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CORROSION OF ALUMINUM AND ITS ALLOYS  
IN SUPERHEATED STEAM

by

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## CORROSION OF ALUMINUM AND ITS ALLOYS IN SUPERHEATED STEAM

by

J. E. Draley, W. E. Ruther, and S. Greenberg

### ABSTRACT

The corrosion behavior of pure aluminum and some of its alloys in superheated steam was found to depend markedly on the method of starting the corrosion test. Pure aluminum samples survived only in tests that were brought to temperature and pressure very rapidly. Resistant Al-Ni-Fe alloys performed well only if a relatively slow starting procedure was used, suffering extensive blistering or complete disintegration in a test started rapidly.

Over the range of temperature and pressure investigated (400-540°C; 150-600 psig) with optimum starting conditions both pure aluminum and resistant Al-Ni-Fe alloy samples quickly formed a very protective oxide film. Interference colors were noted for exposures of several weeks. Samples surviving a 260-day test (at 540°C and 600 psig) had less than 1-mg/cm<sup>2</sup> weight gain.

Nonresistant alloys disintegrated in short corrosion exposures. A penetrating attack, initiated in only a few spots, rapidly destroyed the samples.

The effects of composition, dispersion of second-phase compounds, hydrogen porosity, and pretreatments were investigated for a resistant alloy (5.6% Ni-0.3% Fe-0.1% Ti)\* in 540°C, 600 psig steam. It was concluded that porosity produced by corrosion product hydrogen was a major factor in the survival of samples. A mechanism for the rapid penetrating attack has been proposed as based on observations made during the study of hydrogen porosity.

Pretreatment of resistant alloy samples in dry air (540°C) or in high-temperature water (350°C) greatly reduced the amount of porosity produced by corrosion in superheated steam.

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\*Compositions given in weight per cent.

## INTRODUCTION

Aluminum alloys have proven to be suitable fuel cladding materials for water-cooled reactors operating over a wide temperature range. A corrosion-resistant aluminum alloy would offer the same advantages of low cost and low neutron capture in cladding the nuclear fuel of a steam superheated reactor. Even if such an application were not feasible due to the poor mechanical properties of aluminum near its melting temperature, the development of a corrosion-resistant alloy could provide information concerning the mechanism of aluminum corrosion. The alloy might also prove to be suited for handling steam in non-nuclear applications.

Corrosion behavior of some aluminum alloys in superheated steam at various temperatures and pressures has been reported in the literature.<sup>(1-8)</sup> When consideration of the data supplied by these references is made, the corrosion behavior of resistant alloys can be summarized in the following fashion.

At relatively low temperatures (up to 370°C) and with the vapor only slightly superheated, the general appearance and overall corrosion is roughly that obtained in water at the same temperature. The corrosion by steam tends to be more aggressive and accentuates the corrosion of alloys of marginal resistance. The corrosion coatings are relatively heavy after a few days exposure ( $10^3$ - $10^4$   $\mu\text{g}/\text{cm}^2$ ) and are multilayered as in the case of corrosion in water.

As the temperature (400-540°C) and the degree of superheat of the steam are increased, resistant alloys acquire a thin temper film ( $5$ - $50$   $\mu\text{g}/\text{cm}^2$ ) which grows only slowly with time. The nonresistant alloys fail rapidly by a penetrating corrosion attack. This type of attack usually starts at one or more spots on the sample and rapidly spreads to consume the entire specimen. A serious lack of reproducibility in corrosion results has been noted, particularly for the higher temperatures (500-540°C). The variables contributing to this phenomenon have been of primary interest during this investigation.

Preliminary tests had indicated that some of our alloys had excellent resistance to superheated steam, so an evaluation program of these alloys was undertaken. Reactor designers at ANL suggested that a temperature of 540°C and a pressure of 600 psig would provide data of particular interest to them. Accordingly, the bulk of the testing was performed at these conditions.



## EXPERIMENTAL

The corrosion tests were performed in a refreshed autoclave system. As shown in Fig. 1, double-distilled water (of specific resistivity  $1.1$  to  $1.6 \times 10^6$  ohm-cm) was first passed through a boiler to remove gases. It was then pumped at  $5$  ml/min through a preheater into the autoclave. Thermocouples attached to the preheater at several points monitored the input steam temperature. The electrical input to the preheater sections was adjusted to bring the steam to the temperature of the test before it entered the autoclave.

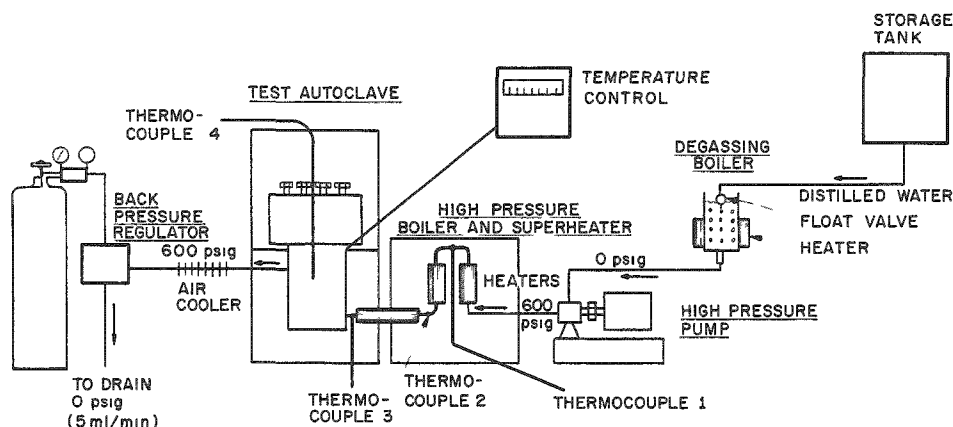


Fig. 1. Schematic Drawing of Superheated Steam Testing Equipment

The test chamber was a 3-in. ID x 12-in. long, stainless steel autoclave. A Flexitallic asbestos-stainless steel gasket was used. Fel-Pro copper base thread lubricant permitted rapid and easy disassembly with the unit still at test temperature. The pressure was controlled by a Grove back-pressure regulator.

Samples were supported inside the autoclave on a perforated stainless steel plate, or suspended on a Nichrome wire or an artificial sapphire rod.

Two types of experimental procedure were investigated. In the first method, the autoclave was preheated, the samples inserted, and the closure completed. A vacuum pump, or in some cases a water aspirator, was attached to the system. Fresh water was allowed to enter the preheater where it flashed to steam. This was pulled through the system to purge the air. This operation was continued 10-15 min, after which the aspirator was valved off and the pump started. Due to the cooling effect of the low-pressure steam flowing during the degassing step, the input steam temperature was low initially, usually about  $100^{\circ}\text{C}$  below the operating temperature. It usually required several hours to reach temperature and pressure equilibrium. This procedure will subsequently be referred to as a "slow" start.

In the second procedure, the system was operated without samples to bring it to temperature equilibrium. The autoclave was rapidly opened and the samples added. A vacuum line was attached while the closure was being completed (about 1 min). With minimum delay the vacuum was valved off and the pump started. Samples in the autoclave reached operating temperature within 5-7 min and operating pressure within 7-9 min of inserting the samples. This procedure will be called a "fast" start to distinguish it from the previous method.

In either case, the samples were removed hot from the test autoclave by venting the steam and immediately opening the autoclave. The specimens were then permitted to come to temperature and moisture equilibrium within a room maintained at  $24 \pm \frac{1}{2}^{\circ}\text{C}$  and  $40 \pm \frac{1}{2}\%$  relative humidity. Buoyancy corrections were made after weighing on a Mettler Microbalance. The specimens were then returned to the interrupted test.

Oxidation in dry air was performed in a small tube furnace. A Vycor tube, one inch in diameter and sixteen inches longer than the furnace, was used as a container. Fresh anhydrous magnesium perchlorate was placed in the cool portion of the tube outside the furnace to remove water vapor. One end of the Vycor tube was sealed, the other was allowed to "breathe" through a drying tube also filled with magnesium perchlorate. The furnace was regulated by a Brown Pyrovane controller. The temperature of the samples was measured with an iron-constantan thermocouple.

Hydrogen analyses were performed after vacuum extraction at  $525\text{-}550^{\circ}\text{C}$ . The pressure of the extracted gas was measured in a known volume. The collected gas was allowed to escape through a heated palladium thimble at the conclusion of the test. In the reported analyses there was no measurable residual pressure, indicating that the collected gas was hydrogen. The samples were prepared for analysis by etching with a dilute  $\text{HNO}_3\text{-HF}$  mixture.

Most of the alloys used were prepared in our laboratory by melting 99.99% aluminum and stirring in the alloying constituents at  $900^{\circ}\text{C}$ . Initially, the melts were made in a high-purity aluminum crucible in a muffle furnace. They were sparged with dry argon gas and poured into a small water-cooled mold. Later alloys were prepared in a reactor-grade graphite crucible in an induction-heated vacuum furnace. The vacuum melts were bottom poured into a water-cooled mold with a heated graphite "hot top." Typically, a casting of about 200 gm was made.

