ANL-6053
Metallurgy and Ceramics
(TID-4500, 15th Ed.)
AEC Research and
Development Report

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CORROSION OF ALUMINUM-URANIUM ALLOYS IN HIGH-TEMPERATURE WATER

by

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Metallurgy Division
Program 10.1.10

November, 1959

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

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ABSTRACT

Sixty-day corrosion tests were performed in water at 290°C with unirradiated aluminum-uranium alloys containing 2 w/o nickel and $\frac{1}{2}$ w/o iron, with several uranium contents from 15 w/o to 53 w/o. The maximum metal penetration rate (4 mils per year by extrapolation) of these alloys was no more than twice that of X8001 aluminum cladding alloy at the same temperature.

Preliminary testing in water at 350°C indicated good corrosion resistance for this alloy system up to a maximum of 80 w/o uranium.

INTRODUCTION

The proposed use of an aluminum-uranium alloy for the fuel of the Argonne Low Power Reactor (ALPR) in 1957 created interest in its high-temperature aqueous corrosion behavior. Since previous experience(1) with aluminum alloys had shown the value of small amounts of nickel and iron in inhibiting corrosion, these elements were incorporated into the fuel alloy from the start of the program. The poor corrosion resistance of some binary aluminum-uranium alloys has since been described by Bowen and Dillon.(2)

Initial success with the relatively low uranium-aluminum alloys led to an extension of the program into the higher uranium region, although no specific uses for these alloys were proposed in current reactor design.

EXPERIMENTAL

Several different techniques were used in alloy preparation. The 15 w/o and 20 w/o uranium alloys were part of production-size melts made in a large vacuum furnace. A thoria-lined graphite crucible was used and the metal was cast into slabs in thoria-lined, hot graphite molds. The slabs were hot rolled to a thickness of about 0.2 in.

The 53 w/o uranium alloy was made in a small vacuum furnace. A thoria-lined graphite crucible was used and the metal was cast into a cylindrical, copper, water-cooled mold. Unfortunately, the center of the casting proved to be slightly porous. The alloy proved to be too brittle to hot roll by ordinary techniques so it was corrosion tested in the as-cast condition.

The high uranium alloys were made in an inert gas tungsten arc furnace. Only about 10-gm buttons of an alloy could be prepared using this furnace. The once-melted buttons tended to fragment when they were turned over and remelted. To avoid this violent fragmentation the buttons were deliberately broken into several pieces and successfully remelted. The buttons were tested in the as-cast condition.

The corrosion testing was performed in double-distilled water at 290 and 350°C. At 290°C, a refreshed autoclave system ($\sim\frac{1}{2}$ liter per hour) was used. At 350°C, small autoclaves were degassed by boiling prior to sealing and placed in a 350°C oven for the duration of the test. In both test systems the alloy was electrically insulated from the stainless steel autoclave by artificial sapphire rods.

Samples were prepared by wet grinding to 240 grit (Durite). They were then measured, degreased and weighed just prior to corrosion testing.

The loss of metal due to corrosion was obtained by difference after dissolving the metal remaining at the termination of the test with methanol iodine solution. The concentration of this solution was 10 gm I_2 per 100 ml CH_3OH.

DATA AND RESULTS

The first testing was performed with material representing possible extremes in the proposed ALPR fuel alloy. The analyzed compositions are shown in Table I and the corrosion curves in Figures 1 and 2.

A comparison of the corrosion rates for the two alloys is difficult due to scatter in the results for the 20% alloy. Experience with aluminum alloys suggests that the corrosion resistance might be sensitive to the distribution of the insoluble phases.(1) Segretation was probably more severe in the 20% alloy and may account for the difference from sample to sample.

TABLE I

Chemical Analysis of Aluminum-Uranium Alloys

Alloy No.	Percent		
	U	Ni	Fe
11	15.03	2.22	0.43
23	20.07	1.98	0.39
	(balance aluminum)		

