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CORROSION RESISTANT ALUMINUM ABOVE 200°C

by

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July 15, 1955

Metallurgy Division

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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ABSTRACT

At elevated temperatures most aluminum alloys in water suffer severe penetrating attack, resulting in relatively rapid destruction of the material. This penetrating attack is explained in terms of mechanical damage as a result of diffusion of corrosion-product hydrogen into the metal.

It is prevented by adding to the water cations which are reduced on the aluminum to form deposits of low hydrogen overvoltage metals. It is also prevented in untreated water by using alloys of aluminum with the same metals. Alloying metals observed to be beneficial are nickel, copper, cobalt, iron, platinum, with nickel probably the most effective.

There has been developed an alloy, containing approximately 1% nickel in 2S aluminum, which appears to be completely safe against the penetrating attack. It is easy to make and is workable. It probably can be used, from a corrosion-resistant point of view, wherever its normal reaction rate with water or a solution is tolerable. Penetration rates in static distilled water are approximately 1, 1-1/2, 3 and 9 mils per year at 250°, 290°, 315° and 350°C, respectively. They are higher where there is significant flow velocity of water past metal.

INTRODUCTION

Commercially pure (2S) aluminum is the time-proven metal of choice for fuel element cladding in water-cooled reactors operated below 100°C. As the temperature is raised, aqueous corrosion rate determinations have shown it to be suitably corrosion resistant up to about 200°C.⁽¹⁾ Several other standard commercial alloys have shown essentially the same behavior.⁽²⁾

Above this temperature, depending on the time in test, a transition in corrosion behavior takes place. The aluminum oxide monohydrate film formed is no longer smooth and uniform. The metal develops blisters of

mixed oxide and metal at an accelerating rate, with penetration into the metal, and it is rapidly rendered useless. The time on test prior to the inception of this damaging attack has been shown to vary with temperature, with alloy composition,⁽²⁾ and with mechanical and thermal condition.^(3,4)

The worst possible aluminum alloy from this point of view is the high purity metal. It is most susceptible to the damaging attack at the lowest temperatures;⁽⁵⁾ it also is sensitive to mechanical condition.⁽⁶⁾ The lack of reproducibility in the amount of corrosion observed in the longer tests run by Strom, Litz and Boyer⁽⁷⁾ is probably explainable in these terms.

If aluminum is to compete with the more expensive materials of construction for use in water at temperatures between 200° and 350°C, this catastrophic corrosion must be eliminated either by suitable inhibitors in the water or by alloying the aluminum. This report describes the investigation which has accomplished both of these objectives.

EXPERIMENTAL

Sample size and shape varied with the material available, but in most cases the specimens were approximately $3/4$ in. x 3 in. x $3/32$ in. A $3/32$ in. hole was drilled near one end. A fresh surface was prepared by wet grinding to 400 grit with Durite abrasive paper on a metallographic polishing wheel. Samples were then measured, degreased in freshly distilled methyl alcohol, and weighed on an analytical balance.

Corrosion tests were performed in two kinds of apparatus. In the first, stainless steel autoclaves (175 ml capacity) were filled approximately $2/3$ full of the test solution. The solution was degassed by boiling in the autoclave just before sealing. The test temperature was maintained by an electrically heated, forced draft oven. Each time the autoclave was opened for inspection the solution was changed. Samples were suspended by an aluminum wire hook and insulated from the stainless steel by a mica washer in the gas phase.

The other apparatus consisted of four high pressure pumps, heaters, autoclaves and pressure relief valves, arranged as shown in Figure 1. With this arrangement it was possible to pump up to 30 ml/minute of replenishing solution at the desired temperature through the high pressure autoclave chambers. The pumping rate was usually chosen to be sufficient to avoid significant change in solution composition, the normal rate being 10 ml/minute. Two of the autoclaves held 470 ml; the other two held 1340 ml. The samples were suspended on racks made of synthetic sapphire rod to insulate the specimens electrically from the stainless steel autoclave.

Figure 1.

Schematic Drawing of Continuous Replenishing System for Corrosion Testing at Elevated Temperature

The solutions were made up using doubly distilled water and Reagent Grade chemicals where required. Quality control tests of incoming and effluent solutions were made with a pH meter, resistivity bridge, and where required, a spectrophotometer for colorimetric analyses. Solutions were deaerated before use and stored in Pyrex carboys under a slight pressure of tank oxygen or tank helium.

Where corrosion rates are reported, samples were periodically removed from the test and weighed. The corrosion product was assumed to be $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The value of x was determined for various exposure times by weighing and removing the corrosion product from some samples at each

period. (The value of x is not indicative of the actual composition, since in its calculation the assumption was made that no corrosion product was lost from the samples.) This value of x was used to compute the average metal loss from the average weight gain of all the samples on test. The rates reported are the slopes of the linear portions of the curves of metal loss per unit area as a function of time on test. The unit used is milligrams per square decimeter per day (mdd).

The corrosion product was removed by an electrical treatment. Twenty milliamperes (AC) per cm^2 was passed between the sample and a platinum electrode with a saturated solution of boric acid (specially purified) at room temperature as the electrolyte. After brushing to remove the loose oxide, the sample was cathodically treated for 2 hours in 4 w/o CrO_3 and 10 w/o H_3PO_4 solution at 80°C . Clean sample runs indicated a loss of 0.06 mg/cm^2 for the over-all process.

In some cases, notably where blistering of the samples occurred, this stripping procedure did not quantitatively remove the corrosion product. Under these circumstances only a rate of weight gain and qualitative description of the samples were obtained.

Aluminum alloys were made in several different ways. Vacuum melting and casting were performed in a suitable furnace using magnesia, alundum, and pure graphite crucibles. Difficulties with ceramic crucible cracking ultimately resulted in the exclusive use of pure graphite crucibles. A minimum vacuum of 10^{-4} mm of mercury was maintained.

