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REPORT

CORROSION EVALUATION OF HIGH-SILICON ALUMINUM ALLOYS

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Chemical Metallurgy Section
Reactor and Materials Technology Department

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CORROSION EVALUATION OF HIGH-SILICON ALUMINUM ALLOYS

INTRODUCTION

This report presents a corrosion evaluation which was done on four types of high-silicon aluminum alloy tubing to determine the best alloy or alloys for in-reactor testing.

K. Videm of Norway has shown that aluminum alloys containing 10 to 12 wt% silicon and 1 wt% nickel have good corrosion resistance to flowing deionized water up to 260 °C.⁽¹⁾ Corrosion rates in his loop studies were substantially less for the high-silicon alloy than for alloys similar to 8001. With the possibility that similar improvements might be observed during exposure to hot process water, four types of high-silicon aluminum alloy tubing were purchased, and corrosion evaluation was done.

SUMMARY AND CONCLUSIONS

A battery of tests was performed on four high-silicon aluminum alloys containing nickel and/or magnesium. The tests included high and low flow isothermal and nonisothermal 140 °C water tests, galvanic couples, stress corrosion cracking tests, and tests in 400 °C steam and 360 °C water. HDA-1 and -4 were decidedly superior to the other two alloys in the non-isothermal high flow, the 360 °C water, and the 400 °C steam tests which are considered the tests of most significance. HDA-4 had better resistance in high temperature water and is considered the most promising alloy.

It is recommended that the testing now be expanded to in-reactor initially with coupons, to determine directly the corrosion of these materials in reactor conditions. The best alloy or alloys then could be selected for fuel cladding on a production test basis.

(1) K. Videm, Aluminum Alloys with Improved Corrosion Resistance in High Temperature Water, KR-19, Institutt for Atomenergi, Kjeller, Norway. May, 1962.

EXPERIMENTAL PROCEDURES AND RESULTS

Four alloys were tested during this program. Table I gives the nominal composition of the alloys.

TABLE I

NOMINAL COMPOSITION OF HIGH-SILICON ALUMINUM ALLOYS, wt%

<u>Alloy</u>	<u>Silicon</u>	<u>Magnesium</u>	<u>Nickel</u>	<u>Iron</u>
HDA-1	10	1	1	0.6
HDA-2	6	1	1	0.6
HDA-3	10	1	None	0.6
HDA-4	10	None	1	0.6

These alloys were received in varying sizes of tubing, all of which were tested. The description of the as-received material is given in Table II.

TABLE II

DESCRIPTION OF AS-RECEIVED HIGH-SILICON ALUMINUM TUBING

<u>Alloy</u>	<u>Description</u>	
	<u>OD, in.</u>	<u>Wall Thickness, in.</u>
HDA-1	1.615	0.085
HDA-1	1.445	0.055
HDA-1	0.421	0.055
HDA-2	1.615	0.085
HDA-2	1.445	0.055
HDA-2	0.421	0.055
HDA-3	1.445	0.055
HDA-3	0.421	0.055
HDA-4	1.445	0.055
HDA-4	0.421	0.055

The heavy wall HDA-1 and -2 were slit lengthwise on one side, flattened, and hot rolled to 0.062 in. thickness. The large diameter 0.055 wall tubing was slit lengthwise on one side and flattened without reduction in thickness. The small tubing was split in half lengthwise and the semicircular pieces tested without further mechanical treatment.

All samples were cleaned and etched before each test. The cleaning procedure consisted of vapor degreasing followed by consecutive etches in hot Turco 4181-19; 20 vol%, room temperature HNO_3 ; 30 vol% HNO_3 - 0.5 vol% HF at room temperature; and room temperature 20 vol% HNO_3 . Between each solution the samples were thoroughly rinsed in flowing tap water, and the final rinse was followed by a deionized water rinse and alcohol dip before air drying. This etching procedure yielded a uniform, smooth, clean sample surface.

The method used for measurement of corrosion varied and is given in the test description.

Chemical Analysis

Wet chemical analyses were done on all the as-received materials (Table III). All were in good agreement with the desired composition.

