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CORROSION EXPERIENCE WITH ALUMINUM POWDER PRODUCTS

by

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ABSTRACT

Extrusions of aluminum alloy powder products were obtained from several sources and evaluated for corrosion resistance to high-temperature (260-350°C) water.

Several types of tubing impact-extruded by ALCOA were tested. The stronger tubing (M655) failed very rapidly. The weaker tubing suffered extensive localized surface attack and penetration of the corrosion attack along the extrusion direction after prolonged (~3 mo) exposure to 290°C water. A precorrosion heat treatment was effective in reducing both types of attack on the weaker tubing.

Armour Research Foundation supplied several types of tubing extruded through a bridge die. All tubes failed on prolonged (~8 mo) corrosion in 290°C water at the longitudinal bond lines. These lines were formed by the rejoining of the metal streams passing over the mandrel supports in the die during extrusion.

Directly extruded tubing supplied by the Torrance Brass Company also failed on extended exposure to 290°C water.

Many experimental rod extrusions (from Armour Research Foundation and Trefimetaux) exhibited corrosion resistance to static 290°C water equivalent to that of wrought alloys. The Trefimetaux specimens were also tested in rapidly flowing water at 315°C. Under these conditions a corrosion rate significantly faster than for the wrought alloy was measured.

INTRODUCTION

The good corrosion resistance of recently developed wrought aluminum alloys(1,2) to low-velocity, high-temperature water suggests application in boiling water reactors as a fuel-cladding material. Unfortunately, the mechanical properties, particularly the low creep strength of these wrought products, tends to limit their usefulness at temperatures of 250 to

300°C to those cases where the fuel material can provide additional strength or to designs which impose very low stress levels on the fuel elements. This limitation could be substantially reduced if it were possible to obtain simultaneously the corrosion resistance of the special wrought alloys and the mechanical strength of some aluminum powder products.

Initial attempts at ANL to secure this desirable combination of properties(3) yielded products with wide variability in corrosion resistance to high-temperature water. Some samples gave very encouraging results, but others manufactured in the same fashion were quite poor in corrosion resistance. Similar results were obtained with powder products fabricated by the hot rolling of laboratory atomized powder in an aluminum can. Since no experimental compacting and extrusion equipment was available at ANL at that time, it was arranged that Armour Research Foundation (ARF) investigate the variables in the production of corrosion-resistant aluminum powder products. At the end of the first year,(4) ARF had produced some rods with very promising corrosion resistance to 350°C water.

At about this time (early 1960), preliminary design studies were being made for refueling the Experimental Boiling Water Reactor (EBWR). The reference design was for a free-standing fuel of uranium oxide pellets contained in a metal tube. There was an interest in aluminum-powder-product tubes for this application, since they would provide data on a new fuel type rather than merely repeating the experience of other reactors with Zircaloy or stainless steel tubes. Accordingly, the emphasis of the second-year contract with ARF was directed towards the production of tubing, starting with powder production. At that time there was no reliable source of powder with the low silicon content required.

The Aluminum Company of America had also been engaged in a research program on corrosion-resistant powder products(5) and had experience in extruding powder-product tubing to close tolerances for the organic-moderated-reactor program. Two groups of tubes, impact extruded to the proposed fuel dimensions, were purchased from ALCOA for corrosion evaluation.

One additional problem with the proposed use of powder-product tubing in the reactor was the end closure. Ordinary welding of aluminum powder products containing more than a small amount of aluminum oxide results in a poor joint and loss of the improved mechanical properties at the weld area. Atomics International had developed a eutectic-pressure-bond technique(6) that appeared suitable for use in organic-moderated reactors, in which the corrosive attack on the aluminum is very slight. Arrangements were made for them to pressure-bond some end caps into our powder-product tubes for corrosion evaluation in high-temperature water.

Before the accelerated corrosion evaluation program had been completed, the original interest in providing a second loading for the EBWR had abated. However, corrosion testing of promising experimental extrusions was continued and a few results have been reported.(7)

This report documents our corrosion experience with aluminum powder products and indicates the problems that can be anticipated in securing consistently high-quality reactor components of this type.

EXPERIMENTAL

Static corrosion testing was performed in continuously refreshed autoclave systems made from stainless steel. The refreshing water was saturated with oxygen at room temperature by first vacuum boiling and then sparging oxygen through the storage carboys.

The dynamic tests also utilized a continuously refreshed system. A high-pressure canned-rotor circulating pump maintained the flow of liquid past the samples. A small pump continuously fed fresh water into the loop. As with the static autoclaves. a Grove back-pressure regulator maintained the pressure at several hundred psi above the vapor pressure of the solution. The discharge from the regulator went to the drain.

Except for one dynamic test of tubing specimens, the aluminum samples were electrically insulated from the stainless steel by artificial sapphire rods.

The amount of unreacted metal remaining in corroded samples was determined by a destructive technique. A corroded sample was weighed and its remaining metal dissolved in methanol-iodine solution (10 gm I_2 per 100 ml CH_3OH) at 50°C. Collecting and weighing the undissolved corrosion product made it possible to calculate the metal weight by difference. The corrosion oxide was separated from the very fine dispersed phases within the powder product by the use of a coarse sintered glass filter and by decanting off most of the liquid (containing the very fine particles in suspension) prior to filtering.

The flow diagram of Figure 1 illustrates the steps in the production of tubing by ARF. For the pilot run of tubing described in this report, no particulate additive was used. Although no details were available, it was assumed that a similar production scheme was also used by the other powder-product suppliers.

Because of the variation in the chemical composition of the various products tested, they will be described as results are given in the next section.

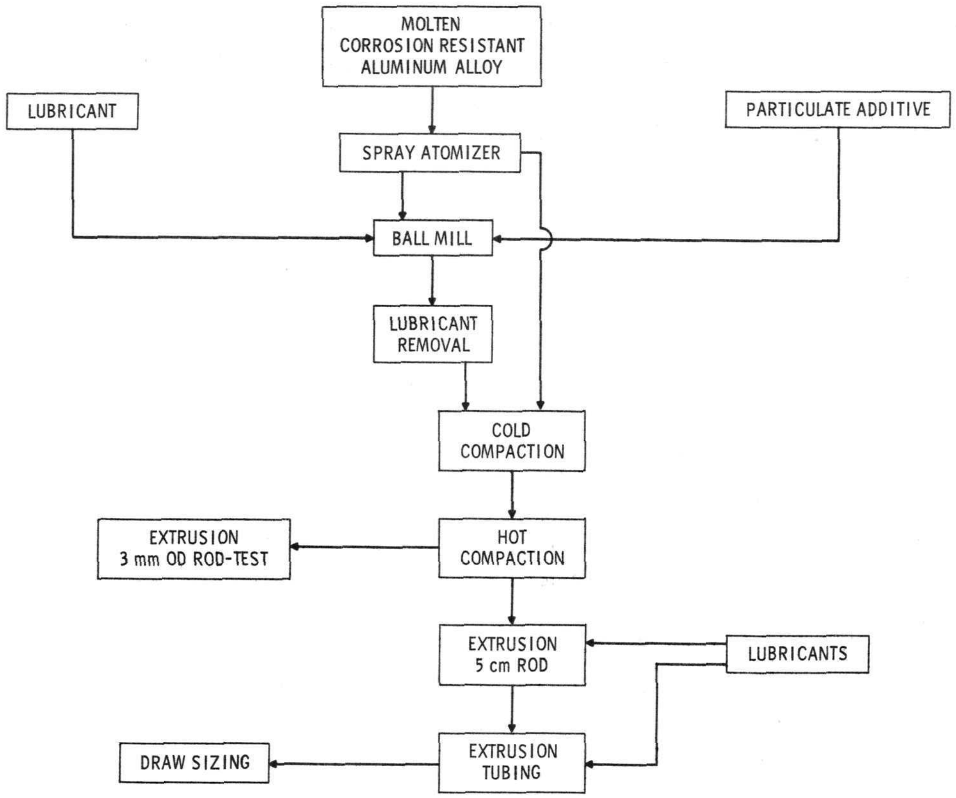


Figure 1. Flow Diagram for the Production of Powder-product Tubing

DATA AND RESULTS

Tubing

Aluminum Company of America: Initially, two types of impact extruded tubing made from as atomized (M654) powder and from ball-milled powder (M655) were supplied. The object of the ball milling was to increase the mechanical properties of the finished product. Subsequently, the same vendor also supplied a limited amount of "modified" M654 tubing with improved mechanical properties. All of the tubes were 1.54 m long by 1.2 cm OD with a 0.089-cm wall thickness. Other pertinent data are given in Table I.