The intermetallic compounds  $\text{NiAl}_3$  and  $\text{FeNiAl}$ , were prepared in a similar fashion, except at  $1200^{\circ}\text{C}$ . X-ray analysis indicated approximately equal amounts of  $\text{NiAl}_3$  and  $\text{Ni}_2\text{Al}_3$  in the first, and only  $\text{FeNiAl}$ , in the second.

The 5.6% Ni-0.3% Fe-0.1% Ti alloy<sup>(1,2)</sup> studied extensively was subject to porosity, and the castings occasionally required cropping to remove the porous metal. The alloys were fabricated by hot or cold rolling into a sheet 0.050 to 0.125 in. thick. One casting of the above composition was obtained from the Kaiser Aluminum Company in the form of 0.125-in. sheet. This was designated K203.

Zone-refined aluminum approaching 99.9999% purity was obtained from United Minerals and Chemical Corp. for another series of experiments. The major impurities were 0.5 ppm Cu and 0.5 ppm Fe.

The specimens were typically wet ground on a metallographic grinding wheel to 240 grit (Durite). Some samples were electropolished in a 9:1 acetic-perchloric acid mixture (by volume). Before weighing, the specimens were measured and degreased in freshly distilled methanol.

## DATA AND RESULTS

### Test Variables

Starting Procedure: Although pure aluminum has extremely poor resistance to distilled water at elevated temperature, our group previously reported<sup>(3)</sup> only slight attack in steam at 450°C and 300 psig in an earlier apparatus. A piece of pure aluminum was therefore included in the series of tests (in our new apparatus) at temperatures from 400°C to 540°C and at pressures from 150 psig to 600 psig. In each case, the aluminum was completely converted to oxide in a brief exposure period. The slow starting procedure was suspected and another test was run using the fast-start method with most severe operating conditions.

In this test the pure aluminum demonstrated good resistance and a very low corrosion rate, as shown in Fig. 2. The dry air results are included for purposes of orientation.

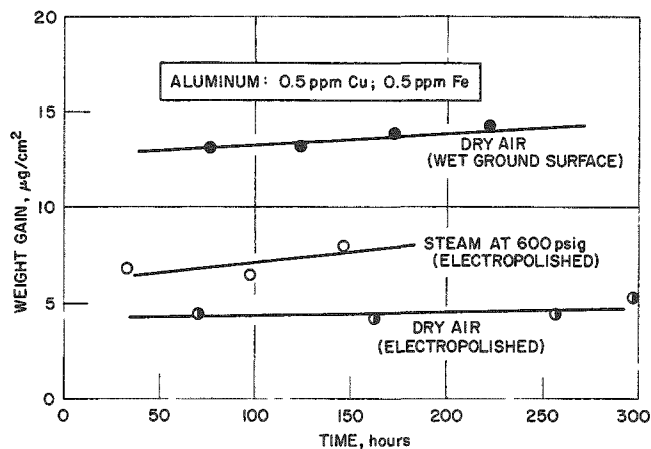


Fig. 2. Corrosion of Zone-Refined Aluminum at 540°C.

The comparison between the wet ground and the electropolished specimen indicates a surface roughness factor of about 3. This is higher than usually obtained from ground specimens and probably reflects differences in the nature of the pretest oxide film.

The electropolished specimens in both dry air and steam were still mirror bright at the conclusion of the tests. Lines on the surface, probably

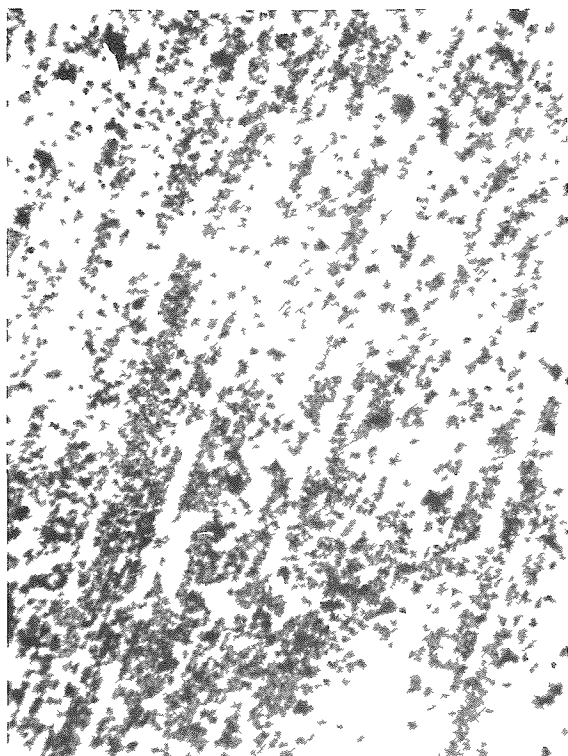
grain boundaries, developed during both the steam and dry air tests. The samples exposed to steam had numerous small, hollow surface blisters which did not grow with time. These were missing in the dry air test. Not all the blisters were located on the surface lines, but those on the lines tended to be slightly larger than average.

The effect of surface preparation on survival of pure aluminum was investigated for the fast-start procedure. Samples of the pure aluminum were prepared by electropolishing, by dry grinding and by wet grinding. One of the electropolished specimens was pre-corroded in boiling distilled water for 45 min to partially hydrate the film. Another was scratched with a needle to break up a possible protective film left by the electropolish. All survived a 26-hr test at 540°C and 600 psi. The ground specimens had more blisters than the electropolished. The test was repeated with a new set of specimens with the same results.

One more exploratory test was made with pure aluminum. A portion of an electropolished specimen that had been exposed for 479 hr in dry air at 540°C was subsequently corroded in 540°C, 600 psig steam for 94 hr. Only a freshly sheared edge showed blisters. The faces of the specimen remained smooth and mirror bright.

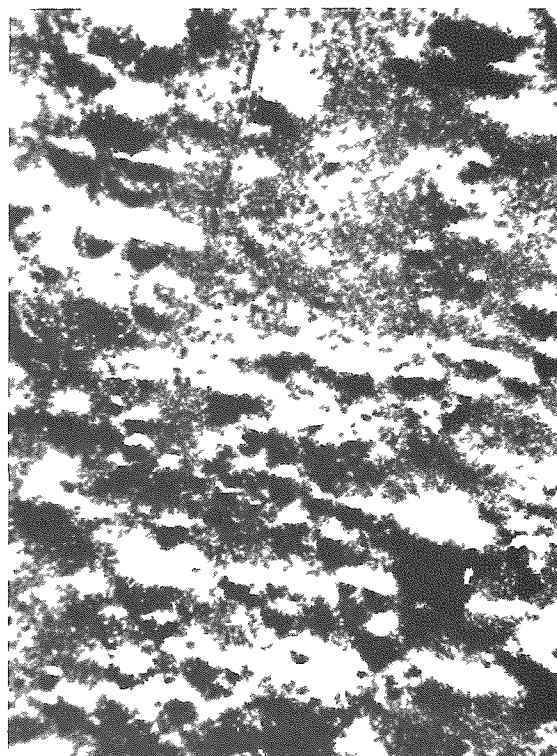
Since the lack of aqueous corrosion resistance makes pure aluminum unsuitable for practical use, the effects of testing variables were investigated for a promising steam alloy (5.6% Ni-0.3% Fe-0.1% Ti) previously described.<sup>(3,5)</sup> At 540°C and 600 psig two tests were made with several specimens from different castings. The fast starting procedure used successfully with pure aluminum was employed. All samples of the alloy disintegrated within 48 hr. Pure aluminum specimens in the same tests were intact.

This was an unexpected result since a number of previous tests had been performed with this alloy at the same conditions, but using the slow starting procedure. The alloy had shown good resistance in these tests. A shorter test exposure using the fast start, was used to investigate further the differences between the fast-start and the slow-start procedures. In this test, samples from adjacent portions of a sheet of the 5.6% Ni-0.3% Fe-0.1% Ti alloy were used. One of the specimens was pre-corroded for two hours in distilled water at 350°C to exaggerate a slow start. The other was tested as ground. The water-pre-corroded sample was identical in appearance before and after the 18-hr test at 540°C and 600 psig. No blisters were noted. The texture shown in Fig. 3 is that of the sample after testing in steam and water. A portion of the oxide film had spalled off. This was not due to the steam test, but was typical of this alloy for water corrosion at 350°C. The surfaces of the "as ground" specimens (Fig. 4) were covered with blisters but the samples were intact.



110303 64X  
5.6% Ni, 0.3% Fe, 0.1% Ti

Fig. 3. Surface of an Aluminum Alloy after 2 Hours in 350°C Water and Then 18 Hours in Steam at 540°C and 600 psig



110304 64X  
5.6% Ni, 0.3% Fe, 0.1% Ti

Fig. 4. Surface of the Same Alloy Exposed Directly to 18 Hours in Steam at 540°C and 600 psig.