TABLE III

CHEMICAL ANALYSES OF HIGH-SILICON ALUMINUM ALLOYS

Alloy	OD, in.	Composition, wt%			
		Silicon	Magnesium	Nickel	Iron
HDA-1	1.615	9.45	0.78	1.11	0.58
HDA-1	1.445	9.74	0.93	1.10	0.57
HDA-1	0.421	9.00	0.85	1.20	0.58
HDA-2	1.615	5.95	0.96	0.97	0.47
HDA-2	1.445	5.99	1.05	1.05	0.50
HDA-2	0.421	5.79	1.15	1.12	0.50
HDA-3	1.445	10.1	1.06		0.57
HDA-3	0.421	10.1	0.90		0.54
HDA-4	1.445	10.1		1.12	0.54
HDA-4	0.421	9.97		1.14	0.56

Metallography of As-Received Material

Metallography to determine the size and distribution of the intermetallic phases in the alloy was done on all the as-received material. Figures 1 through 4 show the flat, transverse, and longitudinal sections of the large diameter thin wall tubing of each of the alloys. The appearance of the other tubing was essentially the same as this material and is not shown. The intermetallic phases present are as well dispersed and as small as could be expected for alloys of this type. No identification of the compounds present was attempted.

Test 1

High Flow Nonisothermal 140 °C Water

This test gave the closest simulation to operating conditions possible with available equipment. The loop exposed the coupons to 25 ft/sec velocity water. After passing over the coupons the water was cooled to room temperature, then reheated to the desired temperature, thus removing from the results any effect of dissolved aluminum in the water. In reactor operation, since it continues to heat as it passes through the process channel, the water never reaches saturation in dissolved aluminum. In the laboratory test, alum flocculated Columbia River water adjusted to pH 6.6 was used. The water contained 2 ppm sodium dichromate as a pitting inhibitor. The temperature of 140 °C was chosen because at appreciably higher temperatures a scale is precipitated from the water onto loop and sample surfaces. The corrosion rates in this test were determined by quantitative dissolution of the oxide in chromic-phosphoric acid.

All alloys except HDA-2 were tested for a total of 2100 hr along with 8001 as a standard material. HDA-2 corroded faster than the other alloys and was terminated at the end of 1400 hr. Figure 5 shows graphically the results of this test. Alloy 8001 oxidized by an approximately linear rate from the very first of

Flat

Longitudinal

Transverse

FIGURE 1

Microstructure of As-Received HDA-1
250X

Negatives 4L923; 4L924; 4L922

Flat

Longitudinal

Transverse

FIGURE 2

Microstructure of As-Received HDA-2
250X

Negatives 4L932; 4L933, 4L931

Flat

Longitudinal

Transverse

FIGURE 3

Microstructure of As-Received HDA-3
250X

Negatives 4L938; 4L939; 4L937

Flat

Longitudinal

Transverse

FIGURE 4

Microstructure of As-Received HDA-4
250X

Negatives 4L944; 4L945; 4L943

FIGURE 5
Corrosion of Aluminum Alloys in 140 °C
Nonisothermal Process Water at High Flow

the test. The oxide of 8001 was evidently very highly stressed, and as soon as it dried, it curled and spalled. Figure 6 shows a 8001 sample after 720 hr exposure with a view of the spalled film. The curling of the film was probably caused by high stress. This effect was not seen on any of the silicon-bearing alloys. The oxide on the silicon-bearing alloys was more adherent and, though a small amount of it could be wiped off when dry, for the most part it was retained by the sample. Because of this non-adherent film, it was not possible to evaluate the thickness of the protective film in detail.

The calculated linear rate for each alloy between 700 hr and test termination is given in Table IV.

TABLE IV

LINEAR CORROSION RATE OF HIGH-SILICON ALUMINUM AND
8001 ALLOYS IN 140 °C WATER WITH A 70 °C ∇ T

<u>Alloy</u>	<u>Linear Rate, mils/yr</u>
8001	31.4
HDA-1	13.0
HDA-2	21.9
HDA-3	18.1
HDA-4	14.4

After 1400 hr exposure HDA-3 showed a shallow pitting type of attack (Figure 7). This was the only nonuniform attack seen on any of the alloys during this test. The results of this test indicate that HDA-1 and HDA-4 are the best alloys tested in this experiment.

A low flow test was run in the nonisothermal loop at the same time as the high flow test. The low flow results were erratic and will not be reported. However, in no case did the penetrations exceed those reported later for a low flow isothermal test in the same water and temperature conditions.

14X

7X

FIGURE 6

Spalled Film from 8001
in Nonisothermal Loop Test

Negatives 4L1878; 4L1876

FIGURE 7
Pitting on HDA-3
in Nonisothermal Loop Test
7X

Test 2

High Flow Isothermal 140 °C Water

This test was run under the same conditions as Test 1, except that the water remained at constant temperature as it circulated. Table V gives the average penetrations for each of the alloys. The 8001, HDA-1, and HDA-2 data are an average of four points for each exposure and the HDA-3, and HDA-4 data are an average of two points.

