

Additive	Analyzed Concentration of Additive, w/o	Average Corrosion Behavior (Rate in mdd for period 3-14 days)
None	0.009 Si-.004 Fe	2.4 mdd (Surface blistering at 14 days)
Mg	0.074 Mg-.03 Si	Disintegrated
Cr	0.20 Cr-0.09 Si	Disintegrated
Fe	0.19 Fe-.05 Si	2.3
Ti	0.15 Ti-.07 Si	1.6
B	0.03 B-.01 Si	Disintegrated
1100 Aluminum and 0.9% Nickel (M-388 Reference)		2.3

The boron alloy was included to try the effect of small ionic size on the corrosion behavior.

A larger casting of the only promising alloy (i.e., containing Ti) was made, and a careful corrosion test run in 290°C distilled water substantiated the results in Table III. A linear rate of 1.4 mdd was measured for the 1% Ni-0.1% Ti alloy, compared with 3.3 mdd for the reference alloy M-388. The film on the aluminum-nickel-titanium alloy was black and resisted attempts to remove it with the usual electrolytic process. The amount of oxide formed during the initial period was about 4 times greater than for the reference alloy.

It should be pointed out that titanium is noted for its grain-refining properties, and it is possible that improved distribution of the second phase is responsible for the improvement in corrosion rate.

Film Conductivity

Experiments were performed in an effort to measure the electronic conductivity of the oxide film on aluminum alloys and to correlate these measurements with corrosion behavior. The reason for interest in the conductivity is based on the hydrogen-blister corrosion hypothesis. The

16

competing reactions for the cathodic corrosion process are presumed to be proton diffusion inward from the solution to the metal and electronic diffusion outward. The proton diffusion results in hydrogen formation beneath the barrier layer with consequent damage. If the film conductivity is increased, the electronic diffusion should be favored at the expense of the proton diffusion, and the hydrogen damage should be reduced.

The dry measurement of electronic conductivity of aluminum oxide on aluminum is difficult because of the excellent insulating properties of the film. This is especially true of aqueous corrosion films in which the film of interest is covered with a thick porous coating. One method of circumventing the difficulties for a relative measurement is to measure the efficiency of formation of an anodic film. The greater the electronic conductivity, the lower the efficiency of formation, since in this case the electronic conductivity is competing with the anode process.

In the search for a solid solution additive which would increase the electronic conductivity and possibly reduce the corrosion hydrogen damage, alloys containing about 0.15% of various metals in high purity aluminum were made. The castings were solution heat treated for 4 hours at 650°C and water quenched. The samples were then electropolished and anodized in purified 1% ammonium borate using 0.5 ma/cm² (platinum cathode). Sample weights were not taken since the relative formation efficiency was compared with high purity aluminum.

There were slight variations in the slopes of the potential vs. time curves for individual specimens, but the average value from start to sparking was chosen for comparison (Table IV).

Table IV

RELATIVE FILM FORMING EFFICIENCY

Alloy	% of High Purity Value	Sparking Voltage
High Purity	100	460 volts
Al - 0.16% Cu	99	460
Al - 0.17% Zr	99	467
Al - 0.13% Si	91	460
Al - 0.34% Ti	90	470
Al - 0.14% Cr	89	490
Al - 0.17% Mn	68	480

The alloy containing manganese showed the poorest anodizing efficiency, so a new alloy was made of aluminum-0.5% Ni-0.3% Fe-0.15% Mn. A test of about 30 days exposure gave a rate of 3.5 mdd (intercept 1.5 mg/cm^2) for this alloy compared with a rate of 3.3 mdd (intercept 0.9 mg/cm^2) for the reference alloy. The metallurgy of this alloy is not known, so perhaps the test was invalidated. Due to the poor showing of the alloy no further work was attempted.

Corrosion Film Study

A micrograph of the cross section of a sample of M-388 exposed 10 days at 290°C indicated the existence of two distinct layers of corrosion film (Figure 6). The layer adjacent to the metal varied between 10^{-3} and 10^{-5} cm in thickness over the sample and was translucent, showing imbedded metallic specks. Using modified Keller's etch these specks were shown to be the second-phase constituent of the alloy. Over this compact layer an outer coating of rough texture was noted. While the thickness of the compact layer varied by a factor of 100 from place to place, the boundary between this layer and the coarse outer coating was a straight line with essentially no dips or rises.