A sample of this same composition alloy was corroded for 402 hr in steam at 540°C and 600 psi, using the slow starting procedure. It then survived without visible change two successive fast start test periods.

Temperature and Pressure: The effect of temperature on the corrosion rate of an alloy of the same composition (5.6% Ni 0.3% Fe 0.1% Ti) was investigated with the slow starting procedure. The results obtained at 600 psig pressure are shown in Fig. 5.

Each point in the figure represents the average for three samples. Agreement among individual samples improved as the temperature increased. At the low temperature, the individual samples had parallel corrosion curves displaced by as much as  $\pm 10\%$  from the average. At the high temperature, the individual displacement was a maximum of  $\pm 3\%$  from the average.

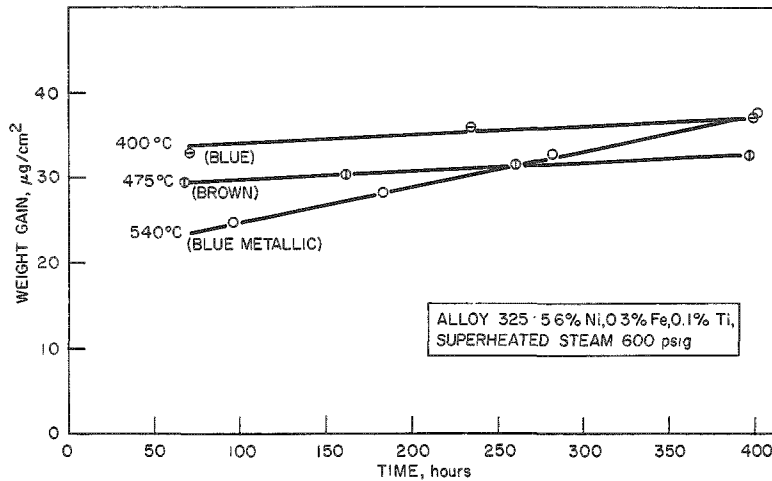


Fig. 5. Effect of Temperature on the Corrosion of an Aluminum Alloy in Superheated Steam

The corrosion rate increased significantly as the temperature rose from 475°C to 540°C. The extrapolated intercept of the linear portion of the curve decreased with temperature. The samples typically acquired a distinct color tint, as indicated in Fig. 5, due to the formation of a uniform, thin oxide film. The tint changed only slightly during the tests.

All of the samples had hollow blisters varying in size from those visible only under a microscope at ~100X to some with a diameter of ~2 mm depending on the particular casting used in the test. These will be discussed in detail in a later section.

The same alloy composition was used to evaluate crudely the pressure effect on behavior. The results are shown in Fig. 6.

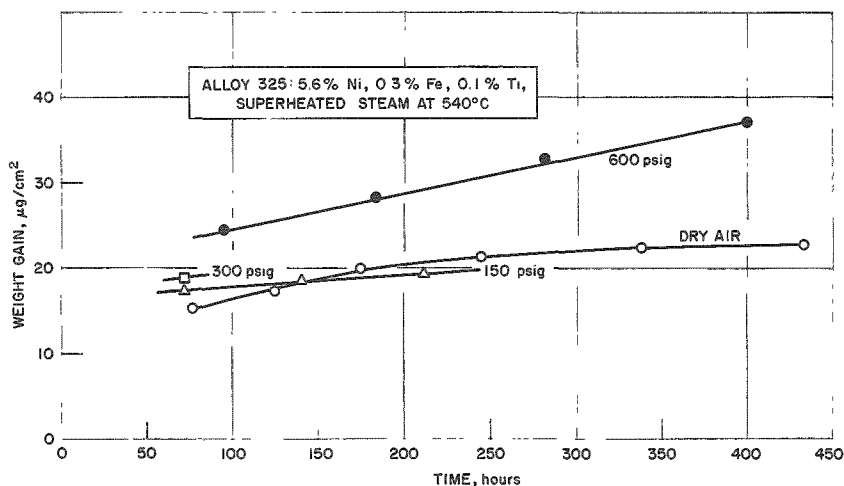


Fig. 6. Effect of Steam Pressure on the Corrosion of an Aluminum Alloy

The dry air experiment was included to allow comparison of the amount of corrosion in steam with that observed in a more familiar environment. The corrosion rate and the extrapolated intercept both increase with pressure, although rather slowly in the range studied. Note that corrosion rate in 150 psig steam was very similar to that in dry air (1 atmos) for this resistant alloy.

### Alloy Evaluation

Unfortunately, the significance of differences in starting technique on survival was not realized at the start of the program. A considerable amount of testing was performed with the slow-start technique. Undoubtedly, some of the test results were clouded by uncertainties in the exact method of starting the experiment. However, a number of tests were performed in which simultaneous corrosion of samples differing in one or more respects was accomplished. Observations of tests of this sort were used to build a qualitative picture of some of the other important variables in corrosion resistance.

As described by Wilkins and Wanklyn,<sup>(6,7)</sup> the percentage of samples of a particular alloy that are intact after a test is rarely 0% or 100%, but is usually somewhere between these limits. In the case of superheated steam at 540°C and 600 psi, a defect in the sample that initiates the penetrating attack leads to the complete destruction of the specimen. At 540°C a number of specimens were partially destroyed during short tests. Upon resumption of the tests, all continued to corrode to destruction.

Factors in the metal leading to initiation of a defect might include alloy composition, trace impurities, distribution and composition of the intermetallic phases, hydrogen content, and other forms of porosity. An effort has been made to investigate these variables qualitatively. Since our early success<sup>(3)</sup> was with a 5.6% Ni-0.3% Fe-0.1% Ti alloy in steam at 450°C and 300 psi, this particular composition was chosen for the investigation.

Composition: Attempts to reproduce the good corrosion resistance of the original casting were not uniformly successful. Many of the subsequent castings rapidly failed in tests which the original casting (A203) survived. In addition, the surface of the A203 was rarely blistered, whereas the subsequent castings were extensively blistered even though the sample was intact.

Several of the alloys were analyzed for the major constituents as shown in Table I.

Table I

## CHEMICAL ANALYSES OF TYPE 203 ALLOYS

Alloy	Ni, w/o	Fe, w/o	Ti, w/o	% Survival at 540°C, 600 psi Steam
A203	5.58	0.32	0.06	Nearly 100%
A203-E	5.69	0.25	0.08	Intermediate
A203-V	5.49	0.31	0.03	
K203	5.42	0.34	0.15	0

Since the results did not indicate the reason for the wide spread in corrosion results, spectrographic analyses of the best and the worst castings were obtained. The results were as follows:

<u>Element</u>	<u>A203 (Good)</u>	<u>K203 (Poor)</u>
Co	0.08%	0.01%
Cr	0.03	0.01
Mn	0.05	0.01
Ti	0.07	0.1

Except for Ni and Fe, all other elements were below the limits of detection.

The survey showed that A203 contained more Co, Cr, and Mn than the K203. These were probably impurities in the nickel and iron used to make the alloy. A portion of K203 was remelted and recast with these additional alloying additions. This casting proved to be as poor as the K203 without these additions.

Recent experience with corrosion in water at 350<sup>o</sup>(9) had indicated a sharp dependence of corrosion behavior on silicon content in the 0.01% region. Silicon analyses confirmed that the K203 casting had 0.06% whereas the A203 had 0.002% silicon. Another alloy of the A203 composition was made with the addition of 0.06% silicon. This had poorer resistance to short exposures (~3 days) at 540°C and 600 psig than had the original casting, but some samples survived while none of the K203 alloy did.

Copper found in the K203 was also suspected as being deleterious. At the same time, it was noted that survival seemed to be higher among samples resting on a perforated plate as compared with suspended samples. Since the supported samples had a hole drilled in them, this operation was also suspected.

Three alloys and three methods of support were tried in the next experiment. Due to space limitations, only duplicate specimens for each



condition could be simultaneously tested. An effort was made to select alternate samples cut from a single narrow strip to insure as much uniformity in the samples as possible. The results of a 69-hr test at 540°C and 600 psig are shown in Table II.

Table II

## SURVIVAL OF SAMPLES\* AT 540°C AND 600 PSIG

Alloy Composition, w/o	No Hole - Lying on Perforated Plate	Drilled Hole - Lying on Perforated Plate	Drilled Hole - Suspended on 0.040-in. Nichrome Wire
5.7 Ni, 0.3 Fe, 0.1 Ti	2	2	2
5.7 Ni, 0.3 Fe, 0.1 Ti, 0.06 Si	1	1	0
5.7 Ni, 0.3 Fe, 0.1 Ti, 0.01 Cu	2	0	0

\*Two samples were tested in each category.