As can be seen from Table V, the results of this test were erratic. This was partially due to difficulty in stripping the film from the samples. The film was much more adherent than the films seen in Test 1. No definite conclusions can be drawn, but HDA-3 did appear to show significantly less penetration than the other alloys in this test.

TABLE V
PENETRATION IN MILS OF ALUMINUM ALLOYS
IN HIGH FLOW, pH 6.6 ISOTHERMAL WATER

Time, hr	Alloy				
	<u>8001</u>	<u>HDA-1</u>	<u>HDA-2</u>	<u>HDA-3</u>	<u>HDA-4</u>
240	1.92	2.05	1.24	1.60	2.10
720	2.37	2.25	2.02	1.56	1.95
1440	(a)	2.76	2.44	2.01	2.71

(a) These samples did not strip completely before the metal was attacked by the stripping solution.

Test 3

Low Flow Isothermal 140 °C Water

The results of this test are given in Table VI. The test conditions were the same as for Test 2 except the water was not at high velocity. The number in parenthesis is the number of samples used to obtain the average penetration.

TABLE VI
PENETRATION IN MILS OF ALUMINUM ALLOYS
IN LOW FLOW, pH 6.6 ISOTHERMAL WATER

Time, hr	Alloy				
	<u>8001</u>	<u>HDA-1</u>	<u>HDA-2</u>	<u>HDA-3</u>	<u>HDA-4</u>
240	0.23 (2)	0.29 (10)	0.25 (10)	0.19 (8)	0.30 (8)
720	0.49 (2)	0.61 (10)	0.49 (10)	0.41 (7)	0.60 (6)
1440	0.70 (1)	0.83 (5)	0.72 (10)	0.48 (4)	0.77 (4)
2160	0.77 (1)	0.88 (5)	0.81 (4)	0.53 (4)	0.89 (5)

In this test all alloys show close to the same penetrations during the entire test except HDA-3 which consistently showed lower penetrations.

Test 4Galvanic Couples in 140 °C, pH 6.6 Water

This test was run in conjunction with Test 3. Flat stock of each alloy was bolted to 8001 and 1245 aluminum, Zircaloy-2, and 304 SS. The observations, made after 1440 hr exposure and stripping of the samples, are given in Table VII. Except where specified, all pitting occurred in the crevice area.

TABLE VIIEFFECT OF GALVANIC COUPLING ON HIGH-SILICON ALUMINUM ALLOYS

<u>Alloy</u>	<u>Couple</u>	<u>Observation of Condition of Aluminum Alloy</u>
HDA-1	304 SS	No deep pitting
	Zircaloy-2	No deep pitting
	1245	One medium pit
	8001	Several medium pits
HDA-2	304 SS	Several deep pits on exposed face in crevice
	Zircaloy-2	Some small deep pits
	1245	Some small shallow pits
	8001	Two deep pits
HDA-3	304 SS	Badly pitted over entire sample
	Zircaloy-2	One deep pit; many medium and small pits
	1245	Many small deep pits; several medium pits
	8001	One deep pit; several medium and small pits
HDA-4	304 SS	Badly pitted
	Zircaloy-2	Several medium shallow pits
	1245	Four medium deep pits on exposed face; one deep and several small pits in crevice
	8001	Several medium shallow pits
8001 and 1245	All HDA	Some minor pitting but no severe attack; appears random as to couple

None of the Zircaloy-2 or 304 SS samples used for coupling showed any evidence of attack.

HDA-3 was obviously the most affected by coupling to the other metals, probably because of the absence of nickel in this alloy. HDA-1 appeared to be the least affected in this test. Similar results were obtained in a 50 °C test.

Test 5Stress Corrosion in 140 °C, pH 6.6 Water

This test was also run simultaneously with Test 3. U-bend specimens of each of the four alloys were fabricated and exposed for 1440 hr. After visual examination the samples were stripped, again visually examined, and checked with dye penetrant. No evidence of cracking was found on any of the alloys. A test in 50 °C water gave the same results.

Test 6400 °C, 100 psi Steam

Tests 6 and 7 were run to determine the resistance of the experimental alloys to high temperature water and steam. The possibility of fuel cladding over-heating exists in any reactor, and a good cladding material should have at least limited high temperature corrosion resistance.