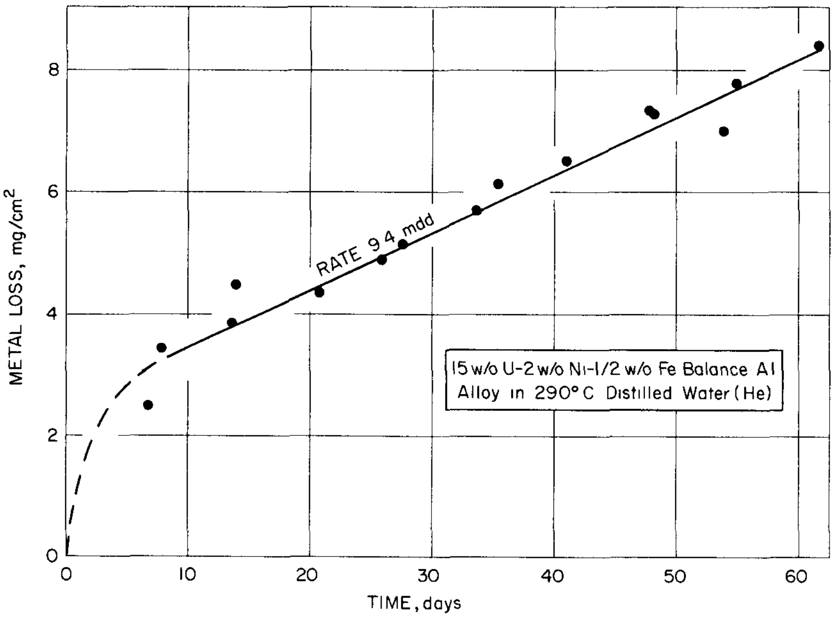

FIGURE 1 CORROSION OF A 15 w/o U FUEL ALLOY

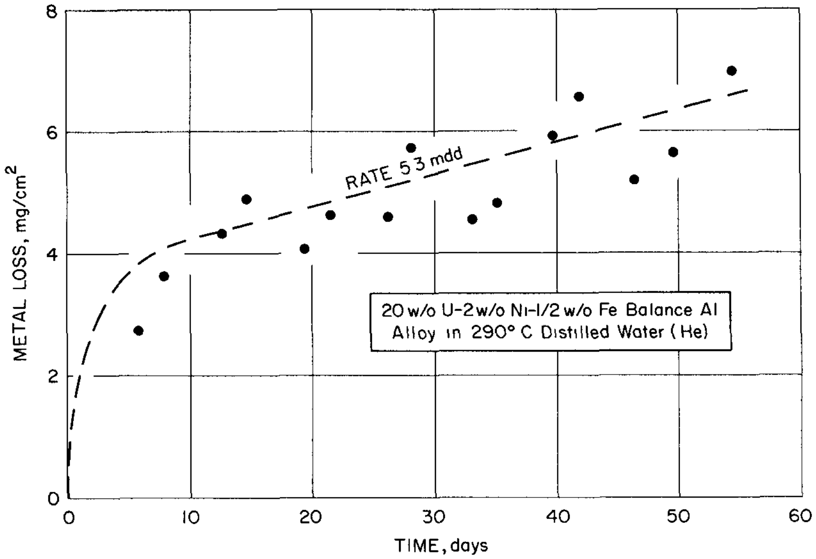

FIGURE 2 CORROSION OF A 20 w/o U FUEL ALLOY

The corrosion rate in Figure 1 can be conveniently compared with that of the X8001 cladding alloy. Allowing for the slight increase in density, the 15 w/o U alloy is penetrated about twice as fast as X8001 at the same temperature (290°C).

An additional test of a similar 16 w/o U-2 w/o Ni-$\frac{1}{2}$ w/o Fe-Al alloy was performed in water at 350°C. Duplicate samples corroded to the extent of 6.06 and 6.48 mg/cm^2 (less than 0.001 in.) in a 38-day exposure. No sign of intergranular or accelerated corrosive attack was noted in any of the above tests.

A 52.7% U-2.1% Ni-0.6% Fe-Al alloy was also tested at 290°C. As mentioned previously, the center of the casting was porous in spots. Two corrosion samples were discarded because of obvious internal corrosion of the central area of the casting. They were eliminated since excessive corrosion was due to casting difficulties rather than to an inherent poor corrosion resistance of the alloy. As shown in Figure 3, the overall resistance is excellent. With an estimated density of about 5 gm/cm^3, the measured corrosion rate of ~6 mg/dm^2-day (mdd) represents a penetration ràte slightly lower than for the X8001 cladding alloy. This alloy also was tested for one day at 350°C without signs of intergranular corrosion.

