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AQUEOUS CORROSION OF ALUMINUM AT 260°C

by

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ABSTRACT

Ten experimental alloys of aluminum containing up to 4% nickel corroded uniformly, without intergranular attack, when exposed for three months to flowing deionized water at 260°C. The average penetration rates were between 1.4 and 1.9 mils per month.

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INTRODUCTION

Aluminum is generally employed as the cladding material for metallic fuel elements operating at surface temperatures below 200°C in water-cooled piles. Commercially pure aluminum, known as 1100 alloy, is widely used for this application because of its availability, well-developed metallurgy, and desirable physical properties. Although the corrosion penetration of 1100 alloy in deionized water is small at surface temperatures up to about 200°C, at higher temperatures the metal is susceptible to severe intergranular attack. In order to use aluminum cladding in power reactors, which operate with surface temperatures of about 250-350°C, an alloy is needed that has the desirable properties of 1100 alloy with improved resistance to intergranular corrosion. As part of an exploratory program, the corrosion rates of experimental aluminum alloys that were designed to meet these requirements were measured.

SUMMARY

Ten experimental alloys of aluminum showed general corrosion only, without evidence of intergranular attack, after isothermal exposure for 95 days to 20 ft/sec flow of neutral, deionized water at 260°C. The average penetration rates were between 1.4 and 1.9 mils/month for all of the alloys. When the alloys were tested statically under the same conditions of water quality and temperature, the average penetration rates were between 0.1 and 0.4 mil/month. The experimental alloys contained either 99.0 or 99.99% pure aluminum to which had been added 1 to 4% of nickel, up to 1.5% of iron, and in some cases less than 1% of chromium, titanium, or copper. The differences between the corrosion rates of the various alloys in flowing water were not significant. The most widely known of the experimental alloys, X8001, had an average corrosion rate of 1.5 mils/month under the dynamic test conditions.

DISCUSSION

BACKGROUND

In water-cooled reactors, cladding is required on the fuel elements to prevent chemical reaction between the uranium and the coolant and to prevent contamination of the coolant system by radioactive material. The commercially pure, 1100 alloy of aluminum has been widely used as the cladding metal where the surface temperature is 100 to 200°C. However, 1100 alloy undergoes intergranular corrosion at temperatures above about 200°C in neutral, deionized water.[1] Intergranular corrosion is the selective attack that occurs at the grain boundaries and causes rapid conversion of the metal to oxide. The addition of about 1% nickel to 1100 alloy produces an alloy that is considered to be strongly resistant to intergranular attack above 200°C[2]. This alloy, designated X8001, is of interest as a cladding material for fuel elements that operate at high surface temperatures. The principal disadvantage of X8001 alloy is that the rate of uniform corrosion, which can be measured in the absence of intergranular attack, is believed to be moderately high above 200°C.

Specimens of X8001 and nine other experimental nickel-aluminum alloys were obtained from the Aluminum Company of America for determination of their rate of uniform corrosion and their resistance to intergranular attack. Six of the alloys were made by adding various constituents to 1100, or 99.0% pure, aluminum; four were made from 99.99% pure metal. In both cases, the principal variable was the relative amounts of nickel and iron, the former being present in amounts from 1 to 4%, the latter from 0.4 to 1.5%. Chromium, titanium, and copper were also added in small amounts to some of the alloys. The composition of all of the alloys is shown in Table I.

TABLE I

Composition of High Temperature Aluminum Alloys

Alcoa Alloy Designation	Weight Per Cent								
	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti
X8001	0.10	0.54	0.03	0.01[(a)]	0.01[(a)]	0.01[(a)]	1.35	0.05[(a)]	0.01
172955	0.07	0.88	0.01[(a)]	0.01[(a)]	0.01[(a)]	0.01[(a)]	1.38	0.05[(a)]	0.01
192263	0.08	1.44	0.03	0.06	0.03	0.02	1.38	0.02	0.02
192264	0.10	0.34	0.02	0.05	0.02	0.35	2.64	0.02	0.02
192265[(b)]	0.08	0.38	0.76	0.05	0.12	0.02	4.34	0.02	0.03
192597	0.00	1.54	0.01	0.00	0.00	0.00	1.42	0.01	0.00
192598	0.00	0.38	0.01	0.00	0.00	0.00	2.89	0.00	0.00
192599	0.00	0.37	0.01	0.00	0.00	0.37	2.85	0.00	0.00
192600[(b)]	0.00	0.47	0.01	0.00	0.00	0.00	4.33	0.00	0.00
205419[(c)]	0.20	0.47	0.01[(a)]	0.01[(a)]	0.03	0.16	2.20	0.01[(a)]	0.14

(a) Maximum value
(b) Alcoa advises that alloys that contain more than 3% Ni are difficult to fabricate and probably cannot become commerical alloys except as APM alloys.
(c) Contains 0.02% Be and 0.04% Zr

EXPERIMENTAL PROCEDURE

Specimens of the test alloys were exposed to deionized water at 260°C in a pressurized flow loop that was built and was being used primarily for other purposes. Two factors known to be of importance in aluminum corrosion under pile conditions - heat transfer through the metal and water quality with respect to products of corrosion - could not be conveniently simulated. The electrical conductivity of the water in the loop was maintained at 0.2-1.5 micromhos/cm, with oxygen content less than 20 ppb.