Every effort was made to obtain low silicon content. This element in trace quantities significantly increases the corrosion of wrought Al-Ni-Fe alloys in 350°C water.(1) It is a difficult element to eliminate since most of the refractory materials used to contain and spray molten aluminum contribute small amounts of silicon to the resultant powder.

The M654 tubing was surprisingly weak for a powder product. Wrought tensile specimens of the same composition have demonstrated 40% greater ultimate tensile strength (UTS) at 315°C. The M654 tubing was therefore too weak for its intended application in the EBWR. The mechanical properties of the modified M654 would have been marginal, whereas the M655 tubing had adequate strength for this application.

Table I

PROPERTIES OF ALCOA POWDER-PRODUCT TUBING

Type	Chemical Analysis(1)				Mechanical Properties at 315°C		
	Ni	Fe	Ti	Si	UTS,(2) kg/mm²	Yield, kg/mm²	Elongation, %
M654	0.99	0.57	0.09	0.006	2.8	2.0	36
M654 (Modified)	1.01	0.52	0.09	0.007	7.7	6.2	21
M655	0.97	0.86	0.09	0.007	12.7	10.5	3

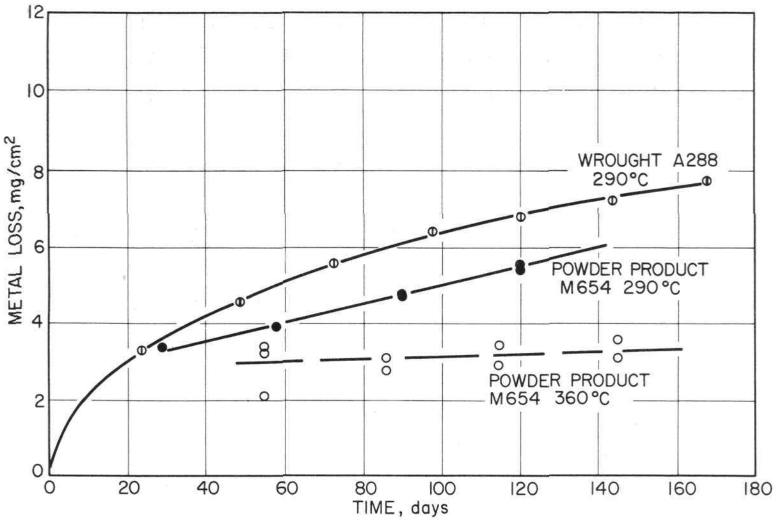
(1)Percent by weight; remainder Al.

(2)One kg/mm² = 1422 psi.

Unfortunately, the strong M655 product corroded exceptionally rapidly in high-temperature water. As much as 80% of the tubing wall was destroyed within 4 days at 350°C. The corrosion was not uniform from spot to spot, and some areas were much more resistant than others. Sharp lines of demarcation outlined these different areas.

A metallographic examination of the corroded tubing revealed no explanation for the exceptionally poor corrosion resistance. Numerous large inclusions with hardness of Rockwell 65C were noted, but they did not appear to play a role in the uniform but rapid attack. The additional iron content of the M655 (see Table I) product suggests that these inclusions were an iron-aluminum compound. It is presumed that iron was picked up during ball milling and converted to the compound during heating and extrusion.

M654 specimens initially showed corrosion behavior equivalent to that of the wrought alloy of the same composition (A288). There were small mounds or blisters in the dark coating, but the corrosion rates were quite satisfactory up to about 120 days (see Figure 2) of exposure at 290°C. Increased corrosion of the cut ends of the tubing was noted at this time. Corrosion penetration and swelling of the sample edge perpendicular to the extrusion direction has previously been noted with powder products. Specimens tested at 360°C suffered less general attack (see Figure 2) and no swelling of the cut ends. A test temperature of 290°C appears to be the most severe for powder products produced from low-silicon alloy powders. This is not surprising, since this is also the temperature of maximum corrosion for the wrought alloy.

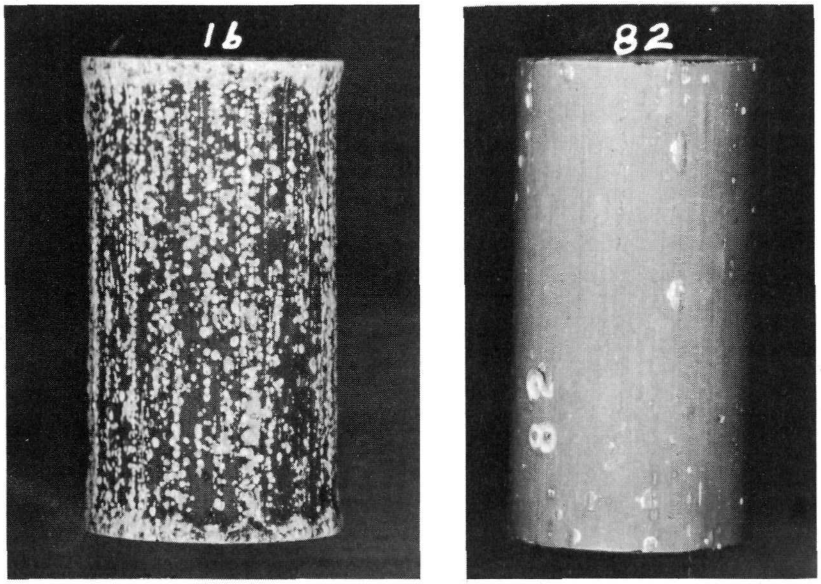


106-6587

Figure 2. Corrosion of Aluminum

Specimens of M654 were also exposed for 29 days at 315°C to water flowing at 2.3 m/sec. No evidence of corrosion swelling or of accelerated attack was noted in this relatively short exposure.

The corrosion resistance of the modified M654 tubing was inferior to that of M654 when tested at temperatures of 350°C and 260°C. Figure 3 illustrates the accelerated corrosion of the cut ends of the tubing at 260°C and the better corrosion resistance obtained at 350°C.