18280

500X

Figure 6

Corrosion Film of Aluminum Alloy M-388 after
10 Days Exposure at 290°C (Distilled Water)

Similar samples were exposed 7 days and 30 days at 290°C. The main differences noted were that the compact layer became more uniform in thickness and the metal surface became smoother as time progressed. The thickness of the rather uniform 30-day compact layer was approximately the same as the thicker portions of the 7-day compact layer. Again the boundary line between layers was reasonably straight. X-ray diffraction indicated that both α -alumina and boehmite were present. Since the outer friable oxide is boehmite, it was deduced that at least part of the compact layer is an anhydrous alumina.

Another sample of M-388 alloy was corroded for a period of about 330 days in distilled water at 350°C. Unfortunately the test autoclave leaked during a one-week period (at ~ 25 days) so that the sample was exposed to steam. Shortly thereafter the corrosion coating was observed to roughen. The rate of weight gain slowly increased from this time to about 120 days and then became roughly linear (~ 35 milligrams/decimeter²-day).

The corrosion coating on this specimen was extremely heavy (~ 85 mg/cm² total weight gain). A microscopic examination of a cross-section of the specimen showed numerous hollow blisters and fragments of metal within the corrosion coating. The metal interface was very rough. These are characteristics of the penetrating attack noted on most aluminum alloys in high temperature water. In this case the corrosion rate did not accelerate to complete disintegration but remained constant at a high rate.

Essentially all of the oxide coating was translucent like the compact layer in Figure 6. No distinct layers were noted, but in most areas the oxide adjacent to the metal appeared darker in color for a band of about 1/10 the total coating thickness. Proceeding out towards the water interface, the oxide became lighter in color and showed a greater tendency to spall away during metallographic polishing.

Aqueous Corrosion Inhibitors

The hydroxyl ion was suspected of causing the degradation of the compact layer. Two requirements of an inhibitor for blister resistant alloys would therefore be: (1) good adsorption of the innocuous anion on the aluminum oxide compact layer, and (2) a reduction of the hydroxyl ion concentration to increase the relative adsorption of the harmless ion.

A standard text on chromatography⁽⁴⁾ indicated that the hydroxyl ion is most strongly adsorbed on alumina columns followed by the phosphate ion. Therefore phosphoric acid, combining the two requirements, should be an effective inhibitor. Such is the case. A 30-day corrosion test conducted at 290°C with phosphoric acid of pH 3.5 (measured at room temperature)

gave a corrosion rate too low for accurate measurement (less than 0.1 mdd) with the existing techniques. The intercept was also very small. Some microscopic pits were noted on the samples, but they did not grow with increasing time.

Preliminary tests of various phosphates were conducted at 350°C with alloy M-388. Monosodium and trisodium phosphate ($3 \times 10^{-4}M$) solutions were tried first. A test for 4 days duration gave metal losses (after defilming) comparable to distilled water for the monosodium phosphate and 15 times the distilled water rate for trisodium phosphate. The rapid corrosion in the latter solution is attributed to its relatively high pH (10 at room temperature).

Additional tests were performed with solutions containing different cations. Sufficient solute was added to the autoclaves to produce a concentration of about 100 ppm PO_4^{3-} . Solutions were changed regularly. Corrosion rates were obtained by removing duplicate samples at one, two and three weeks. For these samples the methanol-iodine defilming method was used. The results are presented in Table V.

Table V

EFFECT OF PHOSPHATE ADDITIONS
ON M-388 CORROSION AT 350°C

Solute	Corrosion Rate
$Mg_3(PO_4)_2$	5 mdd
Bi PO_4	9
$Th_3(PO_4)_4$	6
Al PO_4	4
Distilled water	16

Some improvement was noted in each case but not of the magnitude noted previously with phosphoric acid. It is presumed that the hydroxyl ion was preferentially adsorbed in the presence of phosphate ion and that the reduction of the hydroxyl ion concentration must be achieved before good inhibition is accomplished.

As a practical note, these substances probably are not well suited for addition to flow systems with heat transfer surfaces. Evidence of thermal deposition of magnesium phosphate was obtained in a test run in a replenished system.

Superheated Steam

Suitable Alloys

The corrosion of aluminum alloys by superheated steam presented an interesting variation of the tests performed in an aqueous environment. Aluminum and most of its alloys typically first form blisters and later disintegrate in both media at high temperatures. An investigation by Groot and Wilson⁽⁵⁾ indicated that M-388 alloy, developed for high temperature water resistance, also had better resistance to superheated steam than various melts of 1100 alloy. This suggested a similarity of corrosion mechanism between water and steam.