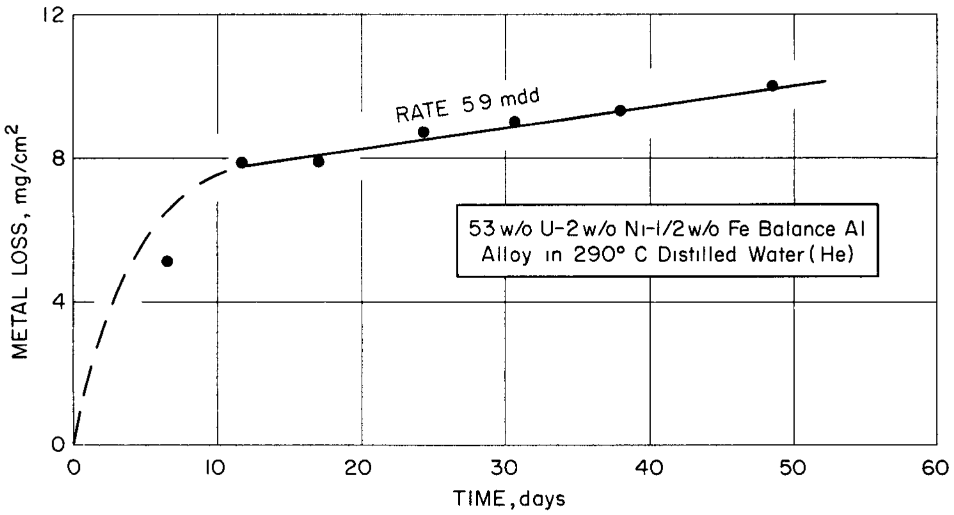

FIGURE 3 CORROSION OF A 53 w/o U FUEL ALLOY

Corroded samples were coated with a heavy, dark corrosion product. Powder X-ray analysis of the corrosion product after removal in the methanol-iodine bath indicated strong $\alpha Al_2O_3 \cdot H_2O$ lines and weak and diffuse UO_2 lines.

The rather good performance of the 53% U alloy suggested possibilities for a corrosion-resistant, high uranium alloy. Small arc-melted button samples and short tests at 350°C were used to explore the high uranium region. The results are summarized in Table II.

It became apparent that a sudden transition in corrosion behavior occurred at 80-82% U. In an effort to extend this limit, Nb, Mo and Ti additions were tried without success.

The alloys which broke into pieces on corrosion test showed a fine network of cracks in the as-cast button. Although other uranium alloy systems fail by corrosion-initiated cracking, these U-Al alloys were so damaged prior to testing that it was impossible to ascertain whether new cracking had been initiated by corrosion.

TABLE II

Exploratory Corrosion Testing of Uranium-Aluminum Alloys

Alloy Nominal Composition, percent					Corrosion Test at 350°C for 1 day
U	Al	Ni	Fe	Other	
60	37½	2	½		Good Resistance
70	27½	2	½		Good Resistance
80	17½	2	½		Good - Broken up
80	19	½	½		Good - Broken up
80	18	2	0		Good - Broken up
80	20				Intergranular attack
82	17	½	½		Disintegrated
82	15.9	1	1	0.1 Ti	Disintegrated
87	10	½	½	2 Mo	Disintegrated
87	10	½	½	2 Nb	Disintegrated

DISCUSSION

The unirradiated corrosion resistance of the ALPR fuel alloy is more than sufficient to insure against a disastrous corrosion failure in a perforated fuel element. In general, the sensitivity of corrosion rate to irradiation varies with the particular alloy system, some systems showing essentially no effect and others a very strong dependence. Since no data exist for this particular system, due caution should be exercised in applying the unirradiated corrosion rates to actual reactor corrosion.

Experiments with higher uranium alloys suggest that the total amount of nickel and iron could be reduced but not eliminated in this fuel alloy and still retain good resistance to high-temperature water.

The sharp transition in corrosion behavior with increasing uranium content occurs at the UAl_2 composition. With more uranium than corresponding to this composition, the alloy would be expected to have an α uranium phase. It seems likely that the presence of this phase destroys the corrosion resistance. An attempt was made, without success, to tie up the α uranium phase with molybdenum or niobium to increase the corrosion resistance. Unfortunately the upper uranium limit of the corrosion resistant alloys falls short of the range of interest of most reactor designers.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Mr. D. Dorman in performing the corrosion testing.

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