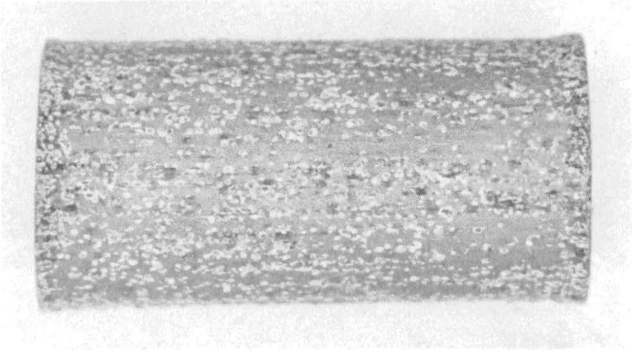
32737 2X

260°C - 124 Days 350°C - 76 Days

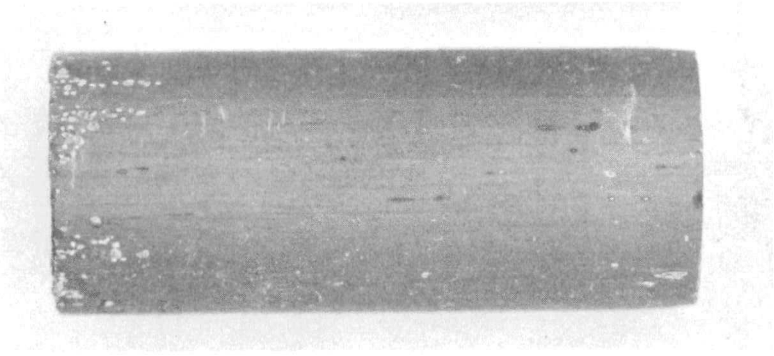
Type M654 "Modified"

Figure 3. Appearance of Corroded ALCOA Tube Specimens

It was assumed that the corrosion penetration at the ends was along unbonded longitudinal areas resulting from oxide stringers, hydrogen-filled voids, and extrusion nonbonds. To ameliorate this condition, a few specimens of the modified M654 were vacuum heat treated for 2 hr at 550°C before corrosion testing at 260°C, and compared with "as received" controls in the same autoclave. That this provided a beneficial effect is evident in Figure 4. At the end of 60 days at 260°C, the heat-treated specimen showed only a very slight tendency for swelling on one end, while the end "belling" is quite apparent on the "as received" control. A large fraction of the surface blistering was also eliminated by this treatment.



As Received



33474

Heat Treated
2 Hour - 550°C

2X

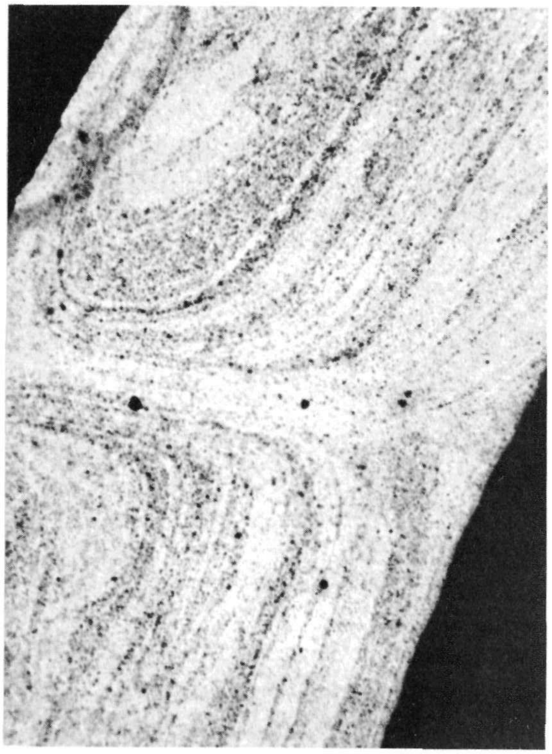
M654 "Modified" - 60 Days - 260°C

Figure 4. Beneficial Effect of Pre-corrosion Heat Treatment

Armour Research Foundation: In this investigation a bridged die was employed in the development of a method for production of powder-product tubing. This method had the advantages of lower cost and better dimensional control than mandrel extrusion, but it was difficult to insure bonding of the metallic streams after they had flowed over the mandrel support. Higher than normal extrusion temperatures and careful control of the extrusion rate were used at ARF in the effort to achieve this objective.

Tubing was prepared at ARF from powder that had been atomized and ball milled there, so that control of each production step was maintained. The removal of the milling lubricant was not satisfactory, as evidenced by the darkening of some of the milled powder in the oven drying following the lubricant extraction step in the procedure.

Tubing for corrosion testing in water at 290°C was prepared from four types of powder. Metallographic examination of the as-received tubing indicated widespread porosity and numerous chunky inclusions. Metal flow lines were visible in the material from 72-hr and 48-hr ball-milled powder in the as-polished condition and became very pronounced on etching (see Figure 5). The as-atomized tubing mostly showed porosity and evidence of short-range longitudinal stringering.



34841 64X

Modified Kellers Etch

Figure 5. Section of ARF Tubing Showing Metal Flow at Bond Line (Powder Milled 72 hr)

Hot tensile tests were performed with the results shown in Table II.

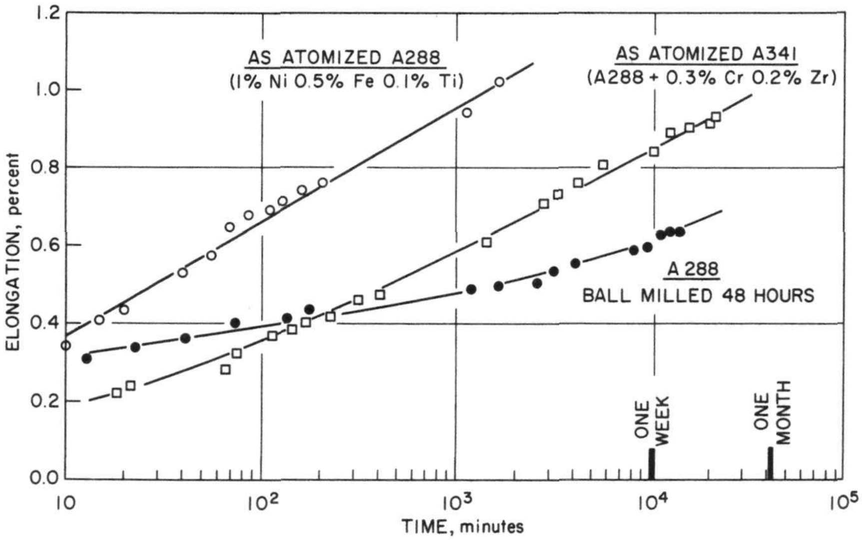
Relatively short creep tests have been performed on three powder tubes at 290°C and 2.8 kg/mm^2. These conditions of temperature and stress were chosen as representative for a tube in an EBWR-type reactor. The creep curves appear roughly linear when the strain is plotted against log

Table II

MECHANICAL PROPERTIES OF ARF TUBING AT 315°C

As Atomized (A288 Alloy) 1 w/o Ni-0.5 w/o Fe-0.1 w/o Ti	5.3 kg/mm^2 5.3
Ball Milled 48 hr (A288)	6.5 6.8
Ball Milled 72 hr (A288)	8.1 8.6
As Atomized (A341 Alloy) 1 w/o Ni-0.5 w/o Fe-0.3 w/o Cr-0.2 w/o Zr-0.1 w/o Ti	6.5 6.7

time (see Figure 6). Extrapolating the plots to 1% creep gave times of 1 day for as-atomized A288 tubing, 30 days for as-atomized A341 tubing, and about 10,000 days for a tube manufactured from powder that was ball milled 48 hr. The time of the creep test (~2 weeks) was too short to have any confidence in the last value, but the numbers serve to illustrate the improvement. A piece of wrought alloy (A288 type) was observed to creep 5% in less than one hour under these conditions.



106-6922

Figure 6. Creep of Aluminum Powder-product Tubing at 2.8 kg/mm^2 and 290°C

Specimens were exposed to 290°C water in the as-received, etched, and the etched and vacuum-heat-treated (2 hr at 550°C) conditions.