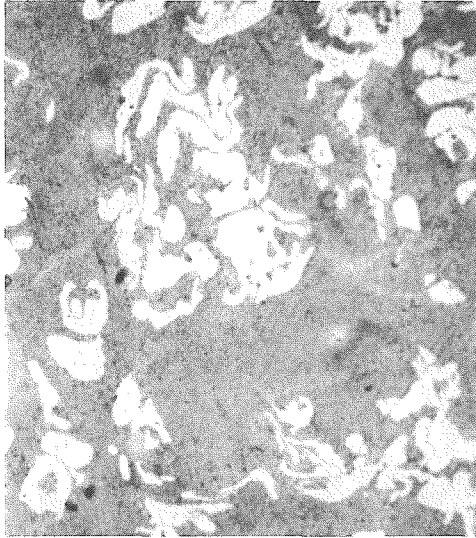
The holes in the suspended samples were elongated slightly in the survivors of this category. Apparently the weight of the specimen was sufficient to distort the holes as the alloy lost mechanical strength. The presence of the copper or silicon was enough to produce marginal corrosion resistance.

Vacuum melting of the poorly resistant Kaiser 203 produced rather heavy deposits on the Vycor walls of the furnace. This indicated that trace quantities of relatively volatile metals, such as zinc and magnesium, were also present in this particular alloy.

Metallography: Previous work<sup>(3,4)</sup> had indicated the need for a uniformly fine distribution of the second-phase compounds for maximum resistance to water corrosion. We have interpreted this in terms of minimizing the dimension of the open areas of the aluminum matrix in a cross section of the alloy. Using this criterion, the microstructure of the complex A203 alloy was studied by preparing intermediate alloys.

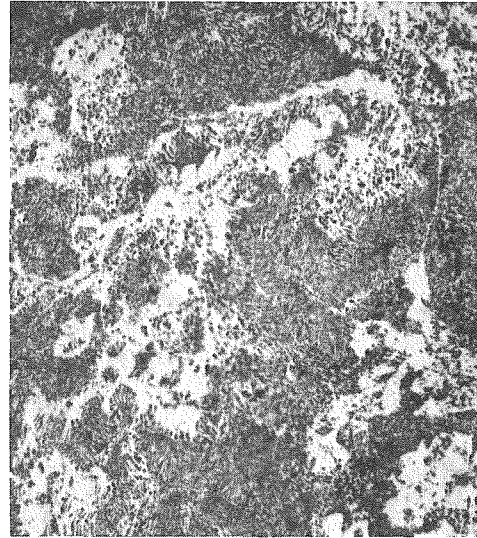
The nickel, in the form of the NiAl<sub>3</sub> phase, provided the bulk of the second phase. A nickel-aluminum binary alloy produced a microstructure in which rather large areas were denuded of second phase (see Fig. 7). The addition of the titanium modified the precipitation and reduced the size of the open areas of aluminum matrix (see Fig. 8).

Addition of the iron to the nickel alloy reduced the size of the open matrix areas by the precipitation of rod-like chunks of NiFeAl<sub>9</sub> (see Fig. 9).



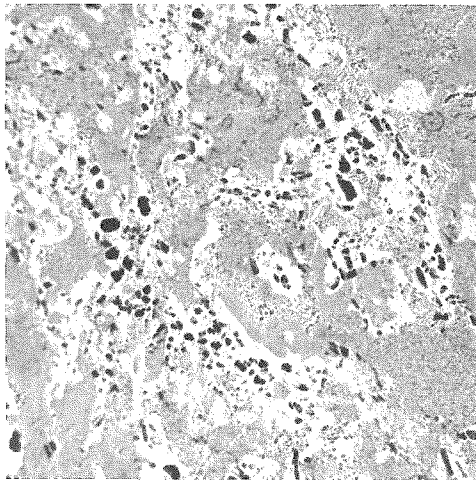
110156 64X

Fig. 7. Microstructure of an Aluminum-5.6% Ni Alloy



110153 64X

Fig. 8. Microstructure of an Aluminum-5.6% Ni-0.1% Ti Alloy



110150 64X

Fig. 9. Microstructure of an Aluminum-5.6% Ni-0.3% Fe Alloy

Finally, a remelt of the same composition as the original casting indicated the difficulty of reproducing the uniformly fine distribution of the original casting. This was particularly noticeable in the size of the  $\text{FeNiAl}_9$  precipitate (see Fig. 10).

The microstructure of the consistently worst casting of this nominal composition is also shown (K203). It also showed the presence of large chunks, presumably of the  $\text{FeNiAl}_9$  compound, but in actual open areas of the matrix it did not differ significantly from other castings that had much better records of corrosion survival. Other metal-

lographic examination of alloys showed that there was considerable variation in the microstructure from one spot to another, presumably reflecting differences in the solidification rate of the casting.

The microstructures of alloys were also examined after exposure to superheated steam (see Fig. 11). The transverse sections were selected from adjacent portions of rolled sheets in order to minimize differences in the original microstructure.

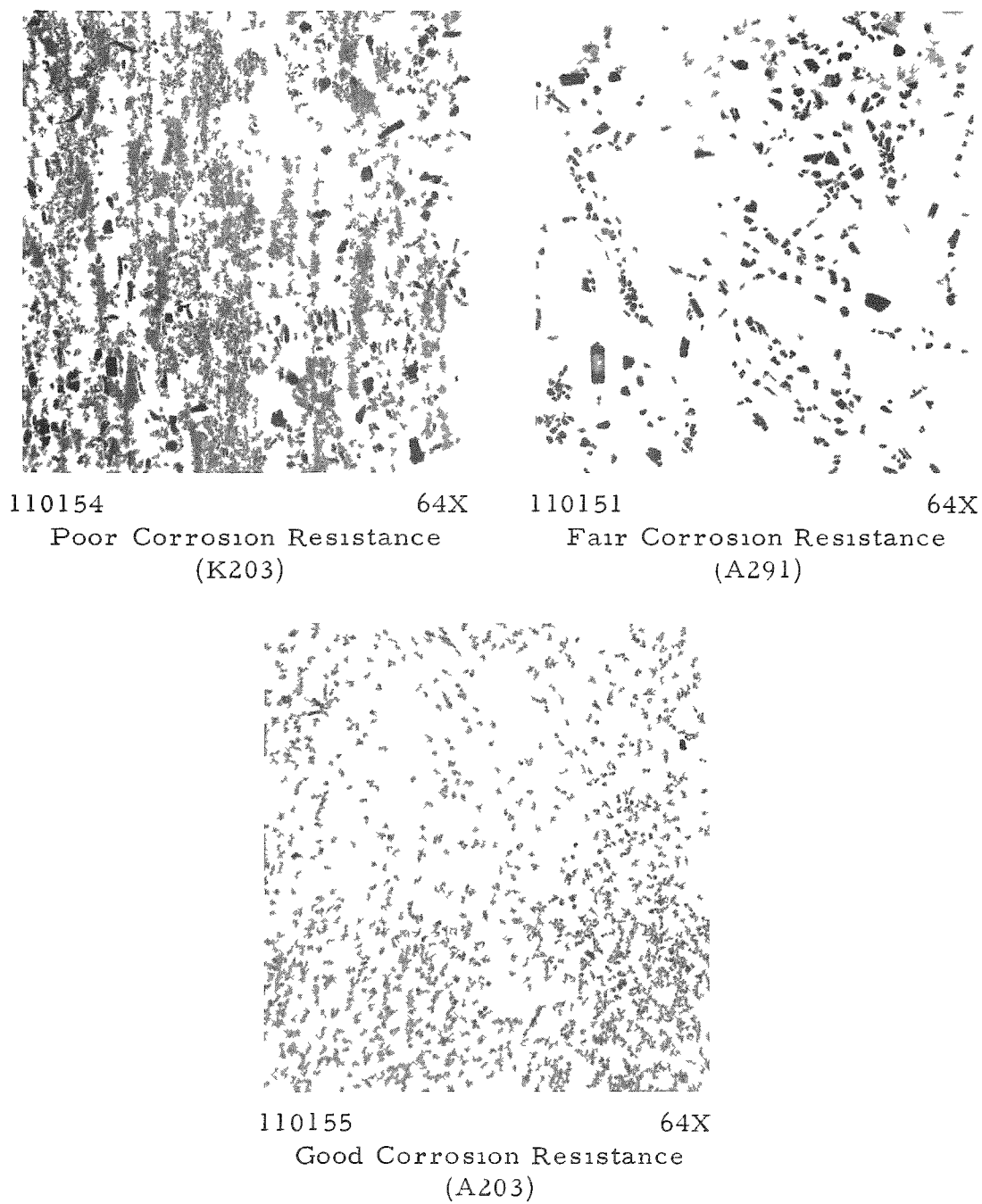


Fig. 10. Comparison of Microstructure and Steam Corrosion Resistance for Several Castings of a 5.6% Ni-0.3% Fe-0.1% Ti-Aluminum Alloy