Air-cast alloys were made in a small resistance-heated furnace, using commercial plumbago and alundum crucibles. Subsequent chemical analyses of the melts indicated considerable silicon pickup from the plumbago, so its use was discontinued.

An Ajax Electrothermic Induction furnace (6 KW) was used exclusively after it became available, since the inductive stirring action rapidly dissolved the alloying elements (air casting).

Silicon was added as 12% master alloy. Iron was added as an 8.5% master alloy. Other elements were added directly and stirred into the melt at temperatures up to 950°C .

All alloys were cold-rolled to approximately one-eighth inch thickness before testing, since it was observed that some as-cast 2S aluminum appeared good without special alloying. Thickness before rolling was about 0.5 in.

DATA

When 2S aluminum corrodes in pure water at temperatures above about 200°C it first develops a smooth adherent coating of α - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. As the time or temperature of testing is increased, the surface of the oxide begins to roughen. Under the microscope the roughening is found to be due to numerous tiny protuberances growing out of the metal surface. On further testing, these protuberances grow into mounds that are clearly visible to the unaided eye. If the mounds are probed they are usually found to contain a mixture of oxide and metal. They form first, and most profusely, at imperfections in the metal lattice, such as at grain boundaries and stringers. The exposure required to cause them to become visible and their rate of growth are dependent on the metal surface condition. Fine-grained material and a less severely distorted structure usually are most resistant to the attack. Relatively thin cold-rolled sheet is bad, although it can be made worse by a grain coarsening anneal, which is believed to result in grain boundary thickening. Extruded bars are generally good. It is guessed that the improvement effected by Lavigne⁽⁶⁾ by careful rolling was due to surface grain orientation and compacting.

The time required for this type of attack to begin varies from a few weeks at 250°C to a few hours at 315°C for annealed sheet stock. The corrosion rate (slope of the metal loss vs time curve) begins to rise rapidly at an accelerating rate as this "blister" type of attack commences. Correspondingly, penetration of the metal occurs at the most active locations.

In the preliminary work⁽¹⁾ it became obvious that until this transition in behavior could be eliminated, it was futile to attempt to measure meaningful corrosion rates. Accordingly the few pieces of information pertaining to this transition were carefully examined.

It was found that electrically coupling 2S aluminum to stainless steel or zirconium would slow the onset of "blister" corrosion and greatly extend its lifetime in 315°C water. These other metals were shown by electrical measurements in a special autoclave (Figure 2) to be cathodic (as expected) to the aluminum at 315°C, so that this is truly a case of "anodic protection." It was first speculated that the anodic protection was due to a continuous repairing of the protective film on the aluminum or to lowered pH at the anodic areas.

Efforts were made to supply an oxidizing agent at lowered pH in the solution to perform these functions. The chemical chosen was potassium dichromate, a well known corrosion inhibitor at low temperatures, in pH 3.5 sulfuric acid. Another common low temperature inhibitor, soluble silica, was also tried (added as Na_2SiO_3). Initial tests in small autoclaves indicated that the autoclaves themselves caused rapid depletion of the inhibitors in the test solutions so the tests were run in the replenishing systems.

Figure 2

Autoclave used for High Temperature Electrical Measurements
During Corrosion

The results of these experiments are shown in Table I. No suppression of blister attack was noted for any combination of pH and oxidizing agent. It will be noted, however, that lowering the pH made a striking reduction in the pre-blistering corrosion rate at 250° as compared with distilled water. Adding the oxidizing agent to the acid actually increased the pre-blistering rate.

Table I

EFFECT OF SOME SOLUTION ADDITIVES ON THE ACCELERATING
BLISTER CORROSION OF 2S ALUMINUM SHEET

Temperature, °C	Gas	Solution	Time when first signs of surface roughening noted, days
250	O ₂	Distilled H ₂ O	16-20 (5.5 mdd)*
250	O ₂	pH 3.5 (H ₂ SO ₄)	16-19 (1.3 mdd)
250	O ₂	pH 3.5 (H ₂ SO ₄) and 50 ppm K ₂ Cr ₂ O ₇	11-17 (2 mdd)
250	He	pH 3.5 (H ₂ SO ₄) and 20 ppm SiO ₂	16-19 (4 mdd)
275	O ₂	Distilled H ₂ O	0-3
	He		0-3
275	O ₂	pH 3.5 (H ₂ SO ₄)	0-3
275	O ₂	pH 3.5 (H ₂ SO ₄) and 50 ppm K ₂ Cr ₂ O ₇	0-4
275	He	pH 3.5 (H ₂ SO ₄) and 20 ppm SiO ₂	0-2

* Numbers in parenthesis indicate linear corrosion rates before blistering was noted. After blisters started wide discrepancies were noted between individual samples.

Originally it was planned to test other solution additives, but another possible explanation of the improvement observed in coupling 2S aluminum to stainless steel was formulated. It was now assumed that the important effect in anodic protection was to move the cathodic corrosion reaction

(liberation of hydrogen) away from the aluminum. Since this greatly slowed the blister attack, the cathodic reaction was considered responsible for the most damaging type of attack on aluminum.

Elaboration of this basic idea with the aid of other clues and comparison of this attack with effects found for other metals, such as the embrittlement of steels, led to the following working hypothesis: Protons from the solution diffuse through the aluminum oxide barrier layer and are reduced to atomic hydrogen at the metal-oxide interface. The hydrogen atoms may combine to form molecules or diffuse into the metal. Apparently neither the atoms nor molecules can readily diffuse back out through the oxide film. It is assumed that at elevated temperatures a significant fraction diffuses into the metal and collects at rifts or cavities to form non-diffusing molecular hydrogen. Pressure builds up within these rifts, cracking or bulging the soft metal into blisters. When these blisters rupture, water is admitted to the fresh metal, producing more hydrogen at a point considerably below the normal metal surface. This process thus may become self-accelerating as is noted experimentally.