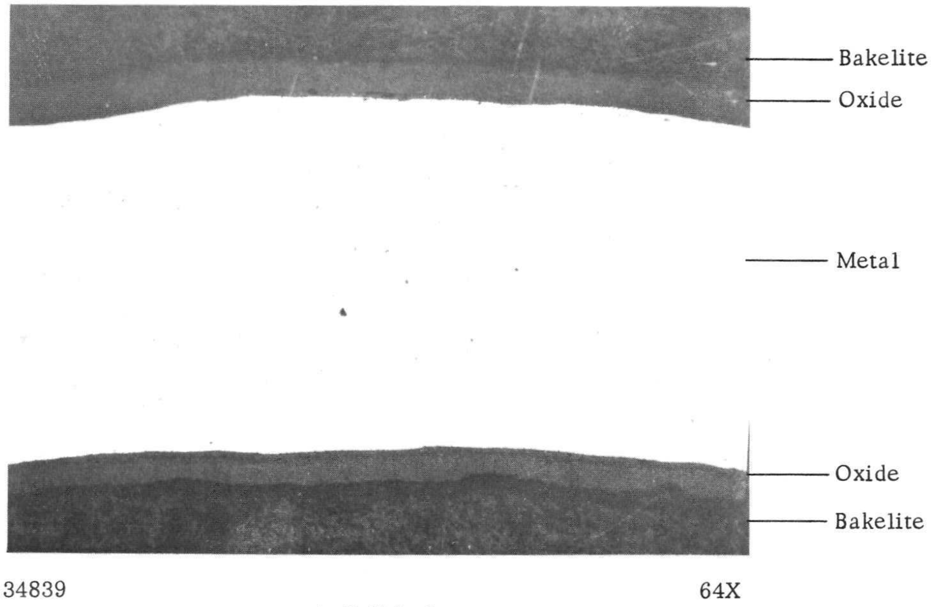
The first material to fail in the 290°C corrosion test was the strong product (72-hr ball-milled powder). Extensive corrosion swelling was noted after one month; by two months, longitudinal streaks of completely oxidized metal were noted on most specimens. No significant effect of the different sample preparations was noted for this material.

The appearance of the as-atomized A288 and the 48-hr ball-mill product (A288) at one-month exposure was quite good. Only a few small blisters and/or mounds were noted in the dark corrosion product. The as-atomized alloy 341 samples were much more susceptible to surface corrosion and roughening, and looked quite poor even as early as one month. Very little change in any of the specimens was noted for the next 2 mo.

By the time a 4-mo exposure had been accumulated, accelerated attack was evident on all types of specimens. Many of the as-atomized specimens of both alloys had suffered edge attack while the 48-hr ball-milled samples were corroded severely in longitudinal streaks. Those samples experiencing severe accelerated attack were removed from the test at this period. The remaining samples were preponderantly those which had received the vacuum heat treatment prior to corrosion testing.

The surviving specimens were examined periodically for exposure times up to about 10 mo. There were great differences in the corrosion behavior of tubing of the same nominal preparation technique. For example, only two of thirty assorted initial samples of the as-atomized tubing appeared in good condition after 10-mo exposure. Only three of fifteen initial samples from one length of the 48-hr ball-milled powder extrusions appeared to be in fair condition. No samples survived in good condition from either the A341 (stronger) as-atomized tubing or the 72-hr ball-milled A288 tubing.

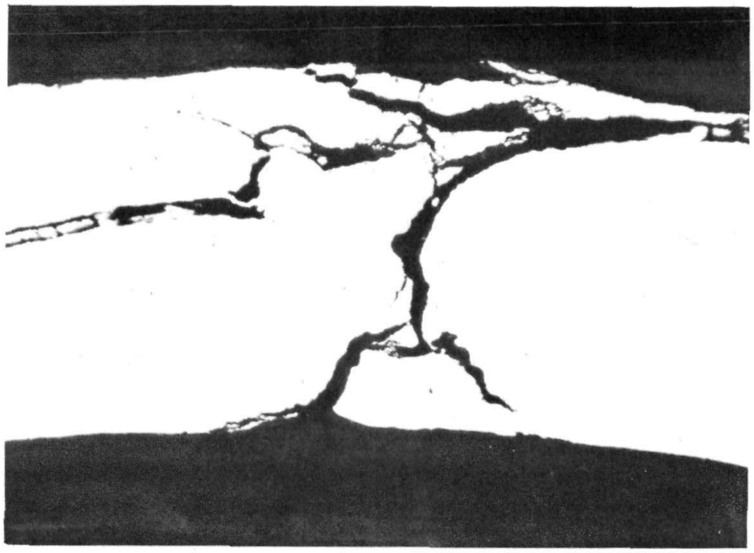
Some samples had still appeared to be free from accelerated corrosion attack, but sectioning of some of these "good" specimens showed internal defects in each. For example, most of the cross section of the 48-hr ball-milled sample was uniformly corroded, as in Figure 7, but at several spots corrosion penetration of the entire thickness was noted, as in Figure 8. By means of the metal flow lines these spots were identified on etching as the bond area between the joined metal streams emerging from the bridge die. All of the tubing types made by ARF exhibited these flaws, although typically only one or two of the bond areas would be attacked out of four possible zones.



As Polished

Figure 7. General Corrosion of 48-hr Ball-milled Powder-product Tube after 8 Mo in Water at 290°C

With this in mind, the few 10-mo survivors were gently compressed laterally with pliers. As expected, all cracked in a brittle fashion in at least one longitudinal area where the metal had been completely penetrated. The attack was quite insidious, since there was practically no external evidence of the severe oxidation.



34842 64X

As Polished

Figure 8. Localized Corrosion of 48-hr Ball-milled Powder-product Tube after 8 Mo in Water at 290°C

Hydrogen analyses were performed on some of the uncorroded tubes. Hydrogen contents were of interest both as a rough measure of porosity and because the vacuum heat treatment (which removes much of the as-produced hydrogen) had such a beneficial effect on the corrosion resistance of the as-atomized A288 powder product. Initially, two tubes with good corrosion resistance and two tubes with poor resistance were analyzed (see Table III A). There appeared to be a correlation of poor

Table III

HYDROGEN CONTENT OF POWDER-PRODUCT TUBES

Type		Corrosion Resistance	Hydrogen, ppm
A	As Atomized A288 Alloy	Good	4.5 4.5
		Poor	11.8 12.2
B	Balled Milled for 48 hr - A288	Good	11.9 20.9
		Poor	18.4 25.6
C	Balled Milled for 72 hr - A288	Very Poor	25.7 27.0
D	As Atomized A341 Alloy	Poor	2.4 3.5

resistance with increasing hydrogen content for the as-atomized tubing. However, the correlation broke down when the other tubing types were analyzed, particularly the as-atomized 341-alloy tubing.

A test was also performed in which as-atomized samples were heat treated in a muffle (air) furnace at 550°C for 2 hr and subsequently exposed to 290°C water. These specimens also showed increased corrosion resistance over the as-received controls. Since these samples and the vacuum treated specimens were not compared for the same period in the same autoclave, it is difficult quantitatively to compare the improvement afforded by the two types of heat treatment. Qualitatively, the vacuum heat treatment appeared to increase the corrosion resistance more than treatment in air.

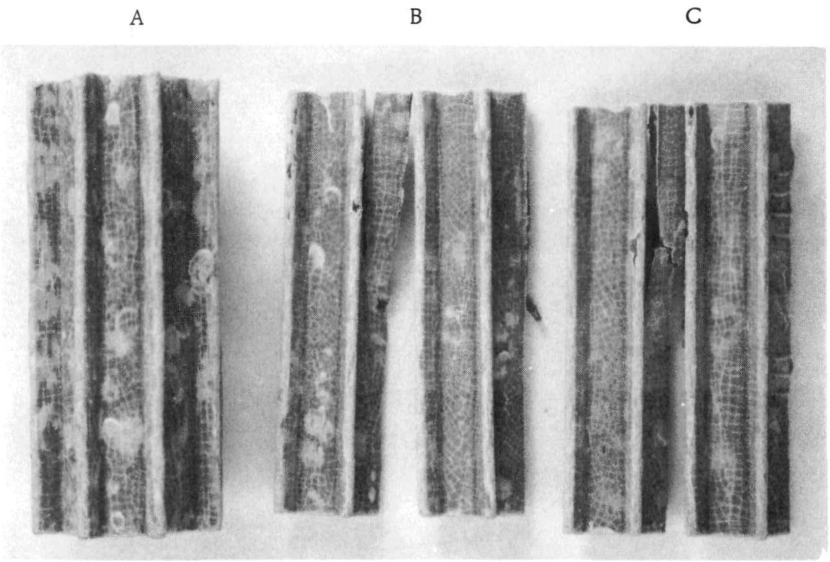
A few samples of the as-atomized and the 48-hr ball-milled tubes were tested for 355 days in a small autoclave in a 350°C oven. No quantitative measure of corrosion was employed except to polish cross sections of the corroded samples and compare them visually with uncorroded tubing. There was little loss of wall thickness and no "end belling." Some of the bond lines had suffered attack, and the tube samples failed along these lines when compressed with a pliers. There was more ductility to these failures than those with the 290°C test specimens.

