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Argonne National Laboratory

SUMMARY
OF
CORROSION INVESTIGATIONS ON HIGH-TEMPERATURE ALUMINUM ALLOYS

February 1955 - October 1957

by

C. R. Breden and N. R. Grant

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C. R. Breden and N. R. Grant

Reactor Engineering Division

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SUMMARY OF CORROSION INVESTIGATIONS ON HIGH-TEMPERATURE ALUMINUM ALLOYS

C. R. Breden and N. R. Grant

I. INTRODUCTION

This report is a compilation of corrosion studies performed during the period February, 1955, to October, 1957, to evaluate aluminum alloys developed for use as cladding material for fuel elements in pressurized water-cooled reactors at temperatures ranging from 500 to 600°F. The alloy compositions included basic 2S aluminum containing nickel, nickel and iron, and special alloys of aluminum and copper.

Specimens of each alloy were evaluated in semistatic and in dynamic streams in isothermal test loops at ANL. These loops were designed to simulate operating conditions of interest (exclusive of radiation) to the pressurized water reactor program, using water conditioning compatible with the most advanced technology for crud and corrosion control for pressurized water systems.

Studies of the most promising alloys of aluminum and nickel were extended to include corrosion-irradiation environments in the test loops at MTR, and boiling heat transfer conditions in heat through-put loops at ANL.

The data include and supplement information published in Reactor Engineering Division Quarterly Reports,(1,2) internal memoranda, and reports to the U.S. Navy Task Group on Aluminum Alloys. Subsequent studies will be described in another report.

II. HISTORICAL

Early in February, 1955, the Argonne Metallurgy Division Corrosion Section, headed by Dr. J. E. Draley, advanced a theory of catastrophic disintegration of 2S aluminum in water at temperatures above 392°F (200°C)(3,4) and three mechanisms of protection:

(1) use of anodic solutions containing nickel ion;
(2) nickel plating of the aluminum;
(3) alloying of the aluminum with nickel or certain other elements.

Method (1) was designed to prevent diffusion of atomic hydrogen through the oxide layer and subsequent blistering and disintegration of the aluminum metal. Draley showed this could be accomplished by adding to the water certain salts which would deposit dendrites of proper overvoltage to effect combination of atomic hydrogen into nondiffusing molecular hydrogen on the surface of the material. The disadvantages of this method were as follows:

(1) The adjustment of pH required to maintain the salts in solution at a level high enough to afford the desired protection. The solutions used by Draley included 5 ppm Ni ion at pH 3.5, 10 ppm at pH 3.7, and 20 ppm at pH 6.

(2) Without pH control, the depletion of the test solution would pose a serious problem of deposition in reactor heat transfer loops. Draley reported that the nickel lost from the test solution went into the formation of a slime which deposited on the samples and the autoclave walls. This deposit also formed in the small-diameter preheater tube, causing experimental shutdowns.

The application of nickel plating on 2S aluminum to provide an atomic hydrogen-combining film achieved considerable success in dynamic corrosion test loops at ANL.(1,5) The nickel plating was applied either by the "Kanigen" dip process or by electrodeposition. Unfortunately, the success was short-lived: both the Kanigen-plated and the electroplated samples lost the nickel-protective layer upon exposure to a combined corrosion-irradiation environment in the ANL Loop at MTR.(5)

With the problems of the first two mechanisms in mind, the use of an alloying agent, consistent with the hydrogen penetration theory, was considered to be the most feasible method of protection against blistering and disintegration of the aluminum. In this connection, Draley had reported the development of blister-resistant alloys of aluminum for use in distilled water at temperatures up to at least 350°C. These were pure aluminum; alloys of 2S aluminum and nickel, nickel and iron; and alloys of aluminum and copper. The alloys of 2S aluminum and nickel, and of aluminum-nickel-iron required the least additions of alloying agents (0.5 to 1.0 wt-%), while copper and iron alone in aluminum required larger weight-percentages (6 to 8%) of additives. Other alloys were also resistant, but made use of high neutron-absorbing materials, such as cadmium.

The ensuing sections describe the series of tests performed to evaluate the behavior of these alloys upon exposure to environments peculiar to high-temperature, high-pressure, water-cooled and moderated nuclear reactor systems.

III. TEST EQUIPMENT AND PROCEDURES

A. Preparation of Samples

Most of the material used in the tests was direct-chill cast and hot rolled by the vendor in conformance with specifications prescribed by ANL. At Argonne, the material was further reduced 50% by cold rolling and machined to size (~2 in. long, $1\frac{7}{8}$ in. wide, $\frac{1}{8}$ in. thick).

The machined specimens were cleaned by immersion for one minute in 10% NaOH followed by one minute in 10% HCl. The samples were rinsed with distilled water, then with alcohol, measured, and weighed on an analytical balance. Certain alloys that could not be cleaned by this method (copper alloys, in particular) were simply degreased. Exploratory loop tests on degreased samples and pickled samples of aluminum-nickel alloys showed that the pickling had no visible effect on the corrosion behavior.

B. Loop Tests

For the most part, the sample alloys were exposed in the semi-static and dynamic test sections of four isothermal test loops at ANL (see Fig. 1).

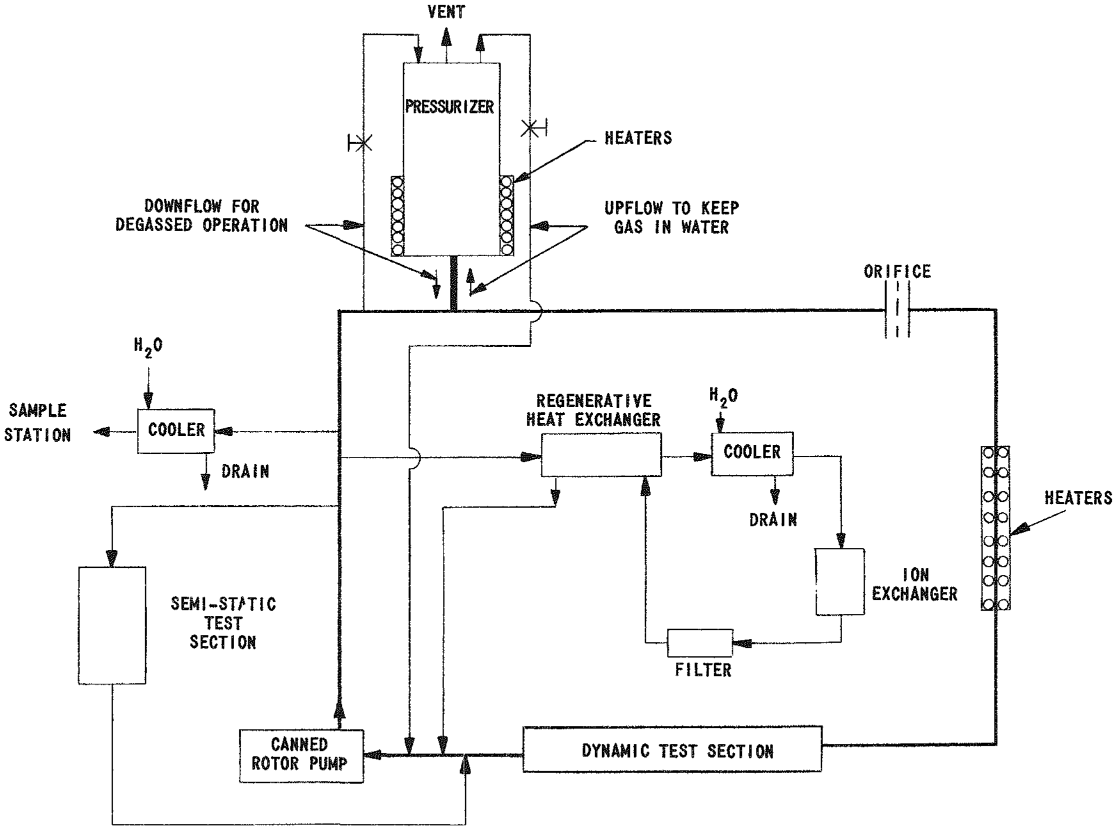


FIG. 1
GENERAL FLOW DIAGRAM FOR DYNAMIC CORROSION TEST LOOPS

Figure 2 shows the manner in which the samples were held in the dynamic test section. The holders were designed to accommodate seven or fifteen sets of samples. The sample holder was positioned within a rectangular flow tube and the entire assembly was installed in the loop test section (3-in. nominal Schedule 80 pipe). Flanges were welded at both ends of the flow tube concentric with the ID of the loop piping; thus the bulk flow was directed through the flow tube.

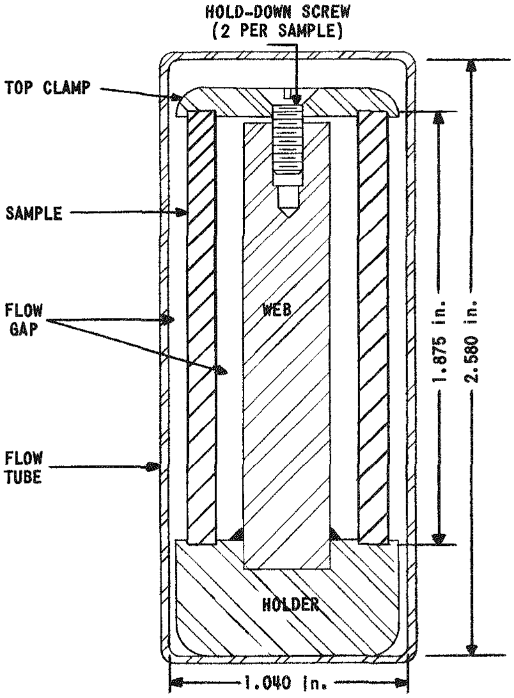


FIG. 2
CROSS SECTION OF SPECIMEN HOLDER IN FLOW TUBE PRIOR TO INSTALLATION IN DYNAMIC TEST SECTION

The bulk flow rate in the four loops was maintained relatively constant: 36 gpm in Loop No. 1, 77 gpm in Loop No. 2, 27 gpm in Loop No. 3, and 55 gpm in Loop No. 4. The velocity through the flow tube was varied from 6 and 7 fps (low velocity) to 16 and 22 fps (high velocity) by increasing or decreasing the thickness of the center web of the specimen holder. The methods employed to establish other loop conditions are described under the respective test series.