Several methods of attack on the corrosion problem were indicated by the working hypothesis:

1. Prepare aluminum without voids or dislocations and the atomic hydrogen will, first, have a low diffusion rate and, second, will not be able to accumulate and form blisters.
2. Provide cathodes, preferably of low hydrogen overvoltage, for the corrosion reaction, liberating hydrogen in a condition (molecular) or at a point where it is not possible for it to diffuse into the aluminum metal.
3. Supply an additive to the aluminum metal which makes it impervious to the diffusion of atomic hydrogen.

Vacuum Casting

One method of securing metal with a minimum of voids is by vacuum melting and casting. This technique was therefore tried with 2S aluminum. Samples of this vacuum-cast material proved to be resistant to blister attack in water at 300°C for as long as tested (30 days). A comparison of the surface appearance of ordinary 2S sheet and the vacuum-cast material after exposure is shown in Figures 3 and 4.

Various methods of working and annealing the as-cast material were used. A summary of the results is shown in Table II. In each case the resultant samples corroded as fast or faster than the parent 2S stock before vacuum casting. From these data it was concluded that the act of working

15,438

20X

Figure 3

Surface of 2S Aluminum Sample After 66 Hours in
Distilled Water at 300°C

15,439

20X

Figure 4

Surface of Vacuum-Cast 2S Aluminum After
132 Hours in Distilled Water at 300°C

as-cast metal provides rifts or dislocations which are not annealed out even after 4-1/2 hours at 550°C and that these rifts provide sites for hydrogen diffusion and blister formation.

Table II

EFFECT OF WORKING ON THE CORROSION RESISTANCE*
OF VACUUM-CAST 2S ALUMINUM

1	Vacuum Cast (As-Cast)	Good Smooth Film - No Blisters
2	As-Cast and Annealed in Air 1 Hr at 350°C	Good Smooth Film - No Blisters
3	As-Cast; Then 1x1x1 cm Cube Compressed to 50 Tons	Badly Blistered; Approximately 40% Metal Converted to Oxide
4	Same Treatment as 3; Then Annealed in Air 1 Hr at 350°C	Completely Converted to Oxide
5	Same Treatment as 3; Then Vacuum-Annealed 4-1/2 Hr at 550°C	Approximately 95% of Metal Converted to Oxide
6	As-Cast; Then Compressed to 25 Tons at 350°C	Approximately 30% of Metal Converted to Oxide

* Corrosion tested 69 hours at 300°C in distilled water.

High purity aluminum (99.99+%) was also vacuum melted and cast. No significant improvement was noted since both the vacuum-cast material and the control were reduced to oxide in 24 hours at 290°C. Since high purity aluminum suffers much more rapid penetrating deterioration than 2S, the prevention of blister type attack would be more difficult. It is not possible to estimate whether the result indicates that the impurities in 2S aluminum can provide a blocking action to the diffusion of hydrogen.

The lack of a practical method of retaining the "as-cast" corrosion resistance while fabricating 2S aluminum diverted attention to the other suggested methods of blister control.

Electrical Protection

Two simple experiments were devised to investigate the possibilities of the second or "remote cathodes" method. In the first experiment an electric current was passed between a 2S sample and a stainless steel electrode, using the autoclave of Figure 2. The experiment was repeated with reverse polarity and also with no current flow. The test was conducted in distilled water at 325°C with a current of $20 \mu\text{a}/\text{cm}^2$ for 4 hours. The weight of aluminum corresponding to the electricity passed is a trivial part of the weight change.

As shown in Figure 5, the results were in accord with the proposed mechanism. The blistering was essentially eliminated (except for a few small ones - maximum height 0.003 in.) on the anodic sample. In this case the bulk of the cathodic reaction (hydrogen liberation) was assumed to take place at the stainless steel electrode. With the current reversed, several strings of large protuberances, about 0.060 in. maximum height, and isolated blisters of about the same dimensions were formed. The control (no current) sample had five large blisters and thus was intermediate between the anodic and cathodic specimens. In each case blistering occurred in the steam phase (where no current was flowing) to approximately the same extent.

The same type of experiment was performed with high purity aluminum at 250°C. The current was increased to approximately $1.2 \text{ ma}/\text{cm}^2$ (computed on the basis of submerged area) and the time decreased to 2 hours to compensate for the much greater corroding tendency of the high purity aluminum. The results are pictured in Figure 6. The voluminous white coating on the upper part of both samples is the corrosion product formed in the steam phase in the test autoclave. The anodic sample below the water line showed some small blisters and otherwise was very slightly corroded, while the cathodic sample corroded slightly more rapidly in the water phase than in the steam phase (as determined qualitatively by cross sectioning the sample and comparing the amount of metal left). The anodic protection was especially striking in this experiment.

Solution Protection

The second simple experiment to investigate the possibilities of the "remote cathodes" method used reducible metal ions added to the test solution. Fifty parts per million solutions of several cations were adjusted to the same pH using sulfuric acid or potassium hydroxide. Freshly prepared samples of 2S aluminum sheet were corroded for 48 hours in the de-gassed solutions at 300°C. The results are shown in Table III.