Torrance Brass Company: Some additional A288 as-atomized, finned tubing was directly extruded over a mandrel from billets supplied by ARF. This material was of about the same corrosion resistance as the as-atomized A288 tubing extruded through the bridge die by ARF and showed the same improvement with vacuum heat treatment. This suggests that a significant portion of the corrosion resistance of the final product is determined in the steps prior to final extrusion. Figure 9A illustrates the appearance of a vacuum heat-treated specimen after 515 days in water at 290°C. Figures 9B and C show the brittle fracture of a similar tube when compressed laterally with ordinary pliers. Essentially all of the metal had been converted to oxide.

Tubing End Closures

Several methods of closing the tube ends were judged feasible. The following methods were based on the experience of others in developing powder-product tubes for organic-moderated reactors and also on fuel-fabrication developments at Argonne:

1) eutectic (Ag or Cu) pressure bonding;(6)
2) flash welding;(8)
3) elemental silicon bonding.(9)



36966 2X

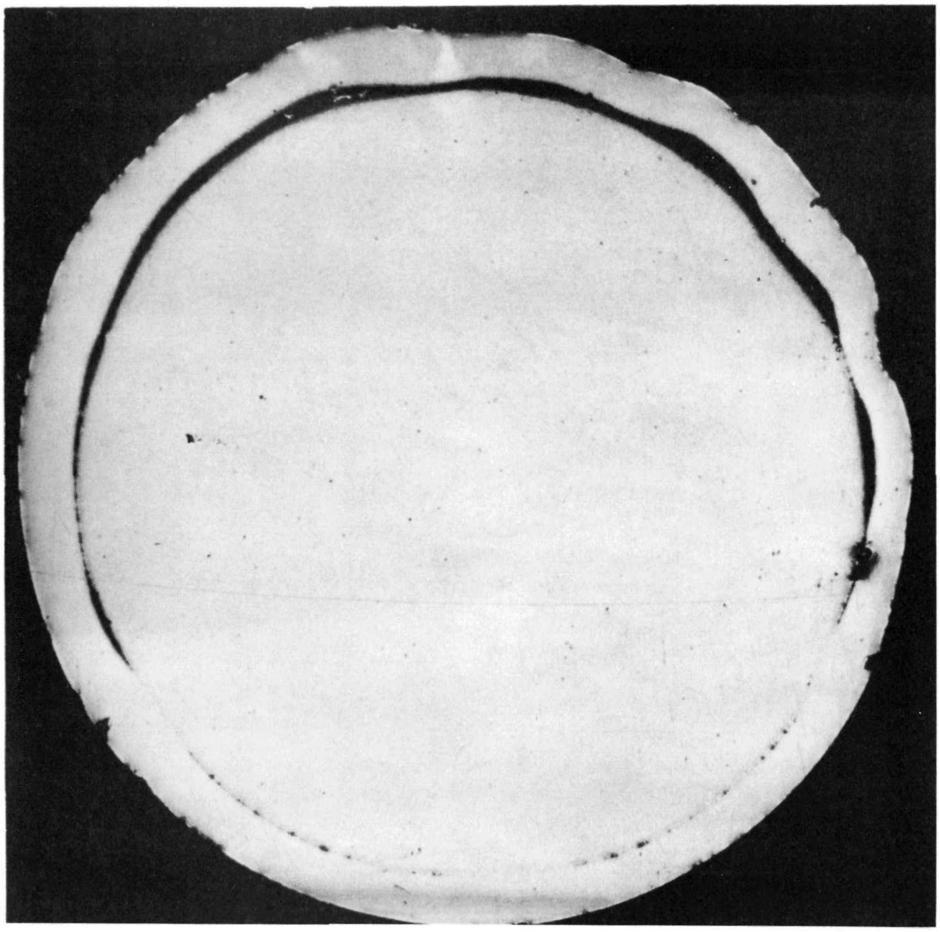
As Corroded Crushed

Figure 9. Appearance of Tubing, Extruded by Torrance Brass, after 515 Days in 290°C Water

Of the three methods, the eutectic pressure bond had been developed by Atomics International (AI) specifically for tubing end closures and thus seemed the most likely prospect for the EBWR program. For this reason, tubes and caps supplied by ANL were joined at AI. After a few relatively short corrosion tests it appeared that the silver eutectic provided better bonding and corrosion resistance than the copper eutectic. Accordingly, a number of ALCOA M654 powder tubes (20 cm long) were sealed by the silver eutectic process with solid end plugs made from wrought alloy of the same composition.

A short (7 days) corrosion test of several of these sealed tubes in 290°C water quickly showed that this bond, although initially helium leak free, had an unsatisfactory resistance to corrosion penetration (see Figure 10). The bulges in the circumference of the sample shown in Figure 10 were larger hollow blisters before the sample was subjected to Bakelite mounting pressures. Although not shown in this figure, some joint areas did exhibit good corrosion resistance. Metallographic examination indicated that these spots had a relatively better bond between the tube and plug than the other areas with poorer corrosion resistance (see Figures 11 and 12).

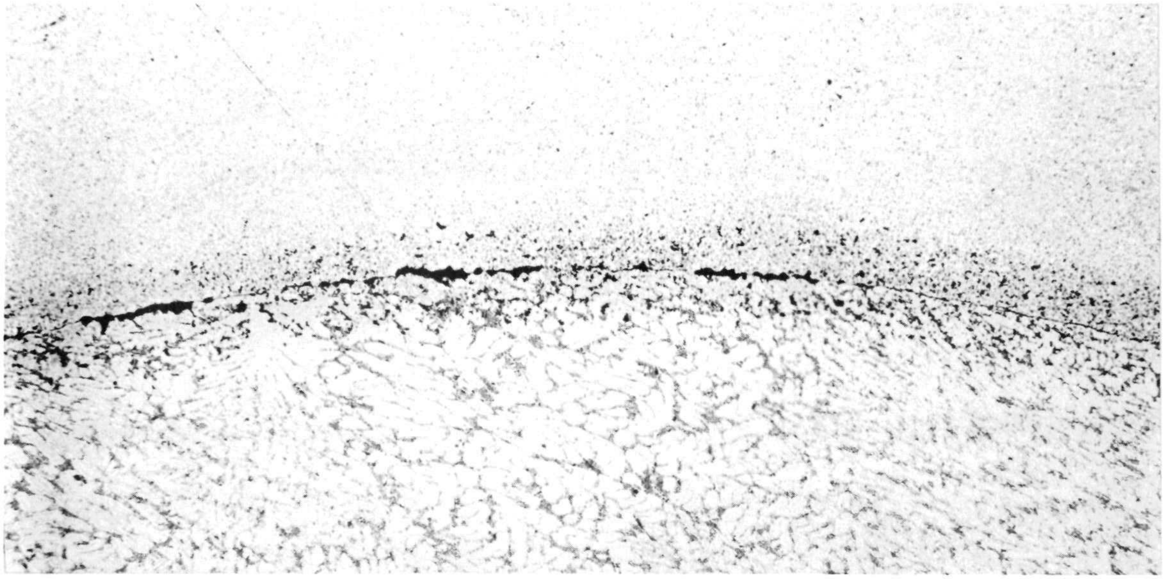
Several modifications of the bonding technique were tried by AI, but high-temperature water selectively corroded the bond line in some areas on all specimens.