In the semistatic test section, the samples were clamped to a center bar, maintaining as little surface contact as possible.

All sample holders were made from Type 304 or Type 347 stainless steel and, except for one test (a test to determine any coupling effect), no attempt was made to insulate the samples from the holder.

Samples were removed periodically from their respective holders, cleaned by the boric acid and chromic-phosphoric acids technique (see Appendix), weighed, and examined visually and microscopically. Samples permanently removed from further testing were replaced with coupons of similar material (replacement samples), and the holder returned to test.

Corrosion and corrosion-irradiation studies were made in special cartridges (designed by ANL) installed in the in-reactor and out-of-reactor sections of the ANL-2 Loop at MTR. These studies included the initial screening tests and subsequent tests on certain aluminum-nickel alloys that held exceptional promise. Both series of tests were made in accordance with established procedures at MTR. Disassembly of the cartridges and examination of the specimens was performed in the high-level caves at ANL.

IV. DYNAMIC SCREENING TESTS OF 2S Al-Ni AND 2S Al-Ni-Fe ALLOYS

From the viewpoint of nuclear economy, the aluminum-nickel alloys were the most attractive for preliminary testing, since the smallest atom percentages of nickel additives to 2S aluminum appeared to give the desired protection against disintegration. Therefore, the first alloys tested were basic 2S aluminum (containing 0.5 wt-% iron) with additions of nickel up to 2 wt-%, and 0.5 wt-% iron.

A. ANL Loop Tests

1. Degassed Water at 600°F (Loop No. 1)

Samples of 2S Al-0.5% Ni alloys, fabricated by ANL Metallurgy Division, were exposed for 8 weeks to degassed, demineralized (1 megohm-cm resistivity) water at 16 fps. All samples showed weight gains (due to adherent corrosion product buildup) during the first two weeks, and weight losses, due to spalling of the outer oxide (see Fig. 3), during the following six weeks. The final stripped weight loss rate for all samples was approximately 13 mil/yr (see Fig. 4).

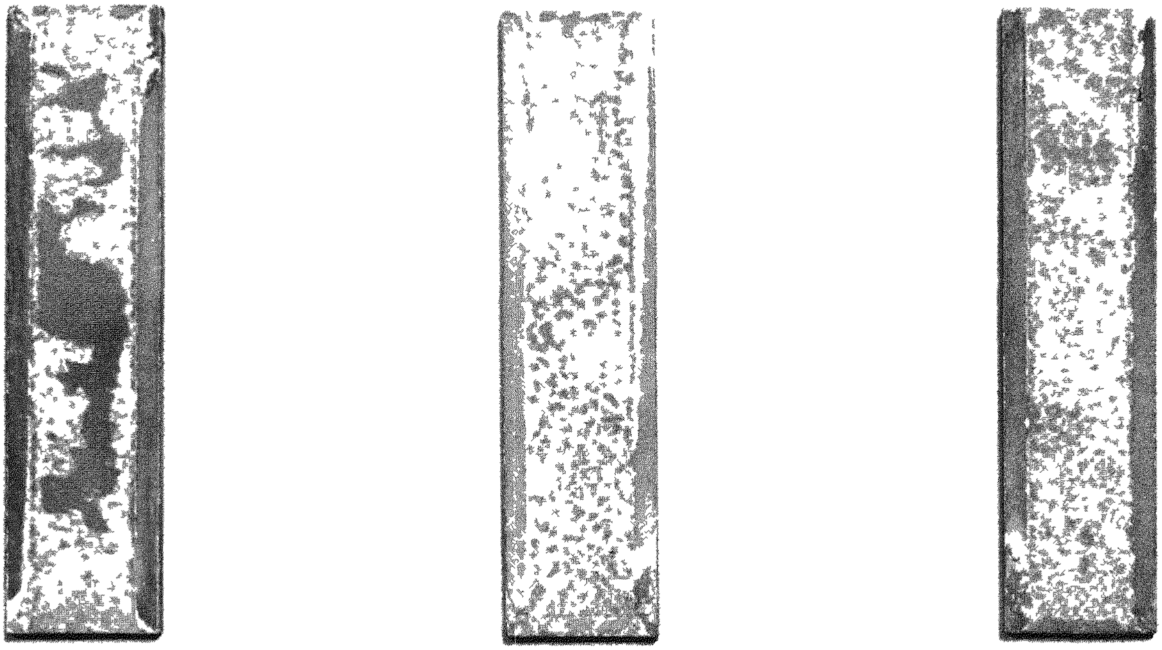


FIG. 3

2S ALUMINUM - 0.5 wt-% NICKEL AS REMOVED AFTER 1375 hr. IN DEGASSED WATER AT 600°F AND 16 fps.

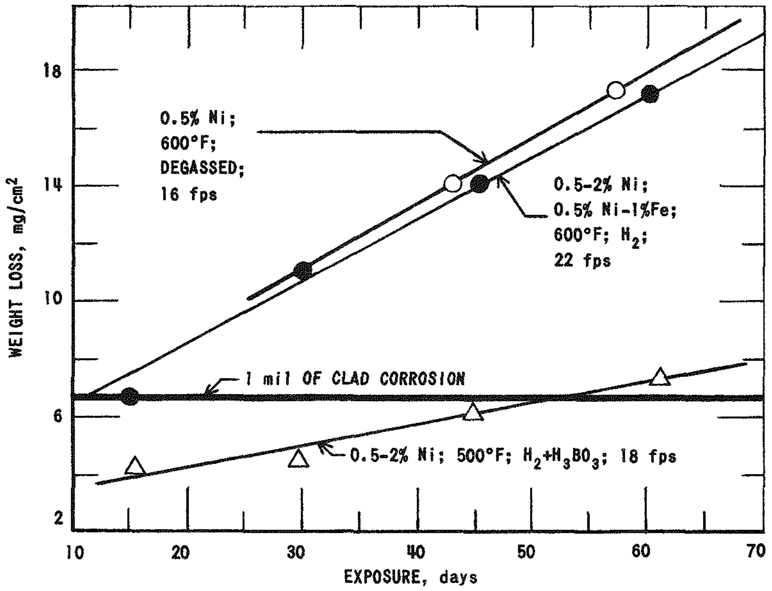


FIG. 4
SUMMARY OF SCREENING TESTS OF 2S ALUMINUM-NICKEL ALLOYS IN DYNAMIC CORROSION LOOPS AT ANL

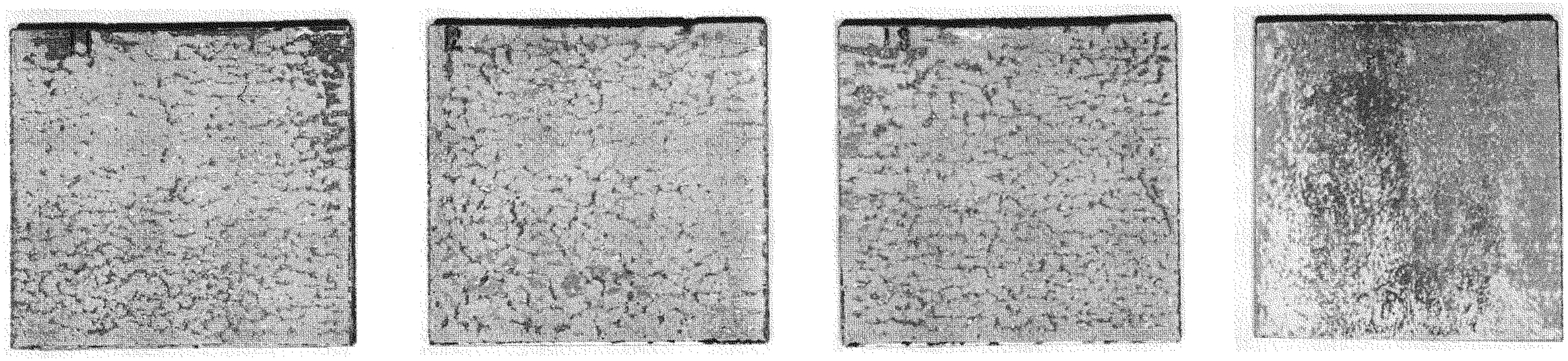
2. Hydrogenated Water at 600°F (Loop No. 2)

Aluminum alloys fabricated by Alcoa were tested for eight weeks in demineralized water (pH 6.8) at 22 fps. Hydrogen gas was added (100 cc H_2/liter of water) at the start of the test. The specimens were 2S aluminum containing 0.5 to 2 wt-% nickel; and 2S aluminum containing 0.5 wt-% Ni and 1 wt-% Fe.

Figure 5 shows the flaky scale (maximum thickness of 0.002 in.) observed after exposures for two and for six weeks. All samples showed a stripped weight loss rate of about 12 mil/yr at the conclusion of the test (see Fig. 4). In general, the stripped metal exhibited heavily etched surfaces and appeared to be uniformly corroded. Some samples showed evidence of erosion-corrosion attack at the leading and trailing edges.