The appearance of the samples correlated with the weight change data. The specimens with small weight changes had smooth, adherent films over most of the surface with isolated microscopic dendritic growths of a

Figure 5

Effect of Electric Current on the "Blister" Corrosion
of 2S Aluminum

($20 \mu\text{a}/\text{cm}^2$ for 4 hours at 325°C)

(White material is voluminous coating of
aluminum oxide)

Figure 6

Anodic Protection of High Purity Aluminum
(2 hours at 250°C - current density 1.2 ma/cm²)

material which glistened in a metallic fashion under the microscope. The appearance of these growths formed in nickel sulfate solution is shown in Figure 7. No blistering was evident on the samples in Co^{++} , Cd^{++} , and Ni^{++} solutions. This protection from blistering was not a short time effect. A sample was tested in 50 ppm Co^{++} solution at pH 3.0 for 24 days at 300°C . At the end of the test period the only blistering in evidence was around a support hole, drilled after the sample had been annealed. The total weight gain for the period was 2.2 mg/cm^2 of which about half was acquired in the first four days.

Table III

EFFECT OF REDUCIBLE CATIONS ON THE CORROSION OF
2S ALUMINUM AT 300°C

Solution*	Weight gain, mg/cm^2 in 48-hour test	Comments
50 ppm Co^{++} pH 4	0.74	Blue Film - No Blisters
pH 7	0.66	
50 ppm Cd^{++} pH 4	0.60	Lt. Blue - No Blisters
pH 7	0.78	
50 ppm Ni^{++} pH 4	0.76	No Blisters; Lt. Grey
pH 7	0.93	
50 ppm Sn^{++} pH 4	0.91	Few Microscopic Blisters Ppt. formed
pH 7	No Test	
50 ppm Cu^{++} pH 4	0.95	Few Microscopic Blisters Ppt. formed
pH 7	No Test	
50 ppm Pb^{++} pH 4	2.68	Dark Grey; Few Blisters
pH 7	1.12	
pH 4 H_2SO_4	3.1	Control Spec. Both badly blistered.
H_3PO_4	4.3	

* Solutions were made up using the sulfate of the required cation except for $\text{Pb}(\text{NO}_3)_2$.

15,446

250X

Figure 7

Dendritic Nickel Deposited on 2S Aluminum
from NiSO_4 Solution (50 ppm Ni^{++})

Because of the possible use in reactors, testing was started using nickel salts rather than those of cobalt or cadmium. Samples of 2S aluminum sheet were used and the temperature was held at 275°C. The combination of samples and temperature was such that with distilled water blistering became noticeable in less than one week. The data are presented in Table IV.

The results were poor with 1 and 5 ppm nickel (nickel sulfate) without pH control. Depletion of the test solution was very serious at the flow rate of 10 ml/min and blister corrosion was not much retarded. As shown in Table IV, increasing the nickel concentration to 20 ppm greatly increased the resistance to blister attack. At the same time the depletion problem was emphasized. The nickel lost from the test solution went into the formation of a slime which deposited on the samples and the autoclave walls. The exact nature of the deposit was unknown. X-ray analysis gave inconclusive results since the clear but complex pattern did not correspond to known nickel compounds. Chemical analysis indicated a basic nickel sulfate with some aluminum. Unfortunately this deposit also formed in the small diameter preheater tube causing experimental shutdowns.

In an effort to reduce this precipitation other nickel salts were tried. The nitrate and phosphate produced similar deposits. In addition, the nitrate did not provide protection against blister attack. The greater oxidizing power of the nitrate ion as compared with the sulfate was assumed to be responsible for this difference, since reduction of nickel ion apparently did not occur in the former case.

Another approach to the deposition problem was to reduce the pH of the solution to a point where the solubility product of the basic salt was not exceeded. After a few attempts a combination of five ppm Ni^{++} (as NiSO_4) at a pH of 3.5 was chosen. As indicated in Table IV, this solution is not depleted by its passage through the autoclave and no deposit results, while the amount of nickel has proven adequate to prevent any blistering in a 70-day corrosion test. The specimens were excellent in appearance, with the 400-grit grinding marks plainly visible through the thin oxide film on the surface.

Several other tests in which nickel sulfate solution was pumped for a period each day followed by continuous flow of distilled water were failures. In each case the blister attack was held off only for a very short time.

Plating Protection

Another method of protection depending on providing "remote" corrosion cathodes was the plating of 2S aluminum with films of nickel. The "Kanigen" dip process was used. The original sample was a piece of plated

Table IV

EFFECT OF NICKEL SOLUTION ADDITIVES ON THE AQUEOUS
CORROSION OF 2S ALUMINUM AT 275°C

Type of Additive	Refreshing Solution	Comments
NiSO ₄ without pH control	1 ppm Ni ⁺⁺ (Helium)	Blisters noted after 4-8 day period. Effluent solution contained 1/2 ppm Ni ⁺⁺ at 10 cc/min.
	5 ppm Ni ⁺⁺ (Oxygen)	Blisters noted after 2-6 day period. Effluent solution 2 ppm Ni at 10 cc/min. Deposition of slime noted.
	20 ppm Ni ⁺⁺ (Helium)	Small blisters only at suspension hole. Test run 120 days. Erratic weight gains and losses after 20 days. Estimated corrosion rates between 12 and 22 mdd, depending on time in test. Deposition of slime very pronounced. Effluent ~ 13 ppm Ni ⁺⁺ at 10 cc/min.
NiSO ₄ with pH control	20 ppm Ni ⁺⁺ pH 3.0 (H ₂ SO ₄) (Helium)	No blisters noted. No change between in- fluent and effluent nickel concentration. No slime deposited. Test stopped after 16 days due to excessive autoclave corro- sion. Corrosion rate ~ 3 mdd.
	10 ppm Ni ⁺⁺ pH 3.7 (H ₂ SO ₄) (Helium)	Small blisters noted only at suspension holes on 2 long term samples. Effluent ~ 7 ppm Ni ⁺⁺ at 10 cc/min. Some slime deposited. Rate ~ 3 mdd between 25 and 58 days.
	5 ppm Ni ⁺⁺ pH 3.5 (H ₂ SO ₄) (Helium)	No blisters noted. No change between influent and effluent nickel concentra- tion. Samples excellent condition after 70 day test. No slime deposited. Corro- sion rate 0.83 mdd.
Other Nickel Salts	20 ppm Ni ⁺⁺ as Ni(NO ₃) ₂ (Helium)	Blistering noted after 0-3 day period. Samples covered with hard green precipi- tate. Test stopped after 6 days.
	20 ppm Ni ⁺⁺ as Ni ₃ (PO ₄) ₂ pH 3.0 (H ₂ SO ₄) (Helium)	Blistering noted only at suspension holes. Samples and autoclave covered with hard green precipitate. Effluent solution ~ 9 ppm Ni. Test run 44 days. No corro- sion rate obtained since corrosion product could not be satisfactorily removed.
Nickel Sulfate "Shots"	Distilled Water 20 hours/day 50 ppm Ni ⁺⁺ 4 hours/day (Oxygen)	General blistering noted after 3-7 day period. Slime deposited.
	Distilled Water 23.8 hours/day *** Conc. NiSO ₄ (To make 50 ppm Ni ⁺⁺ in auto- clave) 0.2 hour/day	General blistering noted after 0-3 day period.
	50 ppm Ni ⁺⁺ 1st hour at temperature; then distilled water thereafter.	General blistering noted after 0-3 day period.