31701 As Polished 11X

Exposed 7 Days to 290°C Water

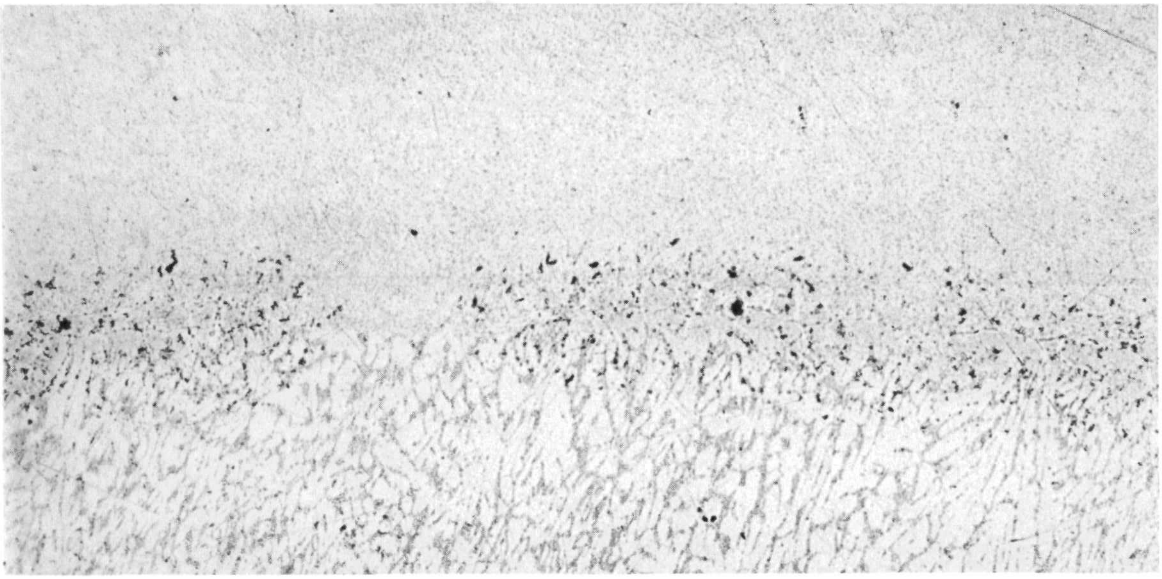
Figure 10. Section through a Failed End Closure



31704 Etched 80X

290°C - 7 Days

Figure 11. Bond Area of Failed Closure

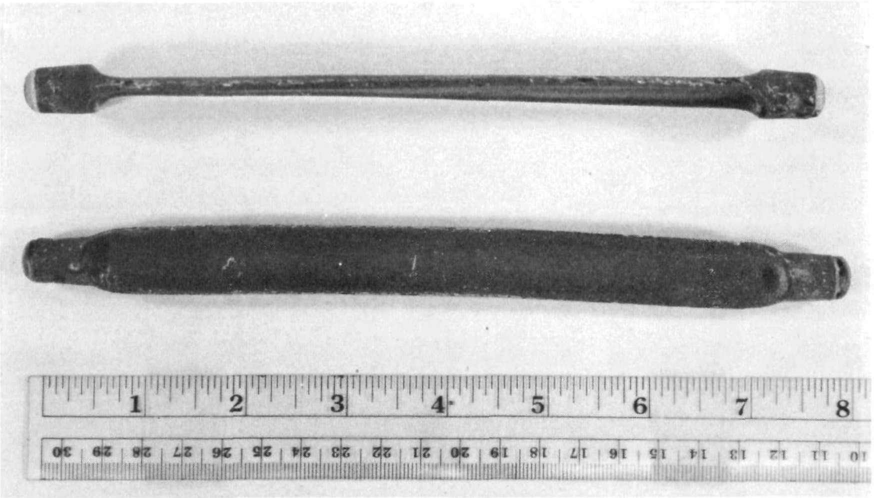


31706 Etched 80X

290°C - 7 Days

Figure 12. Bond Area of "Good" Closure

F. McCuaig of the ANL Coatings and Jacketing Group then used a "motor arc" electric welder to fusion weld the entire end of some of the tubes bonded by AI. The additional welding process greatly increased the resistance to corrosion penetration. For example, five tubes treated in this fashion were tested for a total of 292 days in 290°C water and showed none of the usual visual indications of bond failure (see Figure 13). Transverse sections of several bonded tube ends also indicated no corrosion penetration. Some of the heavy corrosion product flaked off the outside of the tube ends after long exposure, but these relatively bare spots were not attacked on subsequent exposure.



37069 1/2X

Figure 13. Appearance of Sealed Tubes after 292 Days in 290°C Water

The tubes themselves had collapsed since M654 tubing did not have sufficient creep strength to withstand the vapor pressure of the water at 290°C. The internal surfaces of the tubes were still bright, substantiating the observation that penetration of the bonds had not occurred.

Experimental Rod Extrusions

Armour Research Foundation: During the course of the ARF contract many small (0.32-cm-OD) rods were extruded for evaluation of mechanical properties. A smaller number of the promising extrusions were also corrosion tested in 290°C water for extended periods. The pertinent fabrication and mechanical properties data as reported by ARF are shown in Table IV with a generalized corrosion evaluation added in the last column. A graphical representation of the actual corrosion data is given in Figure 14. The spread in values of metal loss of the various extrusions increased as the test progressed. Even for the better extrusions the corrosion rate appeared to increase slightly with prolonged exposure.

Table IV

PROPERTIES OF ARF EXPERIMENTAL ROD EXTRUSIONS

Alloy	Sample Number	Dispersant	Powder Mill Time, hr	Extrusion		UTS, kg/mm^2		YS, kg/mm^2		% Elongation		Corrosion(3)
				Temp, °C	Ratio N:1	27°C	350°C	27°C	350°C	27°C	350°C	
1(1)	2K4	None	72	510	50	21.1	9.4	16.7	8.3	16	8.4	G
1	2U1	None	72	522	90	19.0	-	14.0	-	25	-	G
1	2V1	None	72	448	50	22.0	9.6	17.7	9.1	25	9	F(178)
2(2)	2F1	4 w/o Al_2O_3	340	510	50	24.3	11.0	18.1	10.5	12	4.3	F(29)
2	2O1	5 w/o Al_2O_3	340	510	50	22.6	11.1	18.4	9.6	-	4.2	F(29)
2	2P1	6 w/o Al_2O_3	340	510	50	22.6	9.2	15.1	7.8	15.6	4	F(179)
2	2G1	6 w/o ZrC	340	595/455	50	25.1	-	18.0	-	3.1		G
2	2H1	8 w/o ZrC	340	510	50	25.5	11.7	18.0	10.9	5.5	8	G
2	2I1	10 w/o ZrC	340	510	50	21.8	9.9	17.6	9.5	6.3	4.2	F(87)
2	2S1	3 w/o $AlPO_4$	340	510	50	21.0	-	15.9	-	9.4	-	G
2	2T1	5 w/o $AlPO_4$	340	510	50	24.5	-	16.2	-	3.0		G
2	2Q1	3 w/o SiO_2	340	510	50	23.5	9.0	15.0	8.7	25	8	G
2	2R1	4 w/o SiO_2	340	510	50	23.8	9.8	17.0	9.5	15.6	8	G
2	2E1	5 w/o SiC	340	510	50	25.1	-	17.6	-	-	-	G

(1) Alloy 1 - (A288) 1% Ni, 0.5% Fe, 0.1% Ti, 0.005% Si.