3. Hydrogenated and Borated Water at 500°F (Loop No. 4)

Samples of aluminum-nickel alloys fabricated by Kaiser Aluminum, Inc., were exposed for eight weeks to hydrogenated and borated water at 500°F and 18 fps. The alloys were 2S aluminum with nickel additions ranging from 0.5 to 2.0 wt-%. Hydrogen gas was added (100 cc H_2/liter of water) to the loop at cold startup. Boric acid was added (1 gm H_3BO_3/liter of water) when the temperature reached 500°F.

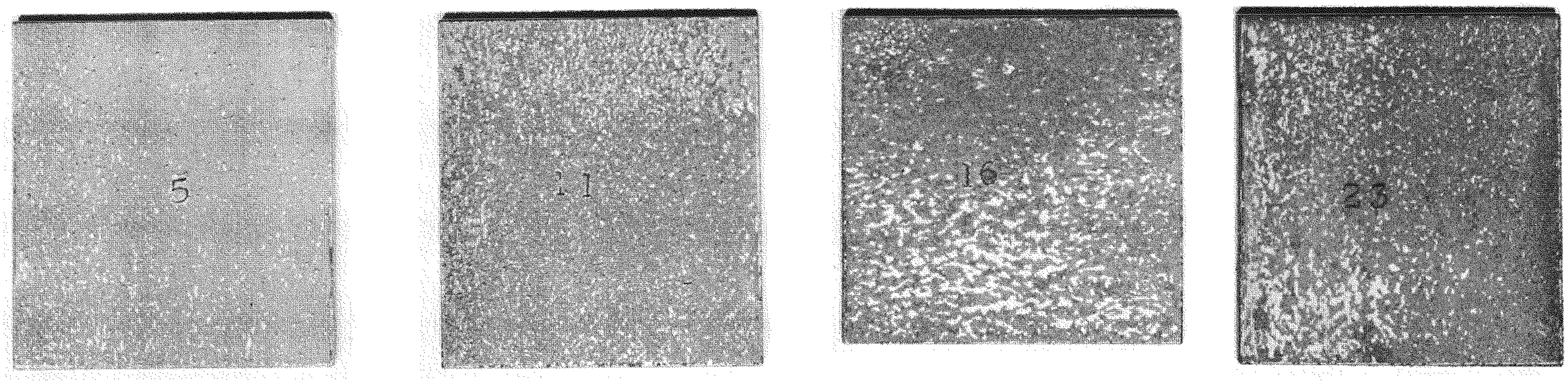


1% Ni
1063 hr

1% Ni
1063 hr

1% Ni
1063 hr

0.5% Ni-1% Fe
342 hr



0.5% Ni
342 hr.

1% Ni
342 hr

1.5% Ni
342 hr

2% Ni
342 hr

FIG. 5

2S Al-Ni AND 2S Al-Ni-Fe ALLOYS EXPOSED TO HYDROGENATED WATER AT 600°F AND 22 fps. (100cc H_2/liter added at start of test)

During the first two weeks, the water was cycled up through the pressurizer to maintain the H_2 gas in the flowing system. However, some difficulty was experienced as a result of the concentration of boric acid in the pressurizer. Therefore, during the following three 2-week periods the flow was cycled alternately up and down through the pressurizer on a 24-hr schedule. As a consequence, the pH varied between 5.3 and 6.3, and the boric acid between 0.1 and 1.0 gm/liter of water.

The originally loaded specimens registered a stripped weight loss rate of about 4 mil/yr, irrespective of the nickel content. The corrosion rate curve (Fig. 4) does not fall along the normal line, probably due to changing water conditions. Upon removal from test, all samples were coated with a smooth, thin (0.001 in.) adherent film of corrosion product.

Replacement samples exposed to similar conditions for four weeks had weight loss rates up to 20 mil/yr. Figure 6 shows the typical appearances of the initial and the replacement samples as removed from test.

B. Corrosion-Irradiation Test Loop at MTR (Cartridge No. MTR-W-5)

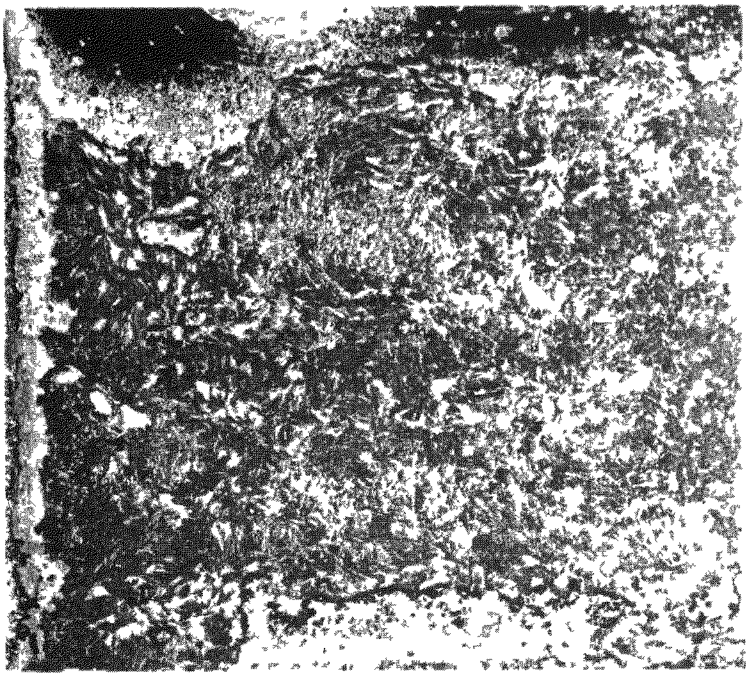
Studies of the combined effects of corrosion and irradiation on aluminum-nickel were performed in the ANL-2 Loop at MTR. Specimens of 2S Al-0.5 wt-% nickel were exposed for 600 hr to demineralized, degassed water at 500°F and 25 fps in the in-reactor and out-of-reactor sections of the loop. The in-reactor specimens, in addition, received a maximum nvt of about 6×10^{20} (equivalent to about 0.1% burnup of all core atoms in a natural uranium fuel plate).

The stripped weight losses were, respectively, 0.014 gm and 0.941 gm for samples A-4331 and A-4332 in the in-reactor section; and 2.727 gm and 4.136 gm for samples A-4333 and A-4334 in the out-of-reactor section. The values are suspect because of a heavy deposit of magnetite (see Fig. 7) on the in-reactor samples; the deposits could not be completely brushed off in acetone.

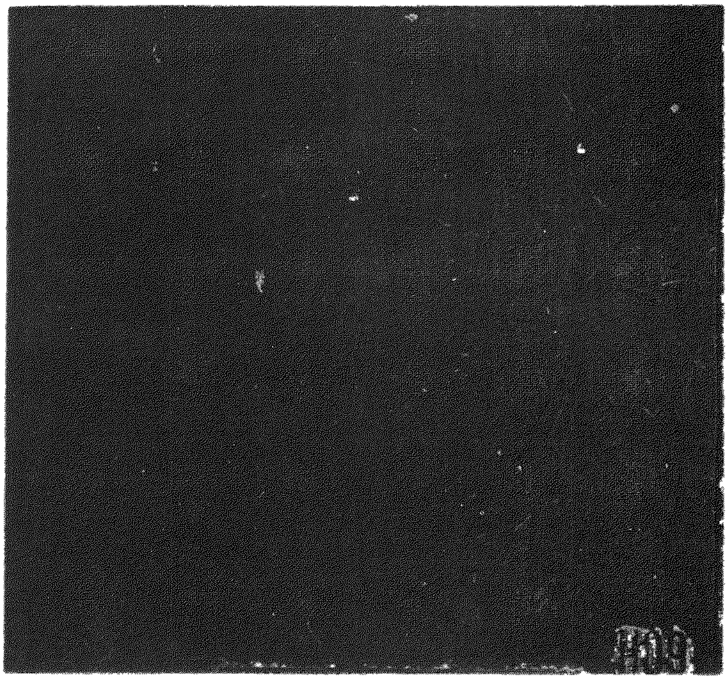
In general, the surface of the in-reactor samples evidenced a more uniform corrosion attack than their counterparts in the out-of-reactor section, with some erosion-corrosion near the holding combs. This observation, along with the disparity between weight losses, suggests the environment in the in-reactor section was less corrosive than the conditions in the out-of-reactor section.

C. Conclusions

Aluminum-nickel alloys were resistant to disintegration for periods up to 60 days in dynamic water at 600°F.