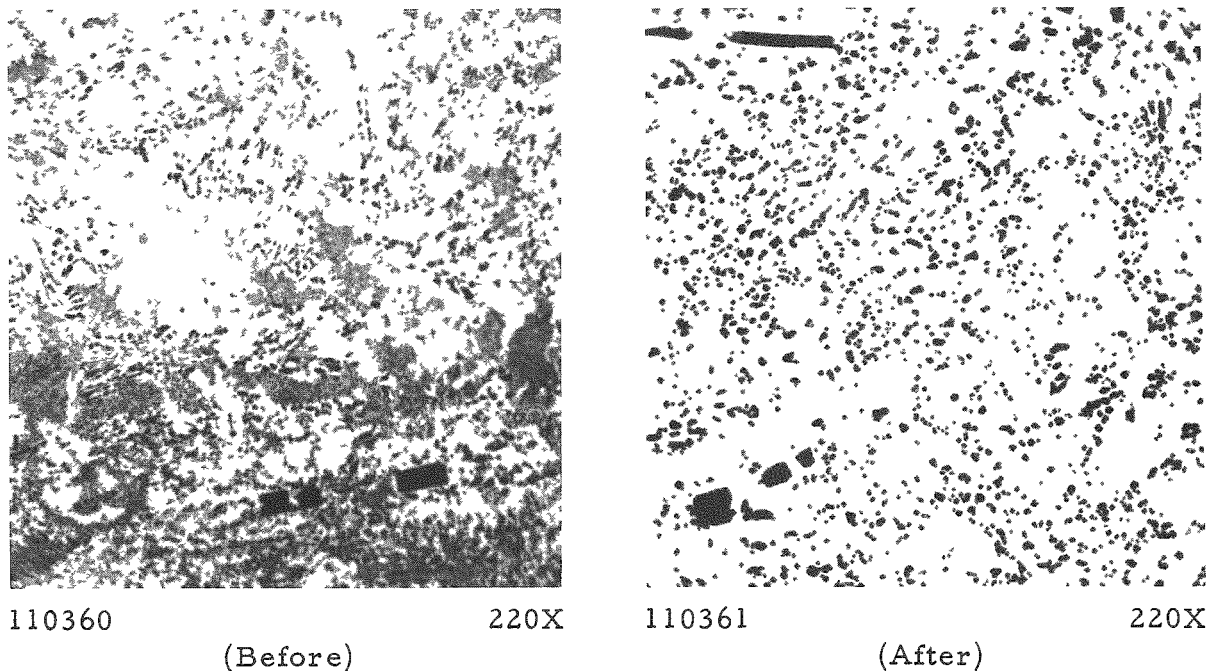


Fig. 11. Coalescence of Second Phase in a 5.6% Ni-0.3% Fe-0.1% Ti-Aluminum Alloy after Exposure to Steam at 540°C and 600 psig for 43 Hours

The very fine  $\text{NiAl}_3$  precipitate agglomerated into roughly spherical particles. The typically rod-like structures of the  $\text{NiFeAl}_9$  did not appear to change as much in size or distribution.

A test in air in a muffle furnace demonstrated that the change in structure is a result of the heat treatment and not particularly attributable to the superheated steam environment.

A test was performed to determine if the coarse microstructure of the corroded alloy would still protect the alloy in the absence of a protective film. Three specimens of a resistant casting were corroded for 69 hr at 540°C and 600 psig. The thin corrosion coating was removed by grinding, and samples were re-exposed for an additional 72 hr under the same conditions. Except for a noticeable increase in microblistering, the samples looked the same at the end of the second exposure as they had at the end of the first.

The intermetallic compounds  $\text{NiAl}_3 + \text{Ni}_2\text{Al}_3$  and  $\text{FeNiAl}_9$  were also corrosion tested in 540°C, 600 psig steam for 102 hr. They formed blue-violet temper films on the surfaces, but were otherwise unchanged in appearance by the exposure. The weight change was not measured. They were unaffected by the fast starting procedure.

Hydrogen and Porosity: As previously mentioned, the difference in appearance between pure aluminum samples corroded in dry air and superheated steam was in the formation of very small hollow blisters only on freshly exposed surfaces in the superheated steam environment. Freshly prepared samples of the corrosion-resistant 5.6% Ni-0.3% Fe-0.1% Ti alloys also blistered in the steam environment to a varying extent (with slow start). Some castings of this composition showed no large surface blisters (~2-mm dia) and only on occasional microblister (i.e., 1 per 50-100 cm<sup>2</sup> surface area). Other castings suffered extensive large and microblistering.

Vacuum melting and casting of the alloys followed by hot pressing and hot rolling to sheet reduced the number of blisters formed in a subsequent corrosion exposure in superheated steam but did not eliminate them.

Vacuum melting and casting followed by 60% cold reduction<sup>(10)</sup> eliminated essentially all of the surface blistering, both large and small, when a slow test-starting procedure was used. However, this particular alloy was severely edge cracked by cold rolling to this extent.

The large blisters (1-3 mm in dia) are much more common in sheet produced from castings which showed shrinkage porosity in X-ray examination. The large blisters also were found in stringers in the rolling direction. It was assumed that they were formed from holes in the original casting that had been rolled into partially cold-welded cracks in the final sheet.

Blisters formed on sheet aluminum during heat treatment have traditionally been traced to hydrogen. The temperature of the superheated steam corrosion test is in the range normally used for the vacuum extraction of hydrogen from aluminum. There was some question initially whether the corrosion hydrogen would be retained by the aluminum samples during their long high-temperature exposure.

Samples about  $1 \times \frac{1}{3} \times \frac{1}{10}$  in. were tested in 540°C, 600 psig steam. Their thin corrosion coating was carefully ground away. A brief etch in 50:50:10 (by volume) H<sub>2</sub>O:HNO<sub>3</sub>:HF prepared them for the hydrogen analysis apparatus. This particular casting did not have more than two microblisters (which were ground away before analysis) on any sample. The results are shown in Table III.

Samples of other alloys also gave postcorrosion hydrogen contents of 2-3 ppm. To evaluate the hypothesis that this represented an equilibrium value, a test was conducted with samples having different ratios of surface area to metal volume. The results are presented in Fig. 12. More hydrogen was obtained from a given volume of metal as the exposed surface increased, eliminating the possibility of an equilibrium value. Rather, it suggested in conjunction with the data of Table III that the bulk of the hydrogen trapped within the specimen was formed during the initial surface corrosion reaction and did not escape due to the impenetrable oxide coating formed by this reaction.

Table III

POSTCORROSION HYDROGEN CONTENT<sup>1</sup>

Exposure, days	Hydrogen, ppm
Apparatus blank	0.04
0	0.04
0.8	2.6
0.8	3.0
7.5	2.0
7.5	3.2
36.4	3.1
36.4	3.0

<sup>1</sup>A203x (5.6% Ni-0.3% Fe-0.1% Ti)  
corroded in 540°C, 600 psig steam.

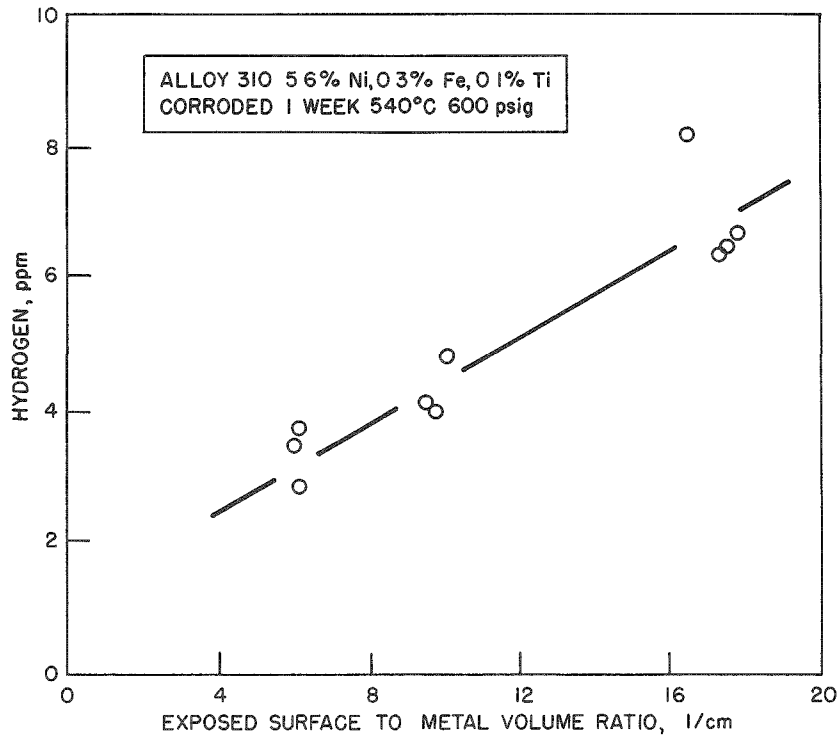


Fig. 12. Postcorrosion Hydrogen Contents of Aluminum Alloy Samples

The hydrogen content of these samples is appreciably above the solubility limit in pure aluminum. While the possibility of the second-phase compound retaining some of the hydrogen in solution cannot be overlooked, the presence of surface blisters on some of the alloys suggested that the hydrogen in the nonsurface blistering alloys probably exist in interior voids.