The samples were first examined after five days exposure. The HDA-3 coupons had been completely destroyed, and most of the rest of the alloys were blistered to some extent. It is known that hydrogen in the steam has an effect on the corrosion resistance of aluminum under these conditions so the test was restarted without HDA-3 coupons. The samples were examined at 5, 10, 15, 20, and 30 days. After 30 days exposure, 8001 coupons were visably blistered while the HDA-1, -2, and -4 coupons showed no evidence of attack. The coupons were sectioned and examined for internal voids which have been seen previously in alloys after steam tests. Alloy 8001 had voids scattered uniformly throughout the metal while the three HDA alloys showed no void formation. The difference is shown in Figure 8. All the HDA alloys appeared the same so just one is shown here. This test confirms Videm's work in which he reported that alloys similar to the HDA alloys were more resistant to steam than was 8001.

HDA-1

8001

FIGURE 8

Appearance of Samples After 30 Days in 400 °C Steam
250X

Negatives 4L2111B; 4L2109D

Test 7360 °C, High Purity, Low Flow Water

This test was done in $>1 \text{ M}\Omega$ water at low flow. This has been the standard evaluation test for alloys in high temperature water for some years and the performance of 8001 in these conditions is well established. Corrosion measurements were made by weighing the sample as removed from the autoclave, dissolving the uncorroded metal in an iodine-methanol solution, and then weighing the film which does not dissolve in this solution. The metal penetration can then be calculated from the metal lost during the test. Table VIII gives the results of this test.

TABLE VIII
PENETRATION IN MILS OF ALUMINUM ALLOYS
IN 360 °C HIGH PURITY WATER

Time, hr	Alloy				
	<u>8001</u>	<u>HDA-1</u>	<u>HDA-2</u>	<u>HDA-3</u>	<u>HDA-4</u>
227	0.43	0.61	0.54	Destroyed	0.62
709	0.80	0.92	0.81		0.87
1438	1.11	1.71 ^(a)	1.62 ^(a)		1.37

(a) Blistered

As can be seen from Table VIII, HDA-3 was destroyed in less than 10 days and HDA-1 and -2 were blistered after 2 mo exposure. HDA-4, although slightly more corroded than 8001, showed no blistering and was by far the best of the experimental alloys in this test. Figure 9 shows the difference between the metal-oxide interface of HDA-1 and HDA-4.

DISCUSSION

From the data of the described tests, the experimental alloys can be ranked in comparative resistance to the different environ-

HDA-4

HDA-1

FIGURE 9

Appearance of Samples After 2 Mo in 360 °C Water
250X

Negatives 4L1980; 4L1985

ments. With such a ranking it is possible to determine the alloys which show the most promise for further testing in- or out-of-reactor. The alloys are shown in Table IX as having good, fair, or poor resistance to the respective environments.

TABLE IX
RANKING OF EXPERIMENTAL ALUMINUM BY RESISTANCE
TO VARIOUS ENVIRONMENTS

Test Type	Alloy			
	HDA-1	HDA-2	HDA-3	HDA-4
1. 140 °C High Flow Nonisothermal Water	Good	Fair	Poor	Good
2. 140 °C High Flow Isothermal Water	Fair	Fair	Good	Fair
3. 140 °C Low Flow Isothermal Water	Fair	Fair	Good	Fair
4. 140 °C Galvanic Couples	Good	Fair	Poor	Fair
5. 140 °C Stress Corrosion	Good	Good	Good	Good
6. 400 °C, 100 psi Steam	Good	Good	Poor	Good
7. 360 °C High Purity Low Flow Water	Fair	Fair	Poor	Good

Alloys HDA-1 and -4 are the two alloys with the best average resistance for the entire battery of tests. If the tests are ranked in relative importance, then probably Tests 1, 6, and 7 are the most significant tests; and HDA-4 is the alloy that would be selected as the most promising.

A further study of the thickness of the retained oxide film under nonisothermal conditions is highly desirable since the film thickness affects the metal surface temperature which in turn affects the corrosion of the material. Such a study could be more easily done in the out-of-reactor nonisothermal loop than with in-reactor coupons, because of the greater ease of handling the non-irradiated material.

The evaluation should now be extended to in-reactor testing, at first preferably with coupons. It is realized that with coupons the effect of heat transfer cannot be evaluated. However, since the planned usage of these alloys involves cladding by an

experimental process, it is felt that the only way to evaluate the corrosion of the alloy separate from the canning process is to use coupons. From the results of this in-reactor test, the most promising alloy for use as cladding could be selected.

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