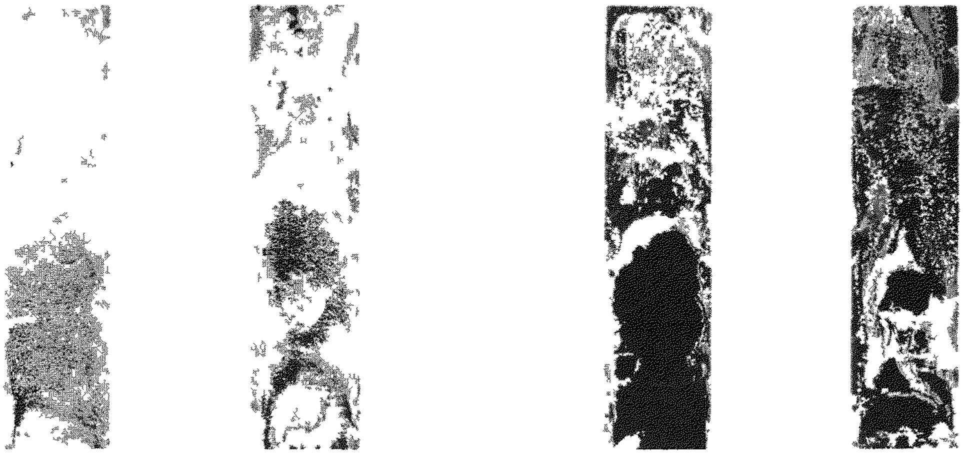
REPLACEMENT
2S Al+2% Ni
4 WEEKS



INITIAL
2S Al+1.5 Ni
8 WEEKS

FIG. 6

TYPICAL APPEARANCE OF INITIAL AND REPLACEMENT SAMPLES OF 2S Al-Ni ALLOYS EXPOSED TO HYDROGENATED AND BORATED WATER AT 500°F AND 18 fps. (X2)



FRONT BACK
SAMPLE NO. A-4331

FRONT BACK
SAMPLE NO. A-4332

FIG. 7
MAGNETITE DEPOSIT ON 2S Al-0.5% Ni ALLOYS EXPOSED FOR 600 hr TO DEMINERALIZED DEGASSED WATER AT 500°F AND 25 fps, AND 6×10^{20} nvt (max) IN ANL-2 LOOP AT MTR.

With respect to corrosion: (1) some inconsistencies in weight losses were evident at 500°F and 600°F; (2) variation of the nickel content had no significant effect; (3) the exposure to the neutron flux appeared to have a beneficial, rather than a deleterious, effect; and (4) nonuniform corrosion attack occurred under certain water conditions.

Consequently, it was decided that the second phase of the test program should focus attention on the influence of water conditioning and velocity with respect to reducing the scale formation and/or buildup of corrosion products on the surfaces of the more promising alloys.

The tests were to be performed primarily on the 2S aluminum-1 wt-% nickel alloy. One ton of this material (alloy M-388) was ordered from Alcoa. One other alloy, Alcoa Alloy No. X-2219, was to be studied to a lesser extent. The compositions of the alloys are listed in Table I.

Table I

COMPOSITION OF ALUMINUM ALLOYS
M-388 AND X-2219

Alloy No.	Composition,* wt-%							
	Ni	Cu	Fe	Si	Mn	Zn	Zr	V
M-388	0.98	0.17	0.49	0.17	-	0.04	-	-
X-2219	-	6.07	0.16	0.08	0.31	-	0.16	0.08

*Average of two or more heats

V. PROGRAMMATIC CORROSION TESTS OF M-388 AND X-2219 ALLOYS

The purpose of the second phase of the loop tests was to evaluate the influence of pH, gas content, and velocity of the water on corrosion of the selected aluminum alloys M-388 and X-2219. The loops were monitored for pH, resistivity, and for H_2 gas buildup.

A. Loop No. 1: 500°F; pH 4.9 - 5.1; Natural H_2 Buildup

The original loading for Run No. 1 consisted of M-388 alloy samples in the dynamic and the semistatic test sections. The holders in the dynamic section were designed to effect flow velocities of 7 and 20 fps past the surface of the specimens. The water was maintained at pH ~ 5 and 200,000 ohm-cm resistivity by means of a cation resin bed (R&H IR-120) regenerated with H_2SO_4.

The corrosion data for the originally loaded specimens are plotted in Fig. 8. Each point represents an average of at least three stripped samples. The variation from this average is not greater than 3%. All samples had a thin, adherent scale at the end of the 8-week test. Removal of the scale revealed uniform corrosion and no pitting or corrosion-erosion of the metal surfaces (see Fig. 9).

The buildup of corrosion product H_2 gas reached a maximum of 150 cc H_2/liter of water in the first 2-week test period before shutdown and sample withdrawal, maximum values of 60 cc H_2/liter were obtained in the subsequent three 2-week test periods.

Replacement samples of M-388 alloy installed at the end of the first 2-week test period showed corrosion weight losses that were higher by a factor of 4 than their counterparts in the original loading.

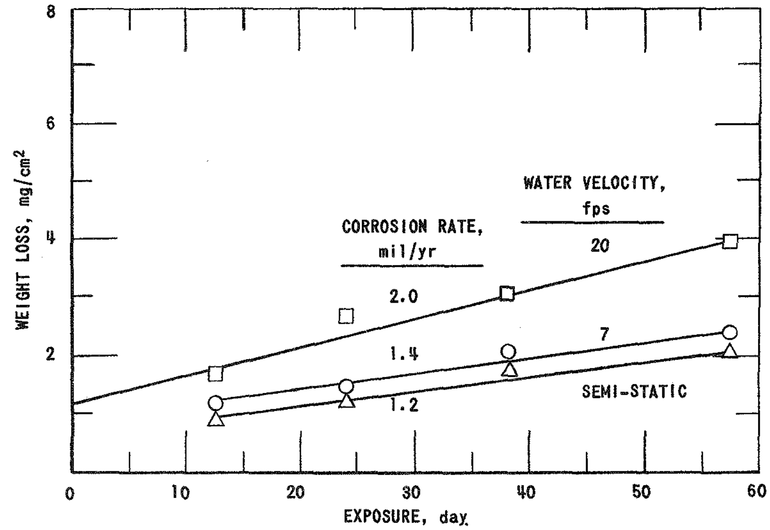
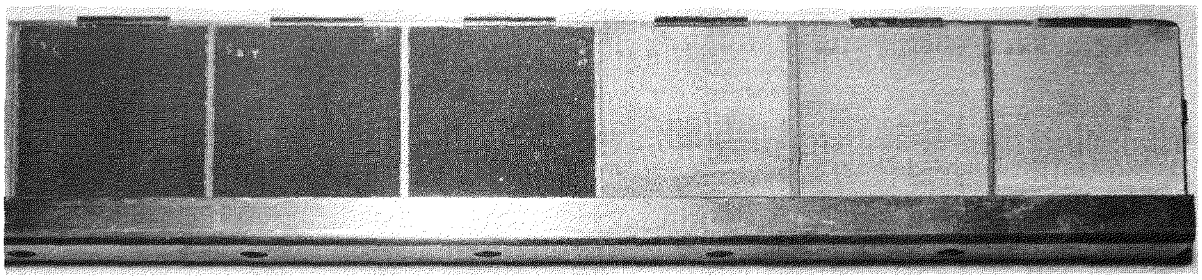
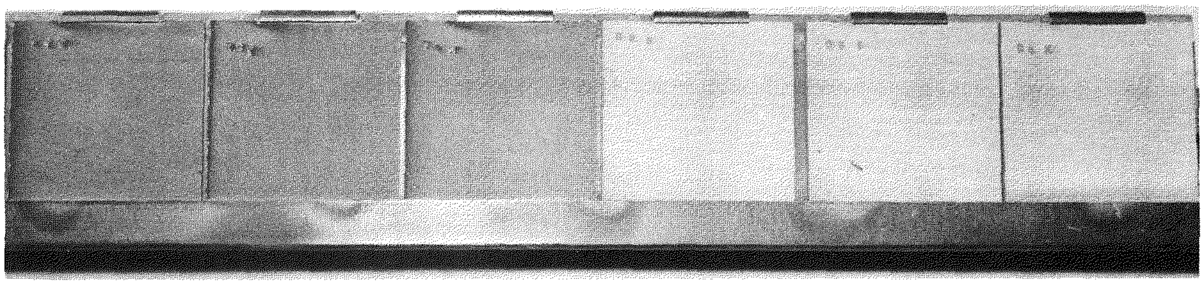


FIG. 8
CORROSION RATES FOR ORIGINALLY LOADED M-388 IN DYNAMIC WATER AT 500°F, pH ~5, AND 200,000 ohm-cm RESISTIVITY. (LOOP NO. 1; RUN NO. 1)



X-2219; 795 hr — M-388; 1376 hr
FLOW VELOCITY: 20 fps →



X-2219; 795 hr — M-388; 1376 hr
FLOW VELOCITY: 7 fps →

FIG. 9
ALUMINUM-NICKEL (M-388) AND ALUMINUM-COPPER (X-2219) ALLOYS AS REMOVED FROM DYNAMIC WATER AT 500°F, pH 5, AND 200,000 ohm-cm RESISTIVITY. (LOOP NO. 1; RUN NO. 1)

Replacement specimens of X-2219 alloy showed more total corrosion than the M-388 alloy, along with slight pitting of the surface and shedding of the outer oxide layers (see Fig. 9).

B. Loop No. 3: 500°F; pH 6.5 - 6.9; Natural H_2 Buildup

The original loading for Run No. 1 comprised 44 samples of M-388 and X-2119 alloy in the dynamic and the semistatic test sections. The holders in the dynamic section were designed to effect flow velocities of 6 and 16 fps past the sample surfaces. The samples were exposed for four 2-week test periods to continuously bypassed demineralized water of pH ~6.5 and 2 megohm-cm resistivity.

The buildup of corrosion product hydrogen gas (Fig. 10) attained a maximum of 350 cc H_2/liter of water during the first 2-week test period, when rapid corrosion of the samples was occurring, but never exceeded a reading of 120 cc H_2/liter during the subsequent three 2-week periods.