A comparison of a corroded (3 days at 540°C and 600 psi) and a non-corroded specimen is made in Figs. 13 and 14. This alloy produced very little surface blistering and was cold rolled initially. No etchant was used in the preparation of these specimens. Note that the cracks or tiny voids in or near the large pieces of second phase in the noncorroded specimen appear to act as sites for gas accumulation when the sample is corroded. The frequency of those holes was approximately constant with increasing distance from the corrosion interface.

110298 640X  
A247 (5.6% Ni-0.3% Fe-0.1%Ti)

Fig. 13. Tiny Voids Associated With Pieces of Second Phase in the As-cold-rolled Condition

110299 640X  
A247 (5.6% Ni-0.3% Fe-0.1% Ti)

Fig. 14. Hydrogen Enlargement of Voids after 3-day Exposure to Steam at 540°C and 600 psig

A few short tests were performed with wet-ground samples of several different alloys, using the fast starting technique. All survivors of alloys depending on iron and/or nickel were badly surface blistered after about a one-day exposure. An Al-3% Pt alloy did not show surface blisters but did show occasional small voids near the pieces of second phase, as in Fig 13.

Long Tests: The short-term behavior of some of the A203 alloys was encouraging. Therefore samples were exposed at 540°C and 600 psi

for long periods of time. Most samples were various castings of the A203 composition, but three others were included because of their excellent initial appearance in a short test. The results are shown in Table IV.

Table IV

CORROSION OF SELECTED ALUMINUM ALLOYS IN  
SUPERHEATED STEAM AT 540°C AND 600 PSIG

Alloy A203 Type Alloys (5.6% Ni-0.3% Fe-0.1% Ti)	Last Measured Weight Gain		Comments
	mg/cm <sup>2</sup>	Exposure, days	
A203	0.34	270	Disintegrated between 305 and 338 days
A203	0.27	267	Intact
A203D	0.35	263	Intact
A203W	0.27	202	Disintegrated between 230 and 263 days
203WA	0.59	204	Disintegrated between 232 and 265 days
203X	0.72	263	Intact
247	0.31	242	Intact
247*	0.15	163	Disintegrated between 181 and 209 days
Other Alloy Types			
122-4% Ni + 1100 Alloy	0.29	243	Intact
193-1% Ni-0.2% Ti	0.57	243	Intact
201-3% Pt	0.39	242	Intact

\*Sample had coating ground off and hydrogen analysis at 46 days, then returned to test.

The weight change was not a reliable measure of corrosion at these exposure times, since not all the corrosion coating was adherent. These data were included in the table to indicate that no preliminary warning of disintegration was obtained from the weight gain.

A number of alloys prepared originally for aqueous corrosion testing up to 350°C were tested in steam at 540°C and 600 psi. Qualitative results are shown in Table V.



Table V

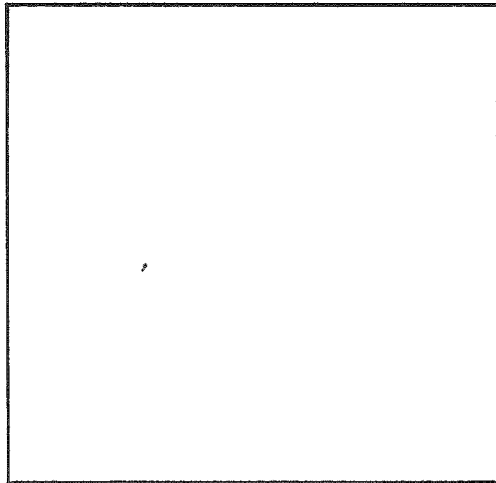
CORROSION OF ALUMINUM ALLOYS IN  
SUPERHEATED STEAM AT 540°C AND  
600 PSIG FOR 18 HOURS (SLOW START)

Alloy	Appearance
122 (4% Ni in 1100 alloy) 133 (0.7% Ni-1% Si-0.03% Fe) 193 (1% Ni-0.2% Ti) 198x (1% Ni-0.1% Ti) 201 (3% Pt) 219 (5.7% Ni-0.3% Fe-0.6% Ti) 220 (5.7% Ni-0.3% Fe-0.6% Zr) 288 (1% Ni-0.5% Fe-0.1% Ti) 332 (1.5% Fe-0.5% Ni-0.1% Ti)	No penetrating attack smooth thin film
128 (0.7% Ni-0.6% Fe-0.06% Si) 129 (0.7% Ni-0.2% Fe-0.06% Si) 131 (0.7% Ni-1% Fe-0.07% Si) 143 (0.7% Ni-0.3% Fe-0.3% Si) 197 (1% Ni-0.1% Nb) 199 (1% Ni-0.05% Ti) 211 (0.01% Ni) 212 (0.2% Ti) Nickeliferous S.A.P. #895 (A.I.A.G.) (0.9% Ni 0.4% Fe) (Powder Metallurgy Product)	Disintegrated

Alloy 332 had only an additional 3 days of testing and was still in excellent condition. As reported in Table IV, alloys 122, 193 and 201 were intact after 243-day exposure. All the rest had failed by disintegration on extended testing. The usual mode of failure was sudden disintegration without previous warning, such as by means of a weight change or a change in appearance. In some cases (for example, 198x), the microblistering of the surface became progressively worse prior to the sudden disintegration.

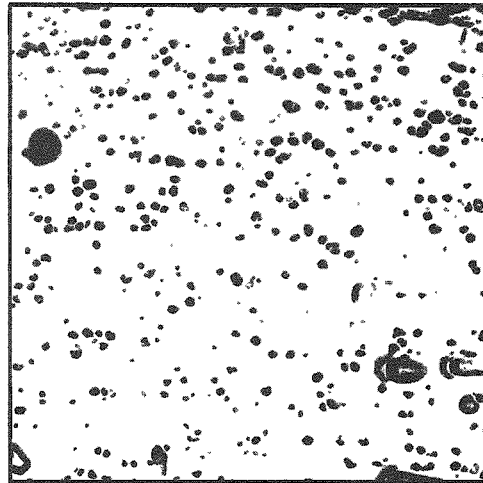
Pretreatment: Experiments described earlier in this report suggested that the surface blistering of the alloys could be eliminated by precorrosion exposure, either to dry air at 540°C or to water at 350°C. Alloy 332 (1.5% Fe-0.5% Ni-0.1% Ti) was chosen for such an experiment. A dozen samples of the as-rolled sheet were exposed for 2 hours to water at 350°C. Another dozen were exposed for 19 hr in air at 540°C (air cooled). Three control samples were wet ground. All were exposed to steam at 540°C and 600 psi (fast start) for 100 hr. The pretreated specimens were all intact and had no blisters visible to the naked eye. Microscopic examination showed that three of the air-pretreated and one of the water-pretreated specimens had

one or more microblisters. Two of the three controls were intact but showed extensive surface blistering (similar to that shown in Fig. 4). The other control had disintegrated. The pretreated samples had still suffered hydrogen penetration and internal blistering, although not to the extent of the wet-ground specimens, as shown in Figs. 15 through 18.



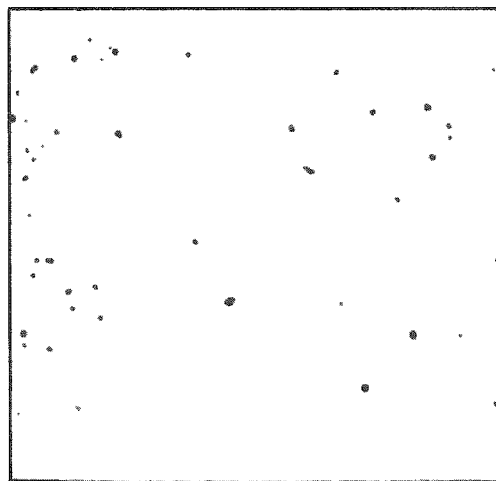
110315 64X

Fig. 15. Alloy 332 (1.5% Fe-0.5% Ni-0.1% Ti); As Rolled - No Exposure to Steam



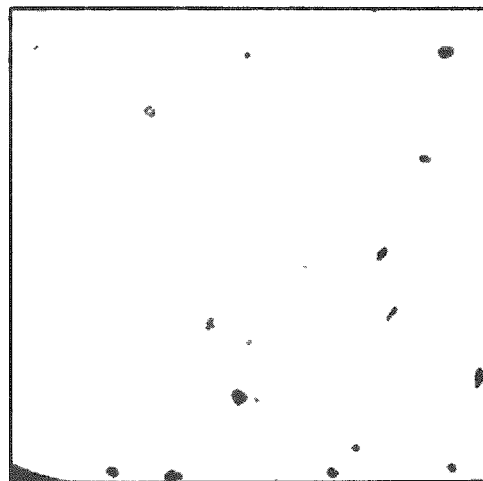
110313 64X

Fig. 16. Alloy 332 - No Pretreatment - Exposed 100 Hours to Steam at 540°C and 600 psig. Note Development of Extensive Hydrogen Porosity.