The test specimens were strips 13/16 inch wide, 1/16 inch thick, and 6 inches long, cut from sheets of the alloys and subsequently polished with 600-grit emery cloth. Each specimen was cleaned and rinsed in acetone and allowed to dry in air at room temperature before being weighed to the nearest 0.1 mg. Figure 1 is a typical flow test specimen. The 1/4-inch-diameter hole near one end and the 1/4- by 1/2-inch slot near the other end fitted over support pins in the test channel. During the flow test, the specimens were supported inside a stainless steel channel and were insulated from each other and from the stainless steel support pins by "Teflon" spacers.

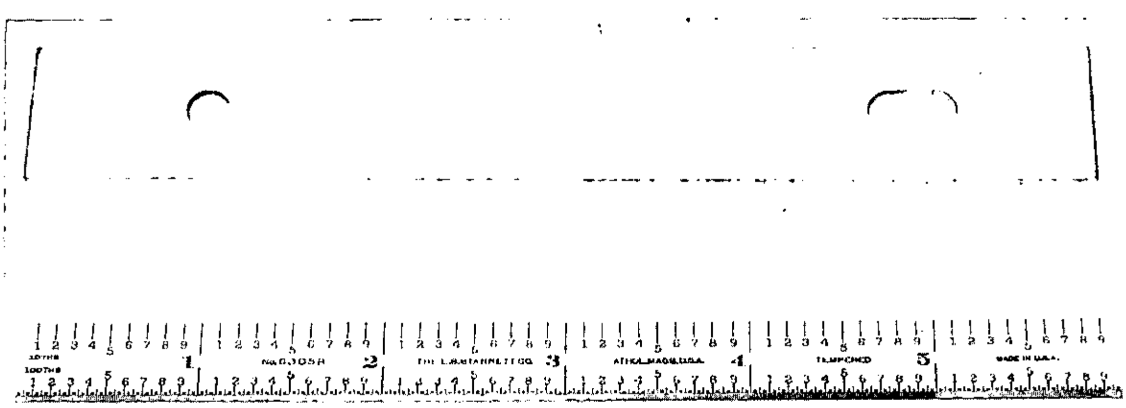


FIG. 1 TYPICAL FLOW TEST SPECIMEN

Figure 2 shows a portion of a test channel, with two groups of specimens in place. The small hole in the baffle beneath the discharge orifices allowed a trickle flow of water past the lower, or static group of specimens. One test channel accommodated six groups, each containing four dynamic specimens between the inlet to the channel and the discharge orifices. Two identical channels were employed to test all of the specimens concurrently. The channels were suspended vertically in the test loop, which was of 1200-gallon capacity and in which neutral, deionized water at 260°C was circulated. The average velocity of water past the dynamic specimens was 20 ft/sec, which corresponded to the downward flow of 55 gpm to each channel. The test loop was constructed of stainless steel except for carbon steel valves and pump. The test conditions are summarized in Table II, page 8.