2S tubing. It was deliberately bent to crack the nickel plate and ground free of the plating on the 1/32 in. cross section to see if a complete or impervious plate was required. A 25-day corrosion test at 300°C produced no blisters in the exposed 2S aluminum and indicated that protection could be achieved without complete coverage. Further testing of plated 2S aluminum was done in a high temperature dynamic loop by the Reactor Engineering Division.

2S aluminum samples, 3/4 in. x 3 in., were plated by the General American Transportation Company Research Laboratory with two thicknesses of nickel: 0.0003-0.0004 in. and a thinner flash coat of about 0.0001 in. The adhesion of the plate on the flash samples was poor. Some plate was inadvertently removed with a piece of Scotch tape.

One set of samples (5 of the 0.0003 in. and 5 of the flash coat) were run for 18 days in distilled water at 274°C. Flow rate was 15-20 ft/sec. All the samples were covered with a thin, dark, uniform coat. No pits or other signs of unusual attack were noted on the heavier plates. The flash-coated samples had small shallow pits on one end. No corrosion rates could be deduced from the weight changes, which were small but erratic. In general, the 0.0003 in. Ni samples lost less than 1 mg/cm² and the flash-coated specimens gained less than 1 mg/cm². This test was terminated to start a test at 315°C.

Fresh samples of the same plating thicknesses were used for the experiment at 315°C. One flash-coated specimen failed by disintegration within 5.7 days. At 41 days the rest of the flash-coat samples were removed. One other had failed and all showed signs of impending failure.

The 0.0003 in. plated samples performed better. One failed between 41 and 52 days. The other four were tested for a total of 109 days without failure. As the flash samples were removed, they were replaced with the 0.0003 in. Ni samples from the previous 274°C test. One of these replacements developed a large blister after 12 days and was removed.

This protection is not peculiar to "Kanigen" nickel plating, as electroplated samples (somewhat thicker plates) prepared by the Reactor Engineering Division have proved equally satisfactory.

Alloys

One of the most interesting phases of this program was the development of blister-resistant alloys of aluminum for use at temperatures up to at least 350°C in distilled water. The same basic hydrogen penetration theory was used to select an alloying agent which would provide a second phase, of low hydrogen overvoltage, to act as local corrosion cathodes for the rest of the aluminum grain. Nickel was the obvious choice.

In a preliminary experiment, specimens of 2S containing 0.01, 0.1 and 0.3 w/o Ni were cast, cold worked, and exposed to distilled water at 290°C. Even the 0.01% sample showed some improvement over typical 2S performance. The 0.3% Ni sample developed only two clusters of blisters at the corners after 17 days; the rest of the surface was in good condition. Ordinary 2S would be largely converted to oxide by this exposure.

Based on the preliminary castings, numerous small melts were made at Argonne and experimental alloys were obtained from commercial sources such as Kaiser, Aluminum Company of America and the Sonken-Galamba Company. The data in Figure 8 show that there was very little effect on corrosion rate caused by varying the nickel content, while other variables were held as constant as possible. This particular series of alloys was prepared by the Kaiser Aluminum Company. The weight gain curves are not reliable measurements of the actual corrosion rate, due to uncertainties as to the composition of the oxide and the amount of oxide lost during the test, but they served for a preliminary estimate when coupled with the known metal loss (obtained by stripping) at the end of the exposure time. Estimated corrosion rates obtained by stripping samples of many castings after various exposure periods are 6 mdd (3 mils/yr) at 315°C and 18 mdd (9 mils/yr) at 350°C.

More accurate corrosion rate determinations in the continuously refreshed autoclave systems have been completed for lower temperatures. The results are presented in Table V. The rates are significantly below those estimated for 2S aluminum by extrapolation of lower temperature data. In reference (1), for example, a short time rate of 24 mdd was obtained for 2S aluminum in distilled water at 275°C.

The slight adverse effect of lower pH on the corrosion rate at 290°C was unexpected. Reducing the pH by this amount for 2S aluminum markedly reduced the corrosion rate at 200°C.

In distilled water the effect of flow rate (of water past samples) is to increase the corrosion rate of the alloy. In a test performed by C. R. Breden in the Reactor Engineering Division at 315°C and 20 ft/sec flow rate, the corrosion rate appeared to be above 20 mdd, an increase of more than three-fold over the static rate. There was some question as to the "corrosion rate" in the dynamic test, since the curve of corrosion versus time did not form a good straight line. Erosive effects on sample leading edges were noted in this test.