110316 64X

Fig. 17. Porosity in Alloy 332 (1.5% Fe-0.5% Ni-0.1% Ti). Pretreated 2 Hours in Water at 350°C, then Exposed 141 Hours in Steam at 540°C and 600 psig.



110314 64X

Fig. 18. Porosity in Alloy 332 Pretreated 19 Hours in Air at 540°C, then Exposed to Steam at 540°C and 600 psig for 141 Hours

An effort was made to determine whether pretreatment would enable essentially all water corrosion-resistant alloys to withstand the superheated steam. The alloys shown in Table VI were precorroded for two hours in water at 350°C and then exposed to steam.

Table VI

## EFFECT OF PRETREATMENT ON CORROSION IN SUPERHEATED STEAM\*

Alloy	No Pretreatment (previous tests)	2 Hours at 350°C (H <sub>2</sub> O) Pretreatment - 540°C and 600 psig for 94 Hr
X8001 (1% Ni in 1100 Al)	Disintegrated	Disintegrated
198X (1% Ni-0.1% Ti)	Intact	Intact
203 (5.6% Ni-0.3% Fe-0.1% Ti)	Intact	Disintegrated
K203 (5.6% Ni-0.3% Fe-0.1% Ti)	Disintegrated	Disintegrated
288 (1% Ni-0.5% Fe-0.1% Ti)	Disintegrated	Disintegrated
298 (5.6% Ni-0.3% Fe-0.1% Ti-0.03% Si)	Intact	Intact
299 (5.6% Ni-0.3% Fe-0.1% Ti-0.01% Cu)	Intact	Intact
313 (5.6% Ni-0.3% Fe-0.1% Ti)	Intact	Intact
332 (1.5% Fe-0.5% Ni-0.1% Ti)	Intact	Intact

\*Slow starting procedure.

Except for the one anomalous test with the 203 alloy, the pretreatment did not alter the final result of the corrosion attack. The 203 sample was one of the last remnants of this casting and may have had unseen edge cracks from rolling. The surfaces of the pretreated specimens were essentially free of microblisters, in contrast with the conditions of the untreated specimens.

#### Mechanism at 540°C and 600 psig

We have described in previous sections the characteristic increase in hydrogen content and the formation of voids for alloys resisting disintegration. The sudden penetrating attack which rapidly destroys an aluminum sample was also examined on an alloy specimen partially destroyed during a short corrosion exposure. Figure 19 is a section through a spot showing this type of attack. The dark areas on the micrograph are a result of the corrosion process. Note the change in size and distribution of these areas with distance from the corrosion interface. Figure 20 illustrates at higher magnification a portion of the sample near A on Fig. 19. The dark areas are shown to be oxide-coated cavities in the metal. The large object in the center is an uncorroded piece of second-phase compound. The smaller particles imbedded in the oxide are also second-phase compound.

A little farther from the corrosion interface (at B on Fig. 19), the oxide coating in the cavities is thinner and the cavities themselves are somewhat smaller and more angular. The pieces of second phase are unattacked (Fig. 21).

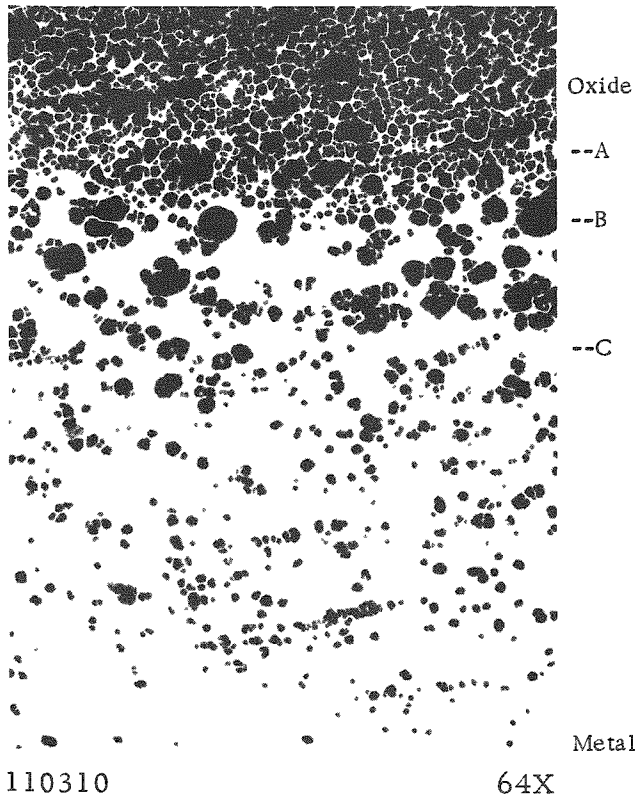


Fig. 19

Corrosion Interface - Penetrating Attack on Alloy 325 (5.6% Ni-0.3% Fe-0.1% Ti) Exposed for 16 Hours in Steam at 540°C and 600 psig

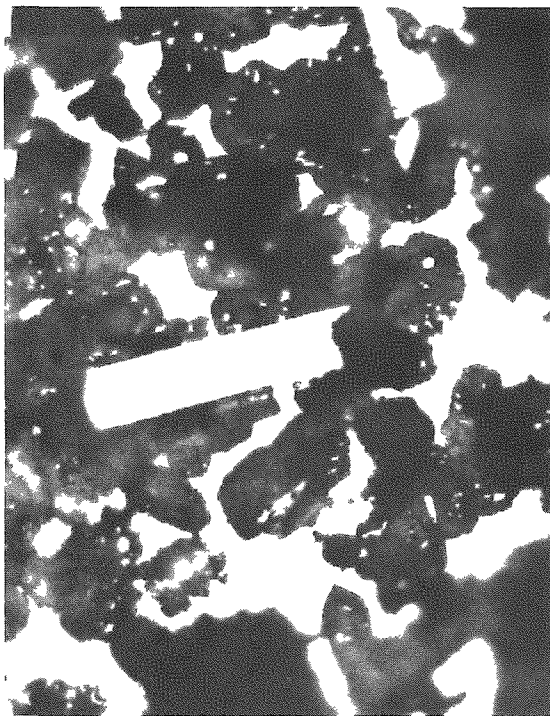


Fig. 20. Area near "A" (Fig. 19) at Higher Magnification. Note Heavy Oxide Layer on Walls of Holes

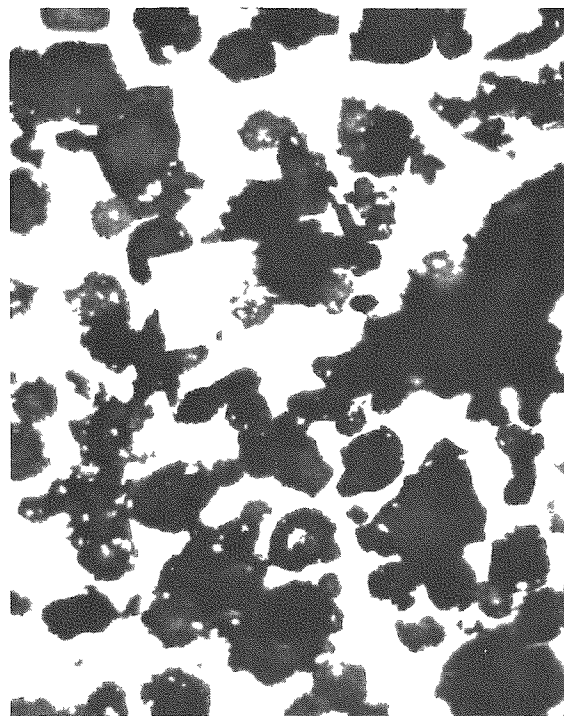
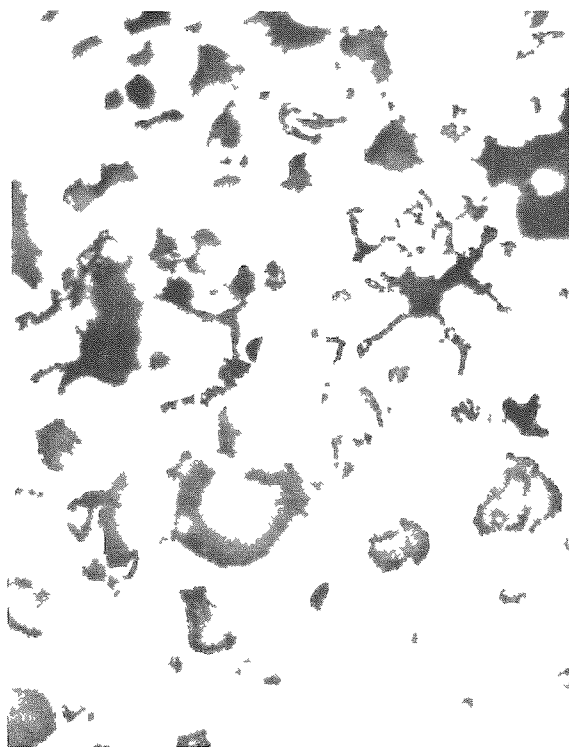


Fig. 21. Area near "B" (Fig. 19) at Higher Magnification

In area C, the next micrograph (Fig. 22) shows the clean voids and angular cracks that are characteristic of gas porosity. Note that most of the cracks are associated with the area immediately adjacent to pieces of second phase. This can be clearly seen in the last micrograph (Fig. 23) of this series taken of an area approximately 1 cm distance from the corrosion interface. Each microvoid is associated with a piece of second-phase compound.