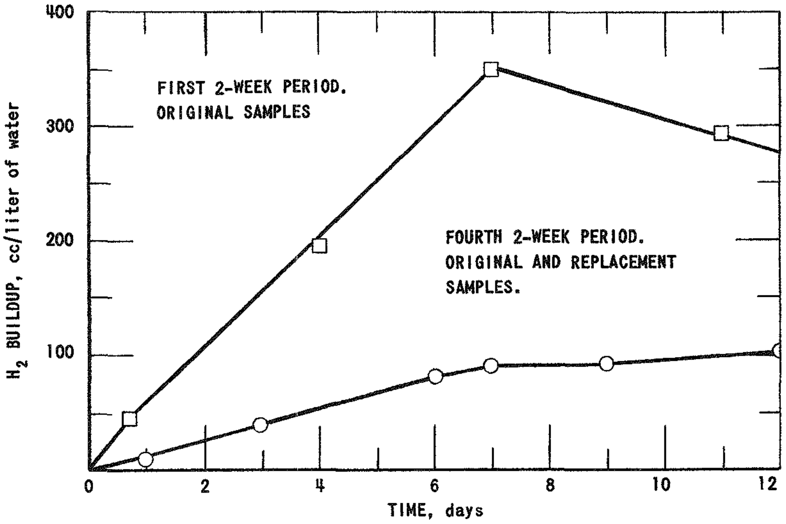


FIG. 10
BUILDUP OF HYDROGEN GAS EVOLVED FROM CORROSION OF ORIGINAL AND REPLACEMENT SAMPLES OF M-388 AND X-2219 ALLOYS IN WATER AT 500°F, pH 6.5-6.9, AND 2 megohm-cm RESISTIVITY.
(LOOP NO. 3; RUN NO. 1)

The corrosion data for the originally loaded samples of M-388 are plotted in Fig. 11. Specimens exposed in the 16-fps velocity region of the holder showed slight erosion-corrosion at the leading and trailing edges. Samples in the 6-fps and the semistatic regions exhibited a uniform corrosion attack. Figure 12 shows the typical appearances of the samples as removed from the test section.

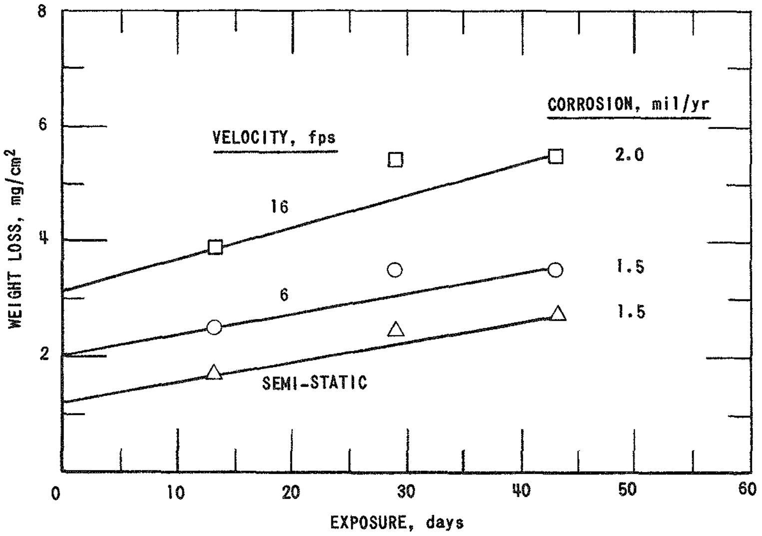


FIG. 11
CORROSION RATES FOR ORIGINALLY LOADED SAMPLES OF M-388 ALLOY EXPOSED TO DYNAMIC WATER AT 500°F, pH 6.5-6.9, AND 2 megohm-cm RESISTIVITY. (LOOP NO. 3; RUN NO. 1)

A comparison of the results of Loop No. 1 tests (pH 5) with values obtained in Loop No. 3 tests (pH ~7) showed that pH 5 water was less corrosive to originally loaded specimens of M-388 alloy. The intercept of the corrosion weight loss curve for pH 5 water was about one-half that for water at pH ~7.

The weight losses for the replacement samples in Loop No. 3 (at 6 and 16 fps) were higher by a factor of 4 or 5 than the values for the originally loaded coupons. The typical stripped appearances of the original and the replacement samples are shown in Figs. 13 and 14, respectively. Replacement samples in the semistatic section showed no change from the corrosion rate of the initial loading.

The original and the replacement samples of X-2219 exhibited slightly higher stripped weight losses than the M-388 alloy. There was some slight pitting and loss of outer layers of the oxide scale on samples exposed in the 16-fps region of the holder.

C. Loop No. 1: 600°F; pH 5.3 - 5.9; Natural H_2 Buildup

Test Run No. 2 was performed primarily with M-388 alloy samples at flow velocities of 7 and 18 fps. The buildup of corrosion product gas ranged from 0 to 210 cc H_2/liter of water during the first 2-week period, and from 0 to 100 cc H_2/liter of water during the subsequent three periods.

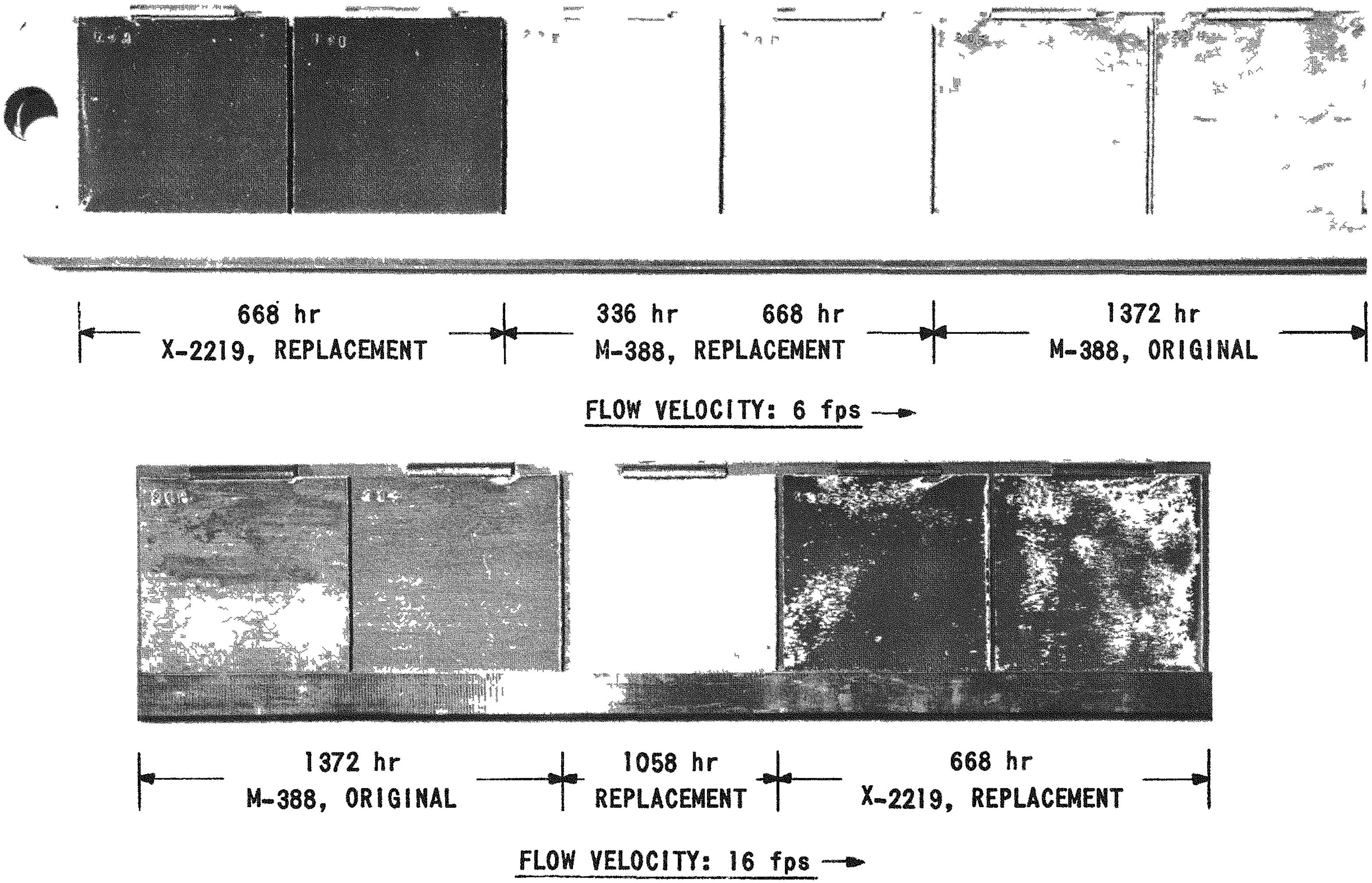


FIG. 12

TYPICAL APPEARANCE OF ORIGINAL AND REPLACEMENT SAMPLES OF M-388 AND X-2219 ALLOY AS REMOVED FROM DYNAMIC WATER AT 500°F, pH 6.5-6.9, AND 2 megohm-cm RESISTIVITY. (LOOP NO. 3; RUN NO. 1)