At this laboratory testing in superheated steam was started initially as a screening test for the development of an alloy with maximum resistance to disintegrating attack. This medium was chosen instead of water because of the comparative simplicity and availability of the equipment. Conditions of 450°C and 300 psig were chosen to cause severe attack on the reference alloy M-388 in a three-day period. A sample of the reference alloy was included in each test as a check on the severity of the conditions.

A number of copper-based alloys developed by the Research Laboratory of ALCOA were tested with the results shown in Table VI. The two alloys tested for 7 days had looked promising at 3 days and so were returned to test, unfortunately before a weighing was made.

Table VI

CORROSION OF ALCOA EXPERIMENTAL ALLOYS IN SUPERHEATED STEAM⁽¹⁾

ALCOA No.	Time in Test (days)	Wgt. Gain Unit Area (mg/cm ²)	Percentage Composition		
			Cu	Ni	Total Others
173168	7	0.07	3.90	2.21	0.91 (Fe, Si)
173164	3	0.07	5.94	0.01	1.83 (.74% Fe)
173165	3	0.10	6.08	0.01	1.64 (.74% Fe)
173213	3	0.09	10.80	0.28	1.33 (.73% Fe, .31% Mn)
173166	7	0.29	2.97	2.94	7.74 (6.97% Si)
173162	3	0.12	6.03	0.25	1.59 (.76% Fe, .30% Mn)
173163	3	0.17	6.18	0.01	1.60 (.71% Fe, .31% Mn)
173212	3	0.11	7.87	0.28	1.55 (.74% Fe, .31% Mn)
173161	3	0.16	6.10	0.00	1.37 (.75% Fe, .30% Mn)

(1) 450°C - 300 psig.

It was assumed, because of the similarity of the attack to that in water, that the same mechanism of hydrogen blister attack was operating in this medium. Therefore, in order to overcome the relatively severe conditions, a very well-dispersed cathodic second phase would be required. For this reason an alloy near the nickel-aluminum eutectic was prepared. Approximately 0.3% Fe was added to cause precipitation of the eutectic within the grains. 0.2% Ti was added for its grain-refining properties. The resultant alloy was compared with the most resistant of the Alcoa experimental alloys. The results are tabulated (Table VII) and also presented pictorially (Figure 7) to indicate the type of attack experienced under these conditions.

Table VII
CORROSION IN SUPERHEATED STEAM⁽¹⁾

Alloy No.	Time in Test (days)	Weight Gain Unit (mg/cm ²) Area	Appearance
A-203 (Argonne) (5.5% Ni)	7	0.02	Thin film - no blistering.
	14	0.03	
173168 (Alcoa)	7	0.07	Thin film - small blisters. Heavy film - badly blistered.
	14	2.40	

(1) 450°C - 300 psig.

The lower right-hand corner of the ALCOA alloy specimen was severely attacked between 7 and 14 days. The M-388 reference alloy was completely converted to oxide, while the A-203 alloy acquired only a very thin uniform film.

Because of the promising results of the steam tests on Alloy A-203 a larger melt was made. This was made in vacuum furnace. Approximately 1.5 kg of material was chill cast. In rolling this relatively large piece of material, edge cracking, due to work hardening, was a much more serious problem than it had been with the original casting. Hot rolling eliminated the difficulty, but the alloy did not stand up to the test conditions as well as the previously cast material. Samples of the material were microscopically blistered after being exposed for only four days.

19585

1X

Figure 7

Aluminum Alloys After 2 Weeks in Steam
(450°C, 300 psig)

Left: Copper alloy 173168 (ALCOA)
Center: M-388 (1% Nickel in 1100 Aluminum)
Right: A-203 (Eutectic of Aluminum-Nickel)

Samples of each of the rolled specimens were observed micrographically. The cold-rolled alloy A-203 showed a finer dispersion of the second phase than the hot rolled material A-203X, again illustrating the desirability of maximum dispersion for "blister" resistance.

Comparison with Zircaloy-2

Samples of this larger melt (A-203X) were compared with Zircaloy-2 in a superheated steam test at 400°C and 4000 psig. The Zircaloy metal loss was estimated from the weight gain. Duplicate samples of the aluminum alloy were removed at about 15, 45 and 75 days and

defilmed. The comparison is made in Figure 8. At the end of the test the black, adherent Zircaloy film was turning white in spots and beginning to flake. The aluminum alloy film remained black and unchanged throughout the test. From the graph it can be seen that the aluminum alloy suffered no attack after the initial film growth, while the Zircaloy continued to react. This aluminum alloy would appear to be potentially very useful under these corrosion conditions.