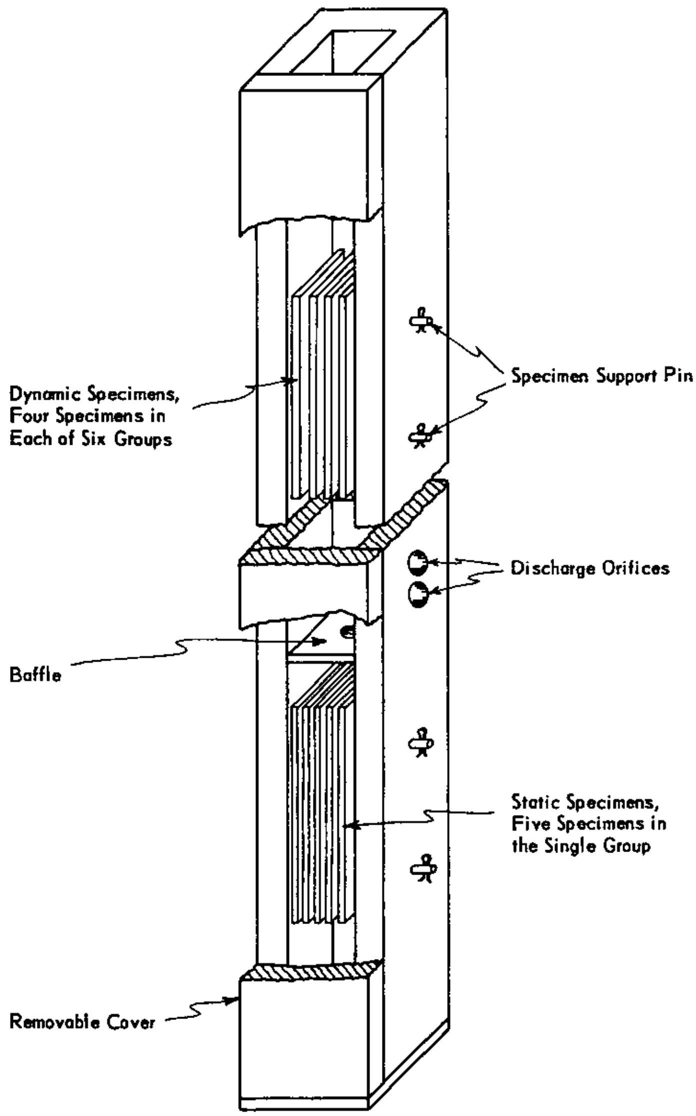


FIG. 2 CORROSION TEST ASSEMBLY

TABLE II

Test Conditions

Temperature	260°C
Pressure	850 psi
pH	6.5-7.5
Conductivity	0.2-1.5 micromhos/cm
Dissolved O_2	<20 ppb
Replenishment	Negligible
Volume of system	1200 gallons
Cleanup rate	1 gallon/minute through deionizer and filter
Ratio of aluminum surface to water volume	1.41 cm^2/liter

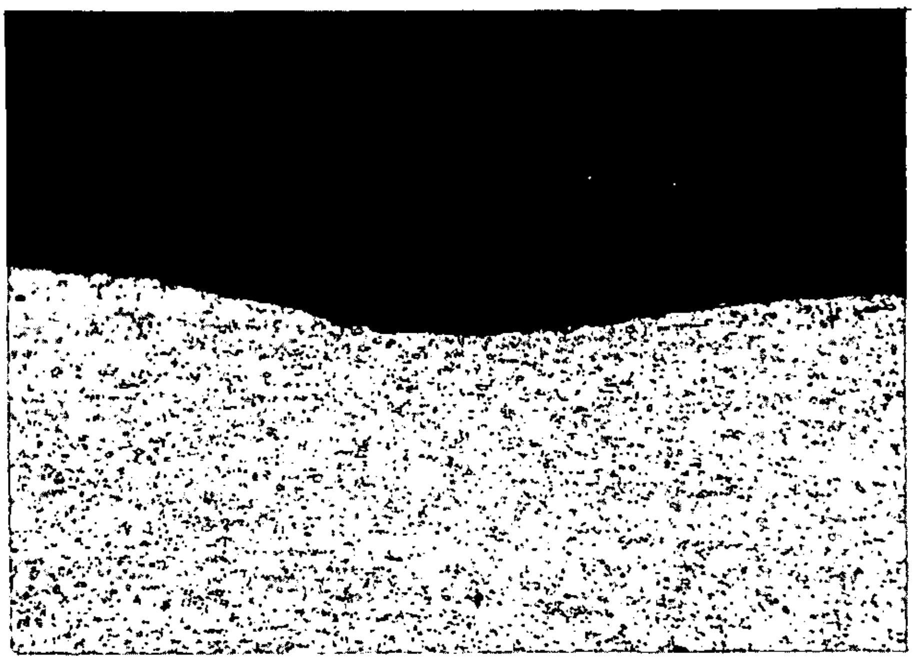
At the conclusion of 95 days of flow testing, the oxide film was stripped from the specimens by an electrolytic method[2], in which an alternating current was passed through a concentrated aqueous solution of boric acid via electrodes that consisted of the test specimen and a clean, uncorroded strip of the same alloy. After being descaled, the specimens were cleaned and rinsed in acetone. The final weighing of each sample was made to the nearest 0.1 mg. The average penetration rates due to corrosion were determined from the metallic weight loss experienced by each specimen during the 95-day test.

After weighing, the stripped samples were mounted in plastic, sectioned, and photomicrographed to determine whether or not intergranular attack had occurred.

RESULTS

Photomicrographs of the sectioned specimens showed no evidence of intergranular attack on any of them. Typical photomicrographs, for the X8001 and 172955 alloy specimens, are shown in Figure 3. The oxide coatings that were stripped off were about 2 mils thick, and the surfaces of the stripped specimens were smooth except for isolated shallow pits and hydraulically eroded regions around the support pins.