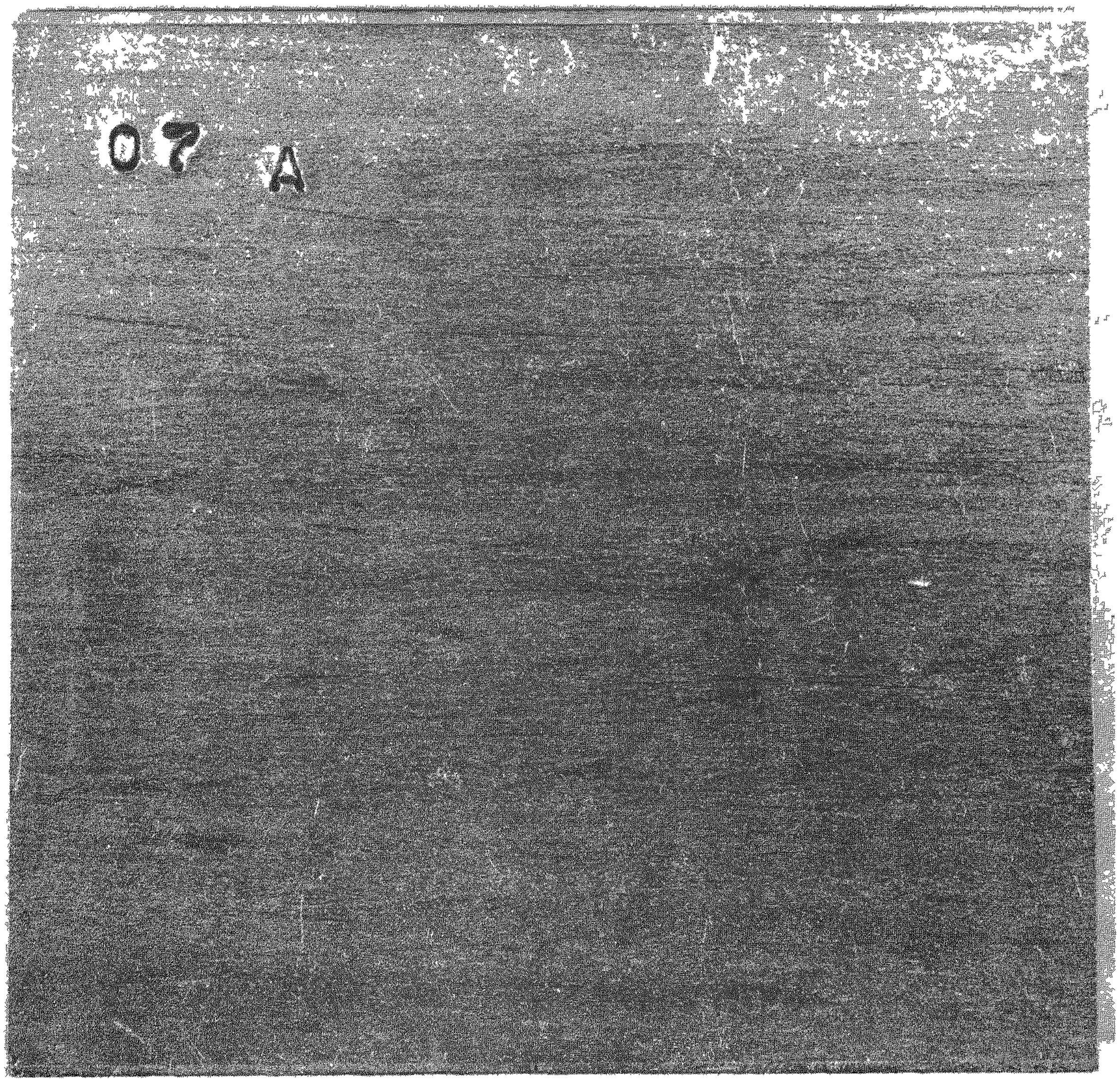


FIG. 13

TYPICAL STRIPPED APPEARANCE OF M-388 ALLOY ORIGINALLY LOADED IN LOOP NO. 3, RUN NO. 1.

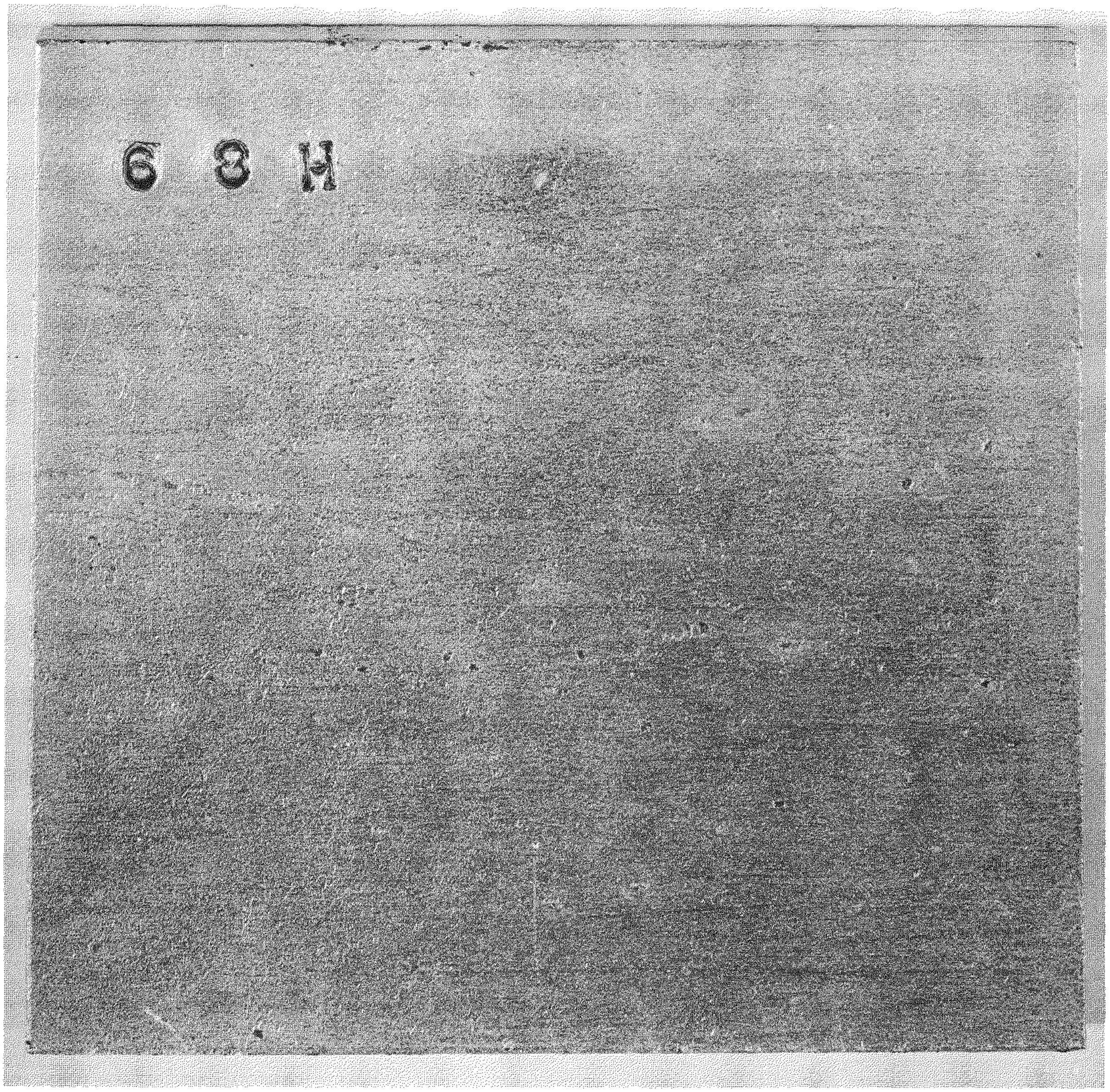


FIG. 14

TYPICAL STRIPPED APPEARANCE OF REPLACEMENT SAMPLE OF M-388 ALLOY EXPOSED IN LOOP NO. 3, RUN NO. 1.

There were no significant differences between the stripped weight losses of the original and replacement specimens, the latter including X-2219 alloy. Samples in the 18-fps region evidenced some cracking and flaking of the oxide scale. Figure 15 shows the scale formation after four weeks of exposure. The corrosion rates and scale thicknesses at the conclusion of the test were as follows:

Flow, fps	Corrosion, mil/yr	Scale, in.
18	6.0	0.0021
7	4.7	0.0018
Semistatic	2.8	0.0016

The final withdrawal of samples from this test also marked the initial appearance of tiny needle-like deposits (Fig. 16) on the specimen holders and elsewhere in the loop. The structure of the needles is typical of the growth of crystals from saturated solutions. X-ray diffraction studies revealed a composition of alpha and beta $Al_2O_3 \cdot H_2O$.

One end of a group of needles was affixed to the metal surface and could not be dislodged other than by scraping with a piece of metal. In the high-velocity region of the holder, the growth of the needles was in alignment (like hairs) with the direction of the water flow. Although the crystals were subsequently found in all loops in which aluminum alloys were tested, the predominant deposits were observed in the loop wherein the water was maintained at the lowest pH value under study.