(2) Alloy 2 - 1% Ni, 0.1% Ti.

(3) G means sample survived 270 days in 290°C water in good condition. F means corrosion failure at the indicated number of days in parentheses.

Those products with added Al_2O_3 (Linde B powder) were most susceptible to failure. Sections through samples of the 2F1 extrusion showed that the Al_2O_3 powder had "balled up" in discrete pockets. Other particulate additives of ZrC, $AlPO_4$, SiC, or SiO_2 apparently improved the corrosion resistance to 290°C water when present in the range from 3 to 8%.

Hydrogen analyses were performed on uncorroded rods. During this operation it was noted that several of the powder products were attracted to a powerful permanent magnet. Analyses of the powder products showed a substantially greater amount of iron was present in the product than in the original alloy. These results are shown in Table V.

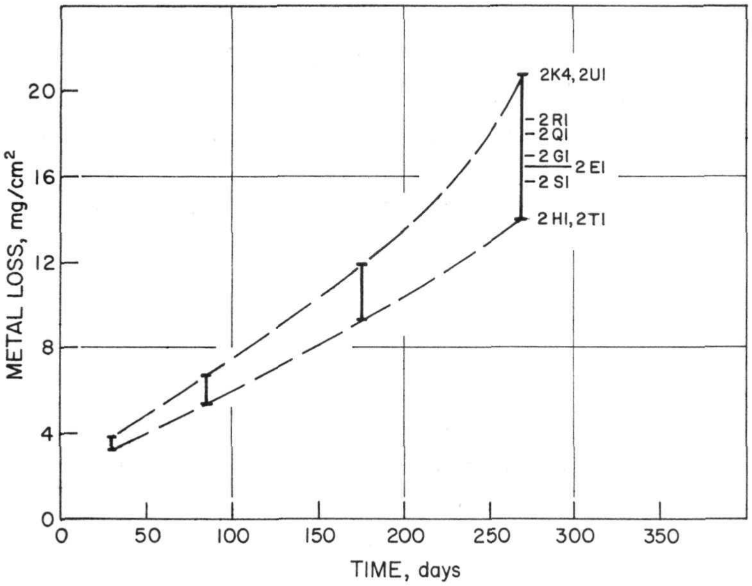


Figure 14. Corrosion of Experimental Rod Extrustions (ARF) in 290°C Water

Table V

IRON AND HYDROGEN CONTENTS OF SELECTED ARF EXTRUSIONS

Sample	w/o Iron		Hydrogen, ppm	Dispersant
	Nominal	Analyzed		
2H1	0	2.9	-	ZrC
2T1	0	0.2	244	$AlPO_4$
2S1	0	0.2	246	$AlPO_4$
2E1	0	3.2	88	SiC
2R1	0	2.3	-	SiO
2K4	0.5	0.5	91	None
2U1	0.5	0.5	67	None
2V1	0.5	0.5	216	None

Arranged in order of increasing total corrosion at 270 days reading down the column. (2V1 failed at 178 days.)

Apparently the abrasive dispersants removed metal from the stainless steel mill and balls. The severely worked stainless steel powder would be expected to be magnetic. There appeared to be no correlation between hydrogen content or iron pickup and corrosion resistance.

Aluminum Company of America: A small quantity of an experimental ALCOA powder product containing 1.4% Ni and 1.4% Fe in relatively pure aluminum was tested in 315°C water flowing at 5.5 m/sec for 147 days.

Observations of the samples were made at approximately one-month intervals. The samples had numerous small blisters after one month, which continued to grow slowly throughout the test. By 2 mo the blisters were large enough to cause the material to be classed as unsatisfactory, but since other wrought alloys in the test were performing well, testing was continued out of curiosity.

At 147 days, several of the blisters had protruded 0.75 mm. Sectioning indicated that penetrations of 1.3 mm occurred under some blisters. The average metal losses of the surfaces not blistered could not be precisely determined because of the blisters, but transverse sections of samples suggested a low uniform rate of attack that would be satisfactory in the absence of the blisters. A single value of the metal loss was obtained at 29 days for an essentially blister-free sample. The metal loss of 4.2 mg/cm^2 compared favorably with a value of 4.7 mg/cm^2 for one of the better wrought alloys in the same test. The powder samples did not suffer the edge corrosion previously described for other powder products.

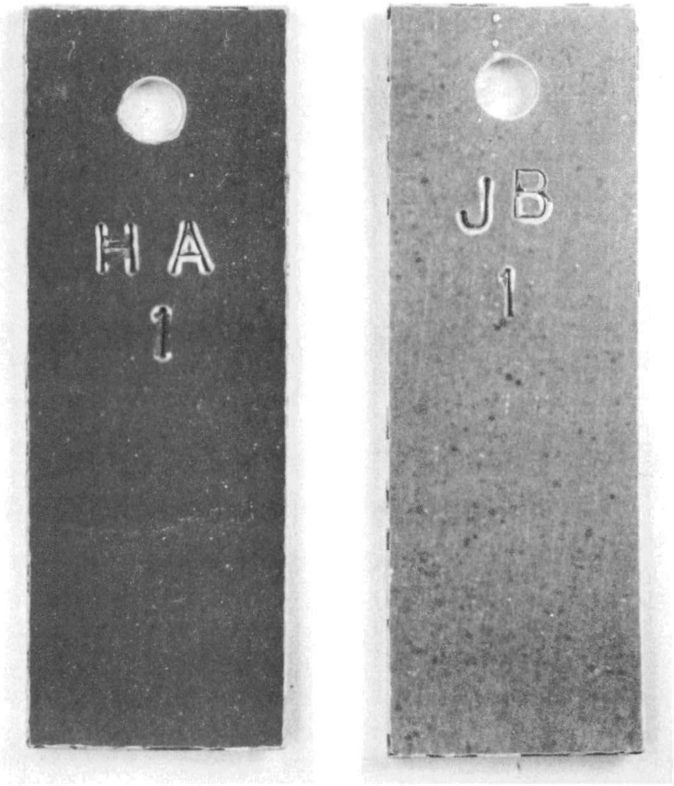
Trefimetaux: Herenguel and Lelong at Trefimetaux, Service des Etudes et Fabrications Nucleaires, supplied small amounts of several different powder products for corrosion evaluation. The pertinent mechanical and chemical data are shown in Table VI. In this table the second letter of the designation, i.e., J, M, G, or H, denotes the extrusion series.

Table VI

PROPERTIES OF TREFIMETAUX POWDER PRODUCTS

Designation	Composition, w/o		UTS, kg/mm^2	
	Ni	Fe	25°C	350°C
BJ4B4 BJ4A4	1	1	25-30	8-9
BM4B4 BM4A4	1	1	22-28	7-8
BG4B4 BG4A4	0.9	2.3	15-20	5-6
BH4B4 BH4A4	0.9	2.3	17-22	6-7

The products were exposed to static 290°C water for 293 days. Both extrusions and thin-sheet samples hot rolled from them were tested. The sheets were used to approximate the sample surface-to-volume ratio of tubing specimens. All demonstrated very satisfactory corrosion resistance, although minor defects, such as small oxide-filled protuberances, were observed (see Figure 15). The M and H series of as-extruded rod specimens developed a saw-tooth attack on one edge of the rectangular cross-section extrusion when first exposed. This did not continue to develop with increasing time and may have been related to poor lubrication of the extrusion die at that point, with resultant defects.