Neg. 419 Alloy X8001 500X



Neg. 415 Alloy 172955 500X

FIG. 3 PHOTOMICROGRAPHS OF FLOW TEST SPECIMENS

Water Flow 20 ft/sec
Time 95 days

The average penetration rates were between 1.4 and 1.9 mils/month for the dynamic specimens and between 0.1 and 0.4 mil/month for the static specimens. The test values are summarized in Table III. None of the alloys showed significantly greater resistance to corrosion than that of the X8001 alloy. The specimens were stripped and weighed only after the conclusion of 95 days of testing; therefore, only the end points for the entire test were established. Curves of penetration vs. time, which ordinarily show a high initial corrosion rate followed by a gradual leveling out to a constant lower rate, were not determined.

TABLE III

Corrosion Rates of Aluminum Alloys at 260°C

Average Values of Penetration Rate During 95 Days of Exposure

Alcoa Alloy Designation	Dynamic (20 ft/sec) Specimens, mils/mo		Static Specimens, mil/mo
	Individual Tests	Mean Values	
X8001	1.40 1.48 1.50 1.53	1.5	0.2
172955	1.93 1.94	1.9	0.2
192263	1.40 1.48	1.4	0.2
192264	1.42 1.46 1.48	1.5	0.2
192265	1.45 1.50 1.47	1.5	0.1
192597	1.73 1.84 1.79	1.8	0.2
192598	1.48 1.36 1.47	1.4	0.1
192599	1.34 1.39 1.36	1.4	0.2
192600	1.55 1.57	1.6	0.4
205419	1.40 1.40 1.43 1.44 1.44	1.4	0.1

Visual observations of the stripped specimens showed no gross localized pitting. Around the support pins, however, there were small regions of either high or low erosion, as produced by locally high or low liquid velocities due to eddies. The erosion at the support pins was up to 15 mils deep and can be seen in Figure 4, which is a photograph of stripped and unstripped specimens of X8001 alloy that were tested dynamically. The appearance of the X8001 specimens in Figure 4 was representative of that of the other alloy specimens. Figure 4 also shows that the descaling was not entirely complete, as evidenced by the small dark areas of unremoved oxide. However, it was estimated that in all cases at least 95% of the oxide originally present on the corroded specimens was removed.

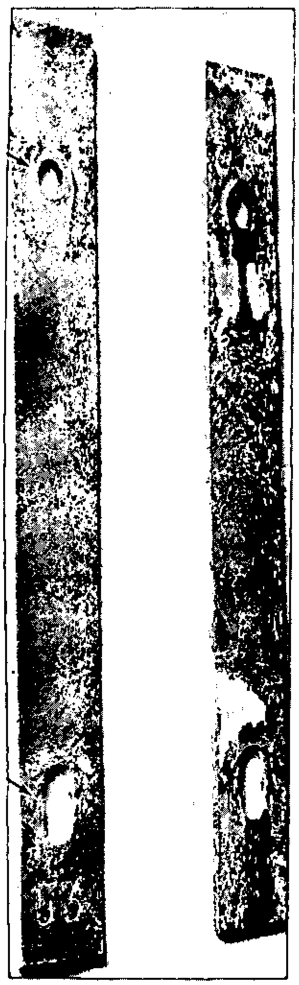


FIG. 4 STRIPPED AND UNSTRIPPED SPECIMENS OF X8001 ALLOY AFTER FLOW TEST

Water Flow 20 ft/sec
Time 95 days

The penetration rates for eight of the alloys tested fell in the range 1.4 to 1.6 mils/month. Differences within this narrow range were considered unimportant. The higher corrosion rates of 1.8 to 1.9 mils/month for the other two alloys, 192597 and 172955, could not be definitely attributed to any factor in the alloy composition. Alloy 192597 had about the same nickel and iron content as an alloy with minimum corrosion rate, 192263, and differed from it only in being made from 99.99% instead of 99.0% aluminum. Alloy 172955 had the same nickel content as X8001 and 192263 and an iron content between the two, but otherwise differed in no particular way from X8001.

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BIBLIOGRAPHY

1. Draley, J. E. and W. E. Ruther. Aqueous Corrosion of 2S Aluminum at Elevated Temperatures. Argonne National Laboratory, Lemont, Ill., AEC Research and Development Report, AECU-2301, 9 pp. (October 1952).

2. Draley, J. E. and W. E. Ruther. Corrosion Resistant Aluminum Above 200°C. Argonne National Laboratory, Lemont, Ill., AEC Research and Development Report, ANL-5430, 37 pp. (July 1955).