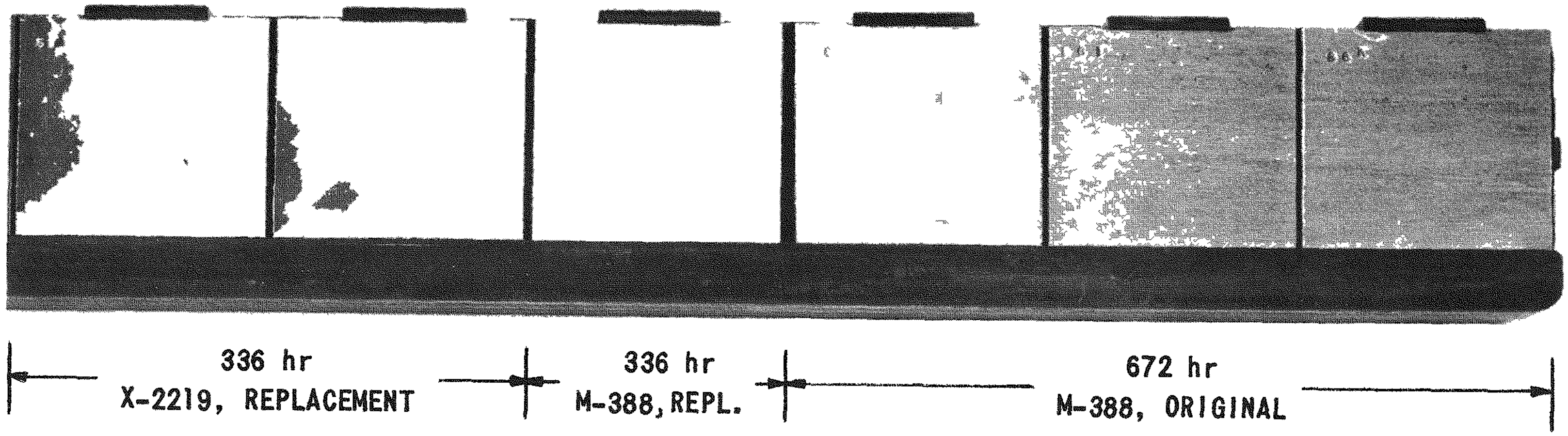
D. Loop No. 3: 600°F; pH 6.8 - 7.0; H_2 Added

Test Run No. 2 was made with M-388 alloys exposed to water velocities of 6 and 16 fps. Hydrogen was added, as necessary, to maintain a concentration of 200 cc H_2/liter of water during the four 2-week test periods.

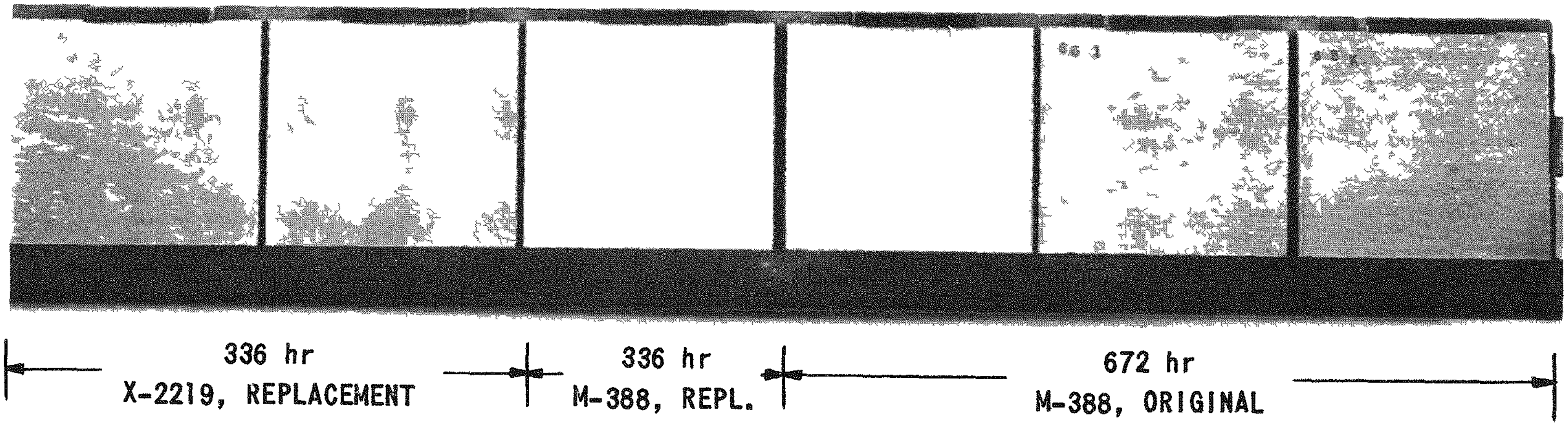
All samples (original and replacement) were coated with an oxide scale, 0.0020 in. thick. The scale on the samples in the semistatic and in the 16-fps velocity region was crusted and ruptured. Some of the scale had been washed away in the dynamic section. The weight losses of the samples were: 8.5 mil/yr (16 fps) and 6.5 mil/yr (6 fps) in the dynamic section, and 5.5 mil/yr in the semistatic section.

E. Conclusions

The corrosion rates of the M-388 alloy in 600°F water above 6 fps (4.7 to 8.5 mil/yr) were adjudged too high to merit consideration as a fuel element clad with surface temperatures of 600°F. Further, the tendency of the oxide scale to rupture and flake could give rise to a difficult crud and filtration problem. The X-2219 alloy was also removed from consideration



FLOW VELOCITY: 18 fps →



FLOW VELOCITY: 7 fps →

FIG. 15
ALUMINUM ALLOYS M-388 AND X-2219 AS REMOVED FROM DYNAMIC WATER AT 600°F AND pH 5.3-5.9. (LOOP NO. 1; RUN NO. 2)

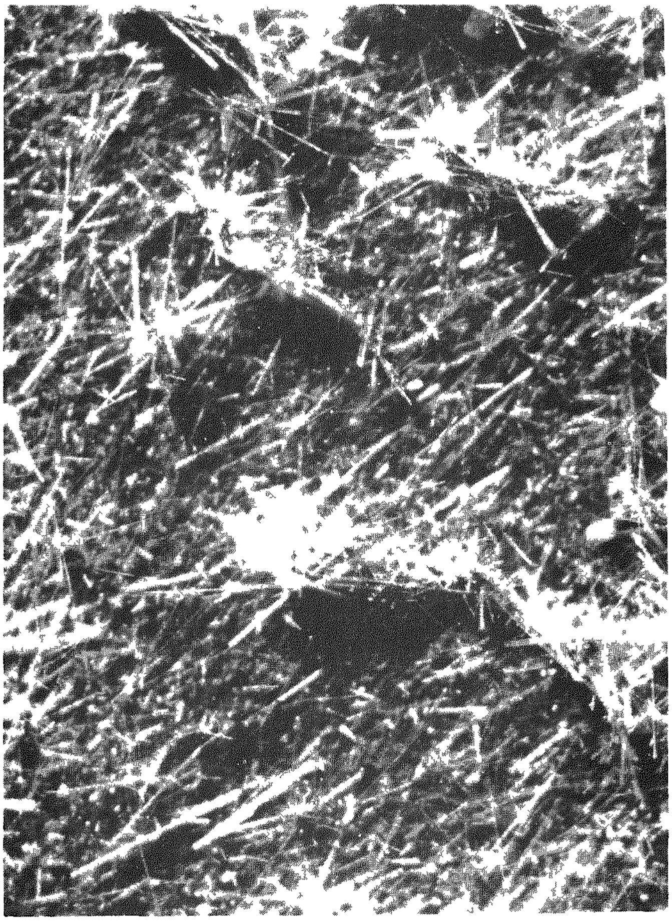


FIG. 16

TYPICAL CRYSTALS OF ALPHA AND BETA $Al_2O_3 \cdot H_2O$ ON SPECIMEN HOLDERS EXPOSED TO DYNAMIC WATER AT 600°F AND pH 5.3-5.9
(LOOP NO. 1; RUN NO. 2)

(18,262) (X 52)

since (1) the corrosion rates were the same or higher than the rates for the M-388 alloy, and (2) almost all of the oxide scale was removed by the flowing water. The latter observation was adjudged especially critical from the standpoints of (1) transport of radioactive material to the external system, and (2) deposition of the corrosion products on other fuel elements and heat-transfer surfaces.

The cause of the disparity between corrosion rates in Loop No. 1 (pH 5.5) and Loop No. 3 (pH 7) at 600°F is obscured by the decision to inject hydrogen gas into Loop No. 3 at startup. Whether the differences are due to pH or H_2 gas injection cannot be decided.

The specimens exposed to 500°F water exhibited two corrosion rates, 2 and 10 mil/yr. Since the 2-mil/yr rate was considered acceptable for reactor design, it was decided that subsequent tests should focus attention on the conditions that effected the difference in corrosion rates at 500°F.

VI. INVESTIGATION OF FACTORS AFFECTING CORROSION RATE OF M-388 ALLOY AT 500°F

The foregoing tests on M-388 alloy had indicated a possible relationship between the hydrogen gas concentration and corrosion rate during the initial two-week exposure, and the corrosion rate measured after subsequent periods of exposure. Accordingly, tests were made in degassed water and in hydrogenated water at 500°F to determine whether the low (~2 mil/yr) or the high rate (~10 mil/yr) could be reproduced at will.

A. Degassed Water at pH 6.3-6.9 (Loop No. 4)

Run No. 2 was operated for six weeks with water of pH ~7 and 2-megohm-cm resistivity, and with intermittent degassing (by venting). The velocity of the water through the specimen holder was 18 fps.

At the end of the test all samples showed a corrosion rate of 11 mil/yr (Fig. 17). The scales on both the original and the replacement samples had ruptured and sloughed off considerably.