36967 2X

Type BH4A4 Type BJ4B4

Figure 15. Trefimetaux Corrosion Specimens after 293-day Exposure to 290°C Water (Static)

Small blisters and minor surface eruptions were noted on the thin-sheet specimens. Dark specks in the eruptions, with a brown-red stain around the spot, suggested that these were the results of iron inclusions in the aluminum. No edge swelling due to corrosion was noted, but on the G and M series a number of slightly raised ridges of oxide ran from one edge of the specimen to the other, parallel to the rolling direction. Attempts to identify the source of the ridges were inconclusive, and they all but disappeared with continued corrosion exposure.

Values of metal loss were obtained for several specimens of the rolled sheet at three different exposure times, with the results shown in Table VII. It is difficult to compare precisely the corrosion rates of aluminum products corroded in different tests since both the amount of aluminum area and the amount of refreshment can cause variations in corrosion rate. Within these limitations, it appears that the Trefimetaux powder products have as good or better corrosion resistance than the best ARF extruded rod previously described.

Table VII

AQUEOUS CORROSION OF TREFIMETAUX POWDER PRODUCTS AT 290°C

Product	Time, days	Defilmed Metal Loss, mg/cm^2	Average Penetration, μ
BJ4A4	189	11.0	40
BJ4B4	189	9.2	33
BH4A4	189	10.3	37
BH4B4	189	11.4	41
BG4B4	251	11.6	41
BM4A4	251	11.7	42
BM4B4	251	11.3	40
BM4A4	293	12.3	44
BG4B4	293	12.0	43
BH4B4	293	12.5	45

Unfortunately, the dynamic corrosion behavior at 315°C (with water flowing at 5.5 m/sec) was not as satisfactory. Cones of a hard, very dark corrosion product (up to 1 mm in diameter and height) were formed on the surface of some of the specimens in as little as 30 days. The number and size of these cones increased in the order: H extrusion samples (lowest); M (intermediate); and G (most and largest). Disproportionately small pits were located under some cones; under others there were none. X-ray analysis of the cones was confused by the large number of lines obtained even after those for boehmite, the normal aluminum corrosion product, were deleted.

After 89 days of exposure portions of the outer layers of oxide tended to flake off as the sample dried, giving the appearance shown in Figure 16. The black cones previously described are particularly noticeable on the lower sample (G2).

Figure 16. Trefimetaux Corrosion Specimens after 89 Days in 315°C Water Flowing at 5.5 m/second

The metal-loss data were limited by the small number of specimens available. The corrosion of these specimens is compared with that of one of the better wrought alloys (measured in the same equipment) in Figure 17. These powder products appear to suffer considerably more corrosive attack in this environment than does the wrought alloy.

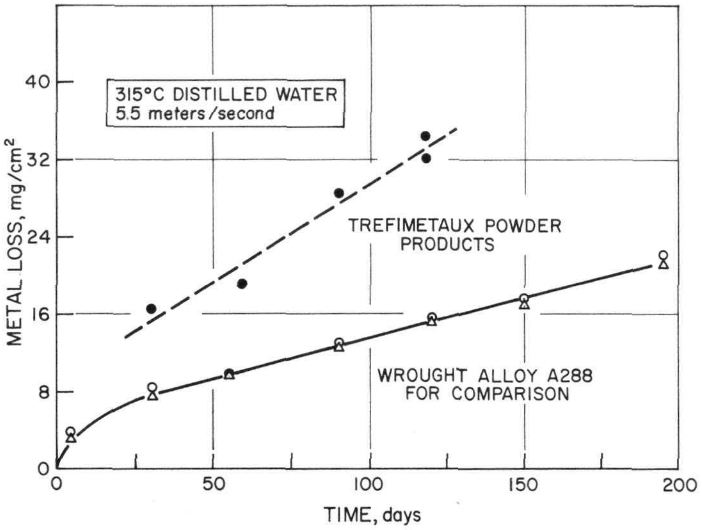


Figure 17. Corrosion of Trefimetaux Specimens in Flowing Water

DISCUSSION

It is obvious from the presentation of the data that the original problem of poor reproducibility of corrosion resistance from one powder product to another has not been eliminated. However, the progress made, particularly by the French at Trefimetaux, is encouraging.

Of all the powder products tested in compiling the data for this report, only three varieties failed rapidly in corrosion testing: M655 tubing (ALCOA), A288 tubing from 72-hr ball-milled powder (ARF), and experimental rods made from aluminum powder milled with added Al_2O_3 (Linde B) powder.

The last named had obvious pockets of porous oxide and metal beneath the surface to explain its poor corrosion resistance. For the other two it has been assumed that the kneading action of the ball mill incorporated milling lubricant (usually of the stearic acid family) into the powder in such a way that it was not subsequently removed. Compacting and extrusion temperatures and pressures would then be expected to decompose the trapped lubricant. The end products might be hydrogen gas (porosity) and an aluminum-carbon compound. A finished product containing a compound of this sort would be expected to have poor corrosion resistance. For example, a casting of an Al-Ni-Fe alloy that was deliberately overheated (to ~1150°C) in a carbon crucible did show very poor corrosion resistance in water.

Powder products with intermediate corrosion resistance appeared to suffer from stringers of inclusions and porosity. These longitudinal stringers result in penetrating attack upon prolonged exposure along the relatively open paths into the metal. Holding the powder products at a sintering temperature prior to corrosion testing may have helped to break the porosity stringers, either by removing the hydrogen (vacuum) or by accumulating the gas into larger disconnected pockets. Discrete microscopic hydrogen bubbles have been observed to form in creep-test specimens held for a long time at high temperature.(9)

A test temperature of about 290°C proved to be more severe than one of 350°C for the low-silicon powder products. Test durations of about 100 days minimum (at 290°C) appeared necessary for the development of the penetrating edge attack on those samples which were intermediate in corrosion resistance. It is not certain that this mode of attack would be significant in reactor fuel-cladding application since the ends subject to penetrating attack would probably be sealed from the coolant.

The corrosion resistance of the small experimental rod extrusions made with particulate additives is difficult to rationalize. The original intent of the additives was to provide increased strength at elevated temperature. This did not occur to any significant extent. However, several of the additives did improve the long-term corrosion resistance. Perhaps their presence in the ball-milling operation modified the kneading process enough to minimize the retention of the milling lubricant within the powder. Hydrogen analyses of these and other products indicated no direct correlation between gas content and corrosion resistance.

The Trefimetaux powder products had the most satisfactory corrosion resistance of all those tested at 290°C. Since the silicon content of the specimens was not analyzed, it is not known if these particular extrusions would perform as well at temperatures of the order of 350°C. If an equivalent grade of tubing (of low-silicon content) could be produced, it would appear to be satisfactory for application in typical boiling water reactors.

The poorer (relative to a wrought alloy) corrosion performance of these powder products in flowing water at 315°C indicated that exact equivalence to wrought alloy resistance has still not been achieved.

Maintaining the corrosion resistance of thin-wall powder-product tubing appears to be somewhat more difficult than for other solid extrusion shapes. Perhaps the large ratio of die contacting surface to aluminum metal volume encourages the incorporation of tramp material and decomposed lubricants into the surface layer of the finished tubing. Such a surface layer of poor corrosion resistance has been noted for some experimental tube extrusions. Inadequate die lubrication, complicated by the large surface-to-volume ratio of the tubing extrusion, could also result in a jerky extrusion with alternate compact and porous sections of the extruded tube.

The use of a bridge die in extruding powder tubing resulted in selective attack (after extended exposure) of some of the seams formed in rewelding the flowing metal streams during extrusion. Since some seams did not suffer selective attack it might be possible to use this extrusion method with powder billets, but only after the seam problem had been overcome.

Kittel(10) has recently observed only minor dimensional changes in prototype elements, consisting of UO_2 pellet fuel in wrought aluminum alloy (A288) jacketing, during reactor irradiation in flowing water at 243°C. This adds a new perspective in considering the requirements for powder products; quite possibly there are reactor applications where the weaker wrought alloys are acceptable.

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