In all corrosion tests, the alloy samples were typically covered with a smooth, dark grey corrosion coating. A network of darker lines was visible on the surface. This same type of network was obtained by etching the metal with sodium hydroxide solution, as shown in Figure 9. It was presumed that the dark lines were nickel-rich grain boundaries which acted as low resistance local corrosion cathodes.

Figure 8

Effect of Varying Nickel Content on the Corrosion
of 2S Aluminum - Nickel Alloys

16,385

100X

Figure 9

Structure of 2S Aluminum - 0.3% Ni Alloy

Table V

CORROSION RATES OF 2S ALUMINUM/NICKEL ALLOY

Alloy	Test Condition	Corrosion rate after initial period	Estimated Intercept
0.5% Ni in 2S (A108, A124)	Distilled Water; 290°C	3 mdd ^a (79 days) ^b	1.0 mg/cm ²
0.5% Ni in 2S (A124)	pH 4.6 (H ₂ SO ₄); 290°C	4 mdd (54 days)	0.3 mg/cm ²
0.5% Ni in 2S (A124)	Distilled Water; 250°C	2 mdd (52 days)	0.5 mg/cm ²

^amdd = milligrams per square decimeter per day.

^bnumber of days the test was run.

Melting and Casting Techniques - The vacuum-cast Argonne series and the Kaiser series were generally superior in surface appearance to the series cast by the Sonken-Galamba Company. The latter gave indications of porosity when rolled by the Argonne Fabrications Group. The 1-1/2% alloy was particularly poor on exposure to 315°C water. It rapidly developed numerous small blisters which continued to grow with further corrosion testing. Since the chemical analyses of this alloy and the 1-1/2% nickel alloys were not markedly different, it was felt that poor casting technique was responsible for the relatively poor corrosion resistance. To test this hypothesis a small remelt of the Sonken Galamba sheet was made here, using chlorine sparging and chill casting. The remelted sample was then corrosion tested. Figure 10 illustrates the improvement effected by remelting. The slight flaking of oxide on the remelted sample was not unusual for this alloy and did not result from excessive corrosion. The edge view of the original sample shows a section through one of the larger blisters. The black areas in the blister are cavities. No such voids were noted in the corroded specimen of the remelted alloy.

In an effort to test the effect of various melting and casting techniques, a series of 1% nickel alloys were made using the same 2S aluminum stock. Vacuum melting and casting, moist air sparging for one minute prior to chill casting, a dry chlorine sparge and also a dry argon sparge were tried. Corrosion tests were performed on this series at 350°C for 6.3 days in an effort to accelerate the corrosion and accentuate any differences. There

Figure 10

Comparison of As-Received and Remelted 2S Aluminum -
1-1/2% Nickel Alloy after Corrosion Testing 15 days at 315°C

was essentially no difference in weight change data from one to the other, as shown in Table VI. The vacuum-melted and cast specimen was the only one not showing at least one microscopic blister. The moist air-sparged sample was covered with a network of dark lines, much heavier and longer than usually noted with the nickel-aluminum alloys, but it did not influence the corrosion behavior.

The tiny blisters noted on these and other alloys could be the result of porosity in the casting. Radiographs of castings prepared in a similar fashion showed considerable microporosity down the center of the 1-1/2 in. x 5 in. x 1/2 in. billet, as well as some much larger holes. The porosity of castings was sharply reduced by using a 1 in. x 1-1/2 in. x 2 in. mold, and subsequent melts have been radiographed to eliminate faulty castings.

Table VI

EFFECT OF MELT SPARGING ON CORROSION OF 1% NICKEL-2S
ALUMINUM ALLOY IN DISTILLED WATER AT 350°C

Treatment	Metal Corroded, mg/cm ² *
Vacuum Cast	2.37
	2.54
Dry Chlorine Sparge	2.34
	2.41
Dry Argon Sparge	2.16
	2.46
Moist Air Sparge	2.28
	2.68

* 6.3 days exposure

Heat Treatment - A few simple tests were made to determine the sensitivity of the 1% Ni in 2S aluminum alloy to heat treatment. The results are presented in Table VII.

The data indicate that the annealed condition is the poorest corrosion-wise but only by a small amount. This finding is concordant with results previously described in the case of vacuum cast 2S aluminum.

Table VII

EFFECT OF HEAT TREATMENT ON THE CORROSION OF
2S ALUMINUM - 1% NICKEL ALLOY

Heat Treatment	Metal lost after 13 days at 315°C in distilled water
Annealed 2 hr at 650°F	3.1 mg/cm ² 3.3
Held 30 min at 950°F; then water quenched	2.9
Held 30 min at 950°F; Water quench - then aged 10 hr at 345°F	2.9 2.8

Welding - One per cent nickel in 2S aluminum was chosen for experiments to determine the weldability of this type alloy and to determine the effect of corrosion on the welds.

Specimens 1/8 in. thick were butt welded (heliarc) using aluminum-nickel alloy filler rod. Standard tensile specimens were then machined. The results of the tensile tests showed no weakness at the weld (Table VIII).

Table VIII

TENSILE TESTING* OF WELDED 2S ALUMINUM - 1% NICKEL ALLOY

Before Corrosion	After 11.7 days in water at 360°C
17,700 psi	16,600 psi
18,200 psi	17,000 psi

*In each case the break occurred at least 1/2 in. from the weld line.

X-ray and metallographic examination of the welds showed them to be sound with a smooth transition in microstructure through the welded area. The welder compared the ease of welding favorably with 2S aluminum.

Some of the same material was rolled to 0.063 in. and spot welded. Two spots were tensile tested in the annealed condition and two were tensile tested after a 6-day corrosion test at 350°C. There was no difference in tensile strength and no unusual corrosion effects were noted.

Crevice Effects - In some instances, most seriously at lower temperatures, increased corrosion has been observed in the crevice formed by close juxtaposition of aluminum samples. This effect has occurred even in water of high purity. The effect has been significantly worse where aluminum has been coupled to cathodic materials such as graphite or stainless steel. To evaluate this type of corrosion for nickel-2S aluminum alloy at elevated temperatures two simple experiments were performed.