Figure 8

Corrosion in Superheated Steam at 400°C - 4000 psig

High Purity Aluminum

A sample of high purity aluminum was included in one of the tests for the purpose of examining the corrosion film formed under these test conditions. After a period of 7 days (450°C - 300 psig) the sample had two small blisters, but had only a very thin corrosion film. It had a weight gain of less than 0.03 mg/cm². A second sample of high purity aluminum was tested in steam at 290°C and 300 psig. After 2 days the sample had been completely converted to oxide.

It is possible that the difference in behavior is associated with the difference in the degree of superheat, or the reduction of the probability of water accumulation in the corrosion product. It is also possible that it is associated with a change in composition of the corrosion product. According to the Al_2O_3 - H_2O phase diagram of Ervin and Osborn,⁽⁶⁾ the equilibrium structure at 450°C is corundum, while at 290°C it is boehmite. The anhydrous oxide might form a more protective corrosion product layer, since it has a more compact structure. An X-ray analysis of the 450°C sample was uninformative since the film was too thin to register. The X-ray pattern confirmed that the corrosion product at 290°C was boehmite.

Alloys containing relatively small amounts of other elements (i.e., 1100 alloy) were attacked more rapidly than the pure metal at 450°C in steam. An explanation may be based on the consideration that these other elements provide a physical or ionic defect structure in the film, permitting diffusion of reactants through the otherwise protective corundum film. Another possibility is that these elements in solid solution tend to produce a non-equilibrium oxide (i.e., boehmite) as a primary corrosion product rather than the resistant corundum.

The superheated steam test program tied in well with the aqueous corrosion program since X-ray evidence indicated that the primary corrosion product in aqueous corrosion at 350°C is alpha alumina. The superheated steam tests provided a method of investigating directly the effect of alloy additions on the resistance and stability of the anhydrous layer.

Several very dilute alloys (Table VIII) were made and tested in steam. Each of these was much less resistant than the high purity metal. It was assumed therefore that a less perfect oxide was formed on these alloys than on the high purity metal.

Table VIII

ALUMINUM ALLOYS

Alloy No.	Analyzed % Composition		
	Ni (w/o)	Ti (w/o)	Zr (w/o)
211	0.0107	-	-
214	-	0.0020	-
215	0.0093	0.0023	-
216	-	-	0.0108

DISCUSSION

Hydrogen Damage Hypothesis

The accumulation of corrosion product hydrogen within 1100 aluminum experiencing "blister" type attack is a significant piece of evidence for this hypothesis. Prior to this measurement it had been difficult to distinguish between this hypothesis and alternative explanations based on the rapid attack of aluminum by alkalinity produced at the cathodic corrosion reaction site:

The "alkalinity" hypothesis does not adequately explain the presence of corrosion hydrogen or the formation of the occasional hollow blisters found in the metal. These experimental observations clearly favor the hydrogen damage hypothesis.

Alloys

The correlation between fine distribution of the cathodic second phase in aluminum alloys and their corrosion resistance to hydrogen damage is excellent. Therefore, in order to achieve the maximum protection from a specific amount of second-phase additive, metallurgical techniques leading to fine dispersions should be employed.

Corrosion Mechanism

It appears that in the absence of "blister" attack, two processes are occurring. One is the formation of fresh compact layer material by oxidation of the aluminum. The other is the transformation of the outer surface of the compact layer into a relatively porous coat. Eventually an equilibrium rate is reached where the rate of growth just equals the rate of degradation. This implies the eventual attainment of a linear corrosion rate. For shorter periods of time the growth mechanism is not well enough understood to predict the rate law. Unfortunately, defilmed sample corrosion measurements made to date are not precise enough to allow determination of the reaction kinetics.

The extent to which hydrogen damage (blister attack) interferes with these processes on a nominally blister resistant alloy is not known. Certainly in the case of the long term M-388 experiment (p. 11) it played an important role.

The impressive reduction in corrosion rate achieved through the use of dilute phosphoric acid is assumed to operate by providing an innocuous competitive reaction for the normal hydration of the protective anhydrous aluminum oxide by water. It is not known at this time whether the phosphate is chemically adsorbed or forms another distinct compound.

Considerably more experimentation is required to assess the practical limitations of phosphoric acid or a similar inhibitor.

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