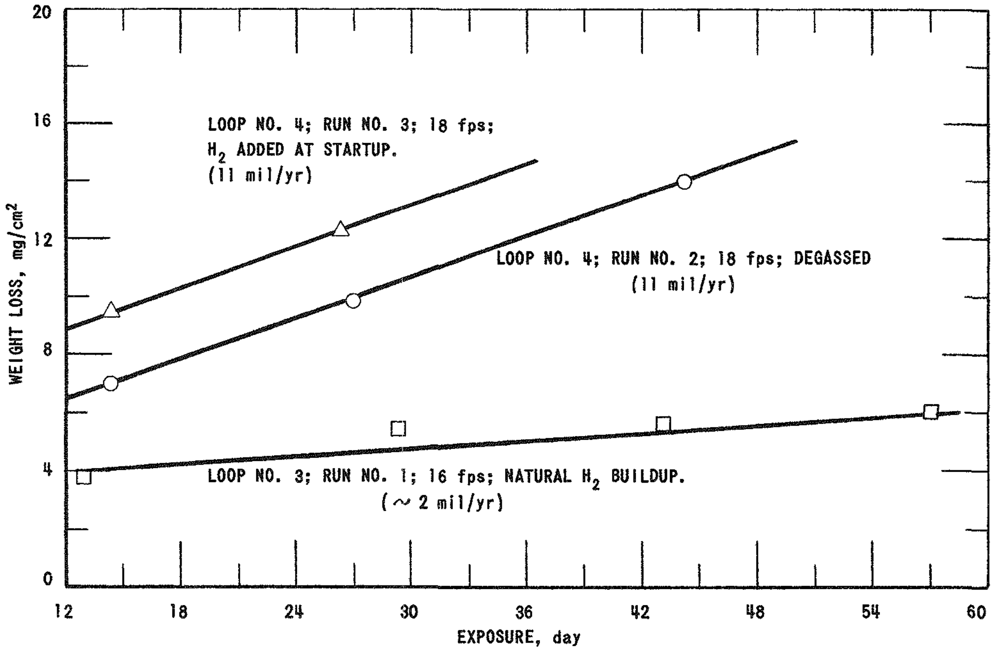


FIG. 17

EFFECT OF HYDROGEN CONCENTRATION ON CORROSION OF M-388 ALLOY IN DYNAMIC WATER AT 500°F, pH 6.3-6.9, AND 2 megohm-cm RESISTIVITY

Consequently, it was concluded that the evolved corrosion product hydrogen gas might be connected with the establishment of the low corrosion rate. Since loop geometry and leakage are important factors in corrosion gas buildup, hydrogen gas was injected at startup in order to effect the low corrosion rate.

B. Hydrogen Added at Startup; pH 6.4 (Loop No. 4)

Prior to startup of Run No. 3, about 150 cc H_2/liter of water were injected in the system. The loop was then operated with water of pH 6.4 and 2-megohm-cm resistivity, and 18 fps past the sample surfaces.

At the end of four weeks of exposure, all samples showed a corrosion rate of 11 mil/yr. Further testing was discontinued.

Figure 17 shows the comparative corrosion rates in degassed water, in water with natural H_2 gas buildup, and in water with H_2 injected at startup.

C. Hydrogen Added Two Days after Startup; pH 6.9

The injection of H_2 gas prior to startup of Run No. 3 in Loop No. 4 appeared to have caused a substantial increase in the intercept of the corrosion curve. It was decided that Run No. 4 would be operated for two days before hydrogen was added, the intent of the late addition of H_2 being to ascertain whether (1) a more durable corrosion film could be established in the absence of H_2, and (2) a reduction in the subsequent corrosion rate could be effected by the addition of H_2 gas.

The test was discontinued after two weeks. The stripped weight losses at this time were equal to those of Run No. 3.

D. Effects of Coupling and Surface Preparation

Twelve samples of M-388 alloy were installed in a high-velocity holder in Loop No. 4 (Run No. 5) to evaluate the effects of coupling on the two corrosion rates. Four samples were Teflon-insulated from the holder; four were held with newly etched stainless steel clamps; and four were held in the regular manner using aged stainless steel clamps.

The stripped weight losses of all samples ranged from 6.73 to 6.92 mg/cm^2 after two weeks in water at pH 6.8 and 16 to 22 fps. Further, coupling to stainless steel had no effect on the corrosion of M-388 alloy in dynamic water of this quality.

Surface pretreatment also proved ineffective. In one case, anodized surface treatment (20°C; 20 minutes; 15 volts; 15% sulphuric acid) increased the corrosion intercept since the anodized film sloughed off before the normal corrosion film could be formed. Surface treatment, with acetone or with sodium hydroxide followed by a nitric acid rinse had no effect on the corrosion intercept or the corrosion rate.

E. Progressive Injection of Hydrogen; pH 6.9

Run No. 6 in Loop No. 4 was designed to simulate the natural buildup of hydrogen gas measured in Loop No. 3, Run No. 3, in an effort to reproduce the low corrosion rate (2 mil/yr) peculiar to that test.

The test was operated for two weeks during which time hydrogen gas was injected, as necessary, to follow the curve of natural buildup of hydrogen in Run No. 3, Loop No. 3 (see Fig. 10). Further testing was discontinued since all samples registered stripped weight losses equivalent to the high corrosion rate of 10 mil/yr.

F. Effect of Pretreatment in Semistatic Water

The purposes of Run No. 4 in Loop No. 1 were (1) to evaluate the corrosion characteristics of a second shipment of M-388 alloy with respect to the initial material received from Alcoa, and (2) to compare the corrosion behavior of samples prepared in the usual manner with the behavior of coupons pretreated for two weeks in the semistatic test section of the loop.

The loop water was maintained at 500°F and pH 5.8-6.1. At the end of the two-week period, the pretreated samples were removed from the semistatic section and installed in the dynamic test section through which water flowed at 18 fps.

With regard to the first purpose of the test, there was no detectable difference in corrosion rate of samples representative of both shipments; the weight losses checked within 2%.

The outstanding difference between the regular samples and the pretreated specimens was the height of the intercept, a measure of the corrosion that occurred during the first two weeks. The scatter in the data (see Fig. 18) precluded a precise determination; however, approximate values were: 10.3 mil/yr for the regular, and 6.9 mil/yr for the pretreated samples. Figure 19 shows the typical appearance of the respective samples.

G. Effect of Radical Change in Gas Conditions after Initial Period with Natural H_2 Buildup

The purpose of Run No. 4 in Loop No. 3 was to determine the effect of radical changes in hydrogen content during the course of a test on M-388 alloy in water at 500°F, pH 6.8-7.0, and velocities of 7 and 18 fps.

Initially, all samples were exposed to 500°F water for two weeks, allowing a natural buildup of gas to 235 cc H_2/liter of water. The samples were then split into two groups. One group was exposed for four weeks to degassed water, and the other group to hydrogenated water (200 cc H_2/liter of water) also for four weeks.

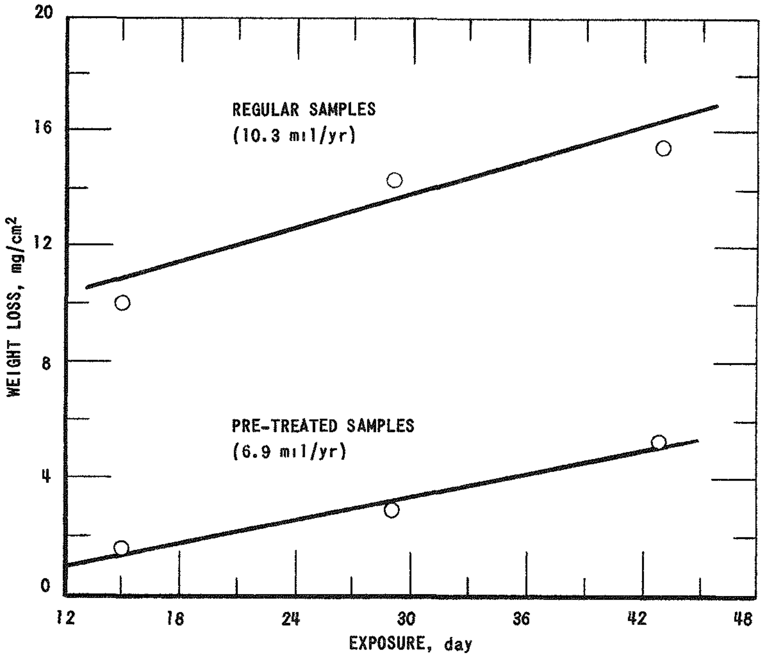


FIG. 18

EFFECT OF SEMI-STATIC WATER PRE-TREATMENT ON SUBSEQUENT CORROSION OF M-388 ALLOY IN WATER AT 500°F, pH 5.8-6.1, AND 18 fps.
(LOOP NO. 1; RUN NO. 4)

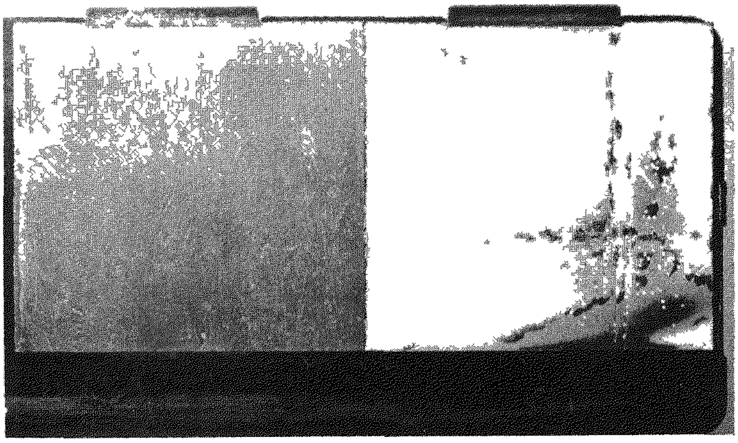


FIG. 19

TYPICAL APPEARANCE OF REGULAR AND PRE-TREATED SAMPLES OF M-388 ALLOY.
(LOOP NO. 1; RUN NO. 4)

The results are shown graphically and pictorially in Figs. 20 and 21, respectively. During the first two weeks in degassed and in hydrogenated water, the samples were only slightly affected. However, in the next period all samples showed an increase in weight loss and accelerated corrosion attack at the leading edges. The final corrosion rates were much higher than those obtained in a previous test with natural buildup of hydrogen gas (Loop No. 3; Run No. 1).