In the first experiment, 1/8 in. thick plates were set in close fitting slots milled in two plates of the same material. A 1% nickel in 2S aluminum alloy was used. The units were then bound together with aluminum-nickel alloy wire or with stainless steel bolts. The exploded assembly is shown in Figure 11.

After 5.7 days in distilled water at 315°C the units were disassembled. Oxide formation caused sticking, but no serious trouble was encountered in separating the units. The samples were examined and reassembled for a further corrosion test to a total of 21 days.

The unit held together with wire gave no indication of crevice effects. The bolted unit produced a series of shallow pits which did not noticeably grow after the 5.7-day examination. The pits were located where the bottom of the milled slots and the sharp corners of the pieces held in the slot were forced together by the bolt tension. The bolts were pulled up enough to slightly bend the slotted member. Since the pitting only occurred on this specimen, the distortion was assumed to be the cause.

Since in use an alloy such as this might be coupled galvanically to stainless steel, the second experiment was devised to evaluate the sort of damage which might result. One per cent Ni in 2S aluminum was used with Type 347 stainless steel.

Four Type 347 stainless steel bolts and washers were tightened in holes drilled in a 1/8 in. sheet of the alloy. Each bolt was removed after a different period of corrosion in distilled water at 315°C. The longest time was 25 days. No large effects were noted. A small trough was formed (0.08 mm deep by about the same width) in the aluminum alloy at the circumference of the stainless steel washer. There was no pitting noted under the washer or in the bolt hole.

17,336

Figure 11

Crevice Corrosion Assemblies

Commercial Impurities - A series of alloys was made using a 0.66% nickel high purity aluminum master alloy to which various additions of iron and silicon were made. The results of one-day corrosion tests at 350°C in distilled water are shown in Figure 12. The added silicon was shown to be disastrous in the absence of iron. No deliberate addition of silicon was made to the iron alloy samples. The small amount present was presumed to have come from the ceramic crucible. The samples that survived one day were replaced for a total of 6.3 days at 350°C. The metal loss (determined after corrosion product removal) is shown in Table IX. It is clearly indicated that in order for a nickel alloy of this concentration to be "good," the presence of a small amount of iron is required.

Table IX

EFFECT OF IRON ADDITIONS ON THE CORROSION RESISTANCE
OF 0.66% NICKEL-ALUMINUM ALLOY

Corroded 6.3 days in distilled water at 350°C

Alloy No.	Composition, %		Metal Corroded, mg/cm ²
	Iron	Silicon	
126	0.02	0.05	Disintegrated
127	0.21	0.06	3.1*
128	0.58	0.06	3.1*
131	0.95	0.07	2.2*

* Corrected for an estimated 0.2 mg/cm² of film remaining after stripping.

A series of alloys was made to determine the minimum iron content necessary to prevent the disintegration at 350° of a 1/2% nickel alloy. As shown in Table X, 0.3% iron was required.

Mixed iron and silicon additions were also made to a 1/2% nickel alloy. The results are given in the last two rows of Table X.

Silicon, even in mixed additions appears to be detrimental, but it can be accommodated by additional iron or nickel in the alloy. For example, a 4% Ni-1% Si alloy was corrosion resistant to 350°C water when tested for

1%

0.5%

0.3%

MASTER
ALLOY

0.2%

0.6%

1%

Silicon Additions

Iron Additions

Figure 12

Effect of Iron and Silicon Additions on the Corrosion Resistance of
0.66% Ni-Al Alloy. Tested One Day in 350°C Distilled Water.

17,247 (1X)

1 day. The metallic interactions which perhaps explain these results have not yet received serious attention, although work has been started in an effort to identify the phases present in these alloys.

Table X

EFFECT OF IRON AND SILICON ADDITIONS ON THE CORROSION
RESISTANCE OF A 0.5% NICKEL-ALUMINUM ALLOY IN WATER
AT 350°C

Alloy No.	Composition, %		Comments
	Iron	Silicon	
165	0	0.04	Disintegrated (1 day)
164	0.10	0.01	Disintegrated (1 day)
167	0.22	0.01	Areas of surface blistering (1 day)
168	0.31	0.02	No blisters - good condition (1 day)
143	0.3*	0.3*	Some blistering after 6.3 days metal loss - 5.1 mg/cm ² .
150	1.11	0.33	Good condition after 7.7 days metal loss - 2.9 mg/cm ² .

* Nominal - no analysis.

Other Alloying Constituents - Alloys with nominally 2% of the alloying metal in high purity aluminum were air cast. Metals used were lead, tin, bismuth, cadmium, cobalt, iron, copper and platinum. Only the last four gave fair results on corrosion test at 315°C. The rest disintegrated. Cobalt and copper alloys were superior to the platinum and iron alloys, but all were inferior to a vacuum-cast 1% nickel alloy. In view of the effect of small amounts of iron on nickel-aluminum alloy corrosion, more work must be done to determine the value of these elements as alloying constituents.

DISCUSSION

Validity of the Hydrogen Penetration Theory

The explanation of the damage to aluminum alloys which occurs as a result of exposure to water at elevated temperature is part of a general theory of the role of hydrogen in aqueous corrosion. It will be presented more completely in a subsequent publication. Sufficient direct proof of the diffusion of hydrogen into aluminum during such corrosion reactions is not yet available. Determination of the hydrogen content of corroded metal has been hampered by experimental difficulties, but at present it is possible to say that there is definite increase in the amount of hydrogen in 2S aluminum samples as a result of corrosion in hot water. The sample shown in Figure 10 offers graphic demonstration that severe disturbance of metal shape does occur from causes other than the formation of solid corrosion products. Many samples showing finer blistering from corrosion have been examined. It has been observed that most of the "blisters" have been filled with a mixture of metal and oxide (corrosion product). However, it has usually been possible to find occasional hollow blisters, and it is believed that this is direct observation of the damage occurring to the metal before the attack has proceeded far enough to produce corrosion product within the blister. The theory fits well with the observed effects of metal texture and distortion. Those things which open parts of the structure to allow more rapid hydrogen diffusion increase the rate of the damaging attack.