110308

640X

Fig. 22. Area Near "C" (Fig. 19).  
Note Absence of Oxide  
Layer in Most of the Holes.

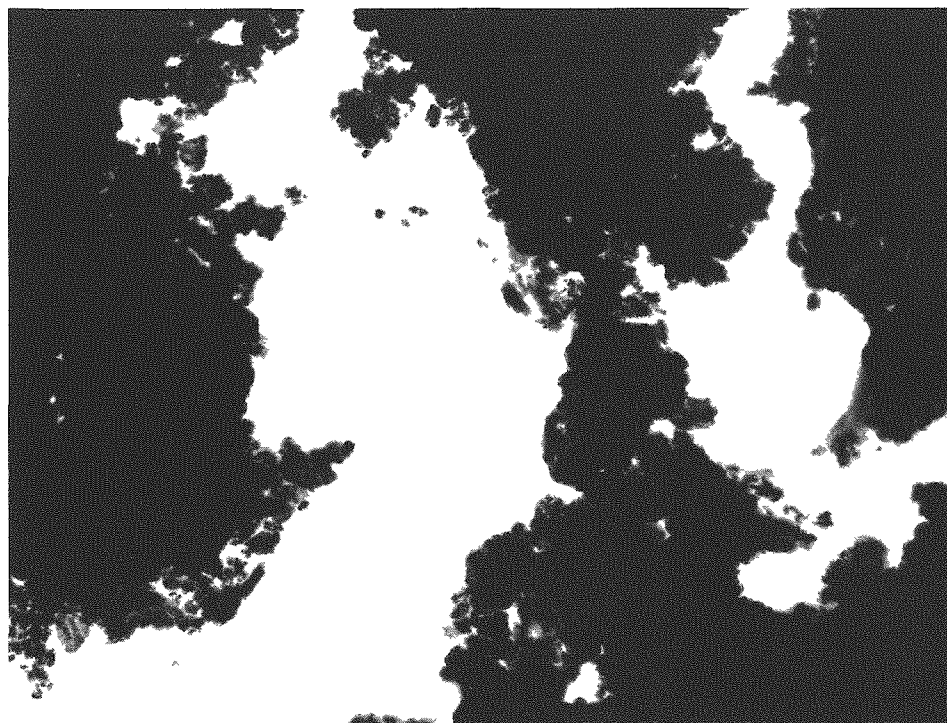


110311

640X

Fig. 23. Area Approximately One  
Centimeter from Corro-  
sion Interface

The oxide on the internal cavities in Figs. 20 and 21 is much thicker than the characteristic temper film found on the exterior surface of a sample. A section of this corrosion interface was thinned down carefully and mounted in an electron microscope. Figure 24 is a direct transmission micrograph showing some of the oxide still adhering to the walls of a tiny void (approximately in area B). A selected area electron diffraction pattern of the oxide in the void was similar to that of diaspor,  $\beta\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ , although not all of the diffraction lines were identical with those listed on ASTM Card 5-0355. The phases  $\alpha\text{Al}_2\text{O}_3$  and  $\gamma\text{Al}_2\text{O}_3$ , which had been identified on the exterior surfaces of similar samples, were not present on the walls of the void. The  $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$  was not found on the exterior corrosion surface.



100757

20,000X

Fig. 24. Electron Micrograph of a Section through an Oxide-coated Internal Blister. Portions of the Oxide Have Been Torn Away during Preparation. (Black  $\approx$  Metal; White  $\approx$  Voids; Gray  $\approx$  Oxide)

In order to measure the increase in temperature attributable to the exothermic nature of the reaction, a test was performed with a sample suspended by a thermocouple in steam at 540°C and 600 psig. This was done to see if thermal runaway was responsible for disintegration. K203 alloy was used to insure rapid reaction. Another thermocouple located in the steam near the specimen was used to measure the bulk steam properties. In this test, the sample ( $1\frac{1}{4} \times \frac{1}{4} \times \frac{1}{8}$  in.) reached a maximum of 15°C above the bulk steam temperature after a period of about 7 hours. It had totally disintegrated after about 10 hours. The increase in temperature does not seem to be sufficient to cause a marked change in the corrosion rate. In one test, due to control failure, a resistant alloy (3% Pt), was exposed to 590°C steam for a period of several hours without ill effect.

#### DISCUSSION

Since the behavior of aluminum in steam at 540°C and 600 psi is so dependent on whether penetrating attack is initiated, a proposed mechanism for this attack is a logical place to start the discussion.

The predominant oxides which form on an exterior pure aluminum surface exposed to superheated steam at 540°C and 600 psi ( $\alpha\text{Al}_2\text{O}_3$  and members of the  $\gamma$  series of  $\text{Al}_2\text{O}_3$ ) appear to form thin and protective films. A portion of the hydrogen produced by the surface reaction with steam enters the metal and produces gas-filled blisters. As long as the interior of the blister is isolated from the steam, the corrosion appears to be limited to the very slow exterior surface reaction.

Finally, mechanical failure or continued corrosion opens a fissure to the interior of the blisters. Depending on the particular alloy and sample suspension, this might occur in a few minutes, hours, or years. Film-free aluminum is then exposed in a predominantly hydrogen atmosphere containing some water vapor. The corrosion product formed under these conditions appears to be a hydrated aluminum oxide, probably diaspore, and relatively nonprotective. A great deal more corrosion-produced hydrogen enters the metal, produces new blisters, and continues the cycle at an accelerating pace. New film-free aluminum surface is exposed to the hydrogen-steam at an increasing rate, and the sample is rapidly destroyed.

It has not been determined whether the oxide formed on the interior of the blister is nonprotective due to the environment in which it is formed (hydrogen-steam) or due to the geometry which tends to expose fresh metal. In either event, the hypothesis offers explanations for the various experimental observations.

Alloys with large amounts of well-distributed cathodic second phases provide a large number of sites for microblisters and effectively distribute the corrosion hydrogen throughout the specimen. Extensive cold working also provides numerous dislocation sites for microblister formation. The time required for a blister to grow to a size that could rupture would be longer for alloys so treated.

Selection of the alloying elements for production of the second-phase compounds also appears important. For example, analysis of the 3% platinum alloy after steam corrosion showed a much lower hydrogen content than for alloys containing nickel and iron. Alloy A332, containing more iron than nickel (1.5% Fe-0.5% Ni), appeared to be more resistant and to distribute the hydrogen throughout the alloy more uniformly than in A288, which contained more nickel than iron (1% Ni-0.5% Fe). Comparison of postcorrosion gas porosity might prove to be a useful tool in developing alloys for this type of environment.

Alloying constituents in solid solution (i.e., small amounts of Cu, Si, Mg, etc.) might be expected to increase the exterior surface rate of reaction by providing a less protective oxide. (Note the extremely low rate of attack of pure aluminum.) The increased surface reaction would result in more hydrogen entering the metal. The induction period before initiation of the rapid penetrating reaction would thus be shortened.

Inclusions in the alloy, such as oxide stringers, would lead the steam relatively deep into the metal and thus decrease the induction period.

The poorest of the 5.6% Ni-0.3% Fe-0.1% Ti alloys tested, K203, probably suffered from a combination of solid solution additives and inclusions.

The extremely pure aluminum has so little surface reaction due to the excellent protective film that not enough hydrogen is produced to produce large blisters and rupture them. However, if the proposed mechanism is correct, it would only be a question of a long induction period before the initiation of penetrating attack.

The mechanism can also explain the sensitivity to method of sample suspension. Marginal alloys would have a great number of blisters that could be opened by mechanical deformation and so initiate the disintegrating attack.

It appears that the bulk of the hydrogen found after corrosion in resistant samples enters before the protective oxide film is completed. Pretreatments which form a similar protective film would be expected to be most effective in those cases where little or no corrosion hydrogen enters the metal during the pretreatment corrosion. Both water (350°C) and air (540°C) pretreatments were useful. In practice, an effort should probably be made to dry the air used for that type of pretreatment.

By careful pretreatment and suitable alloy choice it should be possible to extend the induction period for disintegration to such an extent that practical applications for aluminum-based alloys could be considered.

The penetrating attack of aluminum and many of its alloys in liquid water is in many ways similar to the behavior in steam. This suggests that the proposed mechanism of propagation might be operative in water at lower temperatures as well as in the environment studied here.

#### ACKNOWLEDGEMENT

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