The best argument for the theory is that it satisfactorily explains many unusual corrosion phenomena for aluminum and for other metals. For example, it is predicted that anodic protection can be applied wherever the corrosion rate is influenced by any kind of damage occurring as a result of the penetration of hydrogen beneath the oxide barrier film. Since this is in direct opposition to the simpler version of the electrochemical corrosion mechanism, the few cases in which it had been observed had been considered anomalies. The clearness with which the theory describes such effects is impressive. It is also impressive that upon its formulation, it became possible to predict successful methods of protection of aluminum against the rapid disintegration which has been normal for most commercial alloys.

Alloy Casting Technique

It has not been possible to determine that a particular casting technique is outstandingly better than all others tried for nickel-containing alloys. Variations in crucible materials and in the compositions of alloys produced have tended to obscure relatively small differences. It does seem to have been demonstrated that it is necessary to produce material which is

homogeneous on a macro scale and which is metallurgically sound. The second phase present appears to do its best job when it is quite fine in particle size and nearly randomly distributed.

There have been consistent (but not clear) indications that vacuum castings are better than small experimental castings made in air, with or without sparging. For example, in the series of castings of the same apparent composition, but using sparging by different gases (Table VI), only the vacuum casting (no sparge) formed no blisters (all metal rolled before corrosion testing).

Larger melts have appeared to provide better alloys than smaller ones, as evidenced by the relatively good quality of the castings produced by Kaiser Aluminum Company and the Aluminum Company of America, compared to some of the smaller ones made here.

Alloy Composition

No chemical composition for a "best" alloy can be given. It is readily and reproducibly possible to prevent the accelerating blister attack of typical 2S aluminum by the addition of approximately 1/2% nickel or more. Such alloys appear also to be close to an optimum composition from the point of view of maintaining minimum amounts of alloying constituents. This might be desirable for reactor use where minimum neutron absorption is desired. In such alloys it appears that the sum of iron and nickel should not be less than 0.8%, and that the nickel content should be more than 0.5%. If the silicon in the 2S aluminum stock runs higher than normal, it would perhaps be necessary to add more nickel to counteract its deleterious effect. It is not known whether the copper present in normal 2S aluminum has been of significant benefit in allowing the production of satisfactory alloys. It has been demonstrated, however, that satisfactory alloys can be made from high purity aluminum with the addition of nickel and iron, so that copper is not essential.

In order to minimize the total neutron absorption of a good alloy, it would be desirable to try various small additions of all of the elements which have been shown to be beneficial as alloying constituents. It is intended that some of this type of alloy development will be done in the future, although there is little incentive to provide the absolute minimum in neutron absorption so long as that which exists in an alloy such as 2S aluminum plus 1% nickel is satisfactorily low for typical uses.

There is a considerable incentive, however, to develop alloys with lower corrosion rates than those obtained to date. It is anticipated that a considerable fraction of that part of the effort of this group which is devoted to the development of aluminum alloys will be spent attempting to obtain sizable reduction in corrosion rate.

Another objective which might be considered is the matter of alloy strength at elevated temperature. Alloys of the type which have been discussed in this report do not possess significant improvement in this characteristic over commercially pure aluminum. Alloys considerably higher in copper or iron would appear to offer more promise in meeting this objective, with the hope that they might also prevent the rapid deterioration of the metal by corrosion.

Applicability

Prior to the work herein reported it was clear that aluminum alloys could not be used in water above the temperature at which the penetrating attack occurred, regardless of its corrosion rate before the inception of such attack. There is now an alloy available which eliminates such damaging attack, and it is considered to be usable at whatever conditions of temperature, pH and flow rate its corrosion rate is tolerable. Alternatively, commercial alloys of the 2S type can be used in a solution which will prevent the penetrating attack. This latter approach probably requires more compromise on the part of the designer than does the use of special alloys. In particular, it is probably not feasible to use stainless steel in the same solution which makes 2S aluminum safe. Increased corrosion and the appearance of corrosion product in the solution is observed for stainless steel in solutions such as that containing 5 ppm nickel ion in sulfuric acid solution (pH 3.5).

It is to be noted that in most applications it is probably undesirable to use the alloys so far developed without any pH control. As was pointed out in the earlier publication⁽¹⁾ there is a pH of minimum corrosion rate for 2S aluminum, on both sides of which higher rates of attack are observed. At elevated temperatures this optimum pH is considerably more acid than neutral, appearing to be of the order of 3 from 200° to 300°C (to be published). Consequently, the use of aluminum in neutral water at elevated temperatures is in a sense equivalent to the use of aluminum in alkaline environments at ordinary temperatures. Under these conditions there is a definite effect of solution flow rate on the corrosion rate of the metal. The effect becomes greater as the pH is increased and as the temperature is increased. By analogy with the corrosion behavior of alloys such as 2S, it is hence anticipated that smaller increases in alloy corrosion rate should be induced by solution flow at lower pH. Preliminary data on this point seem to verify the opinion, but information is not yet sufficient to justify such a conclusion. Consequently it is felt that a slightly acid environment is desirable. Increase in pH above neutral should definitely be avoided.

It would similarly be predicted by analogy with nickel-free alloys that corrosion rates in static tests would be lower in acid environment. This does not seem to be true, judging by the single corrosion rate determinations at pH 4.5 and 6.7 at 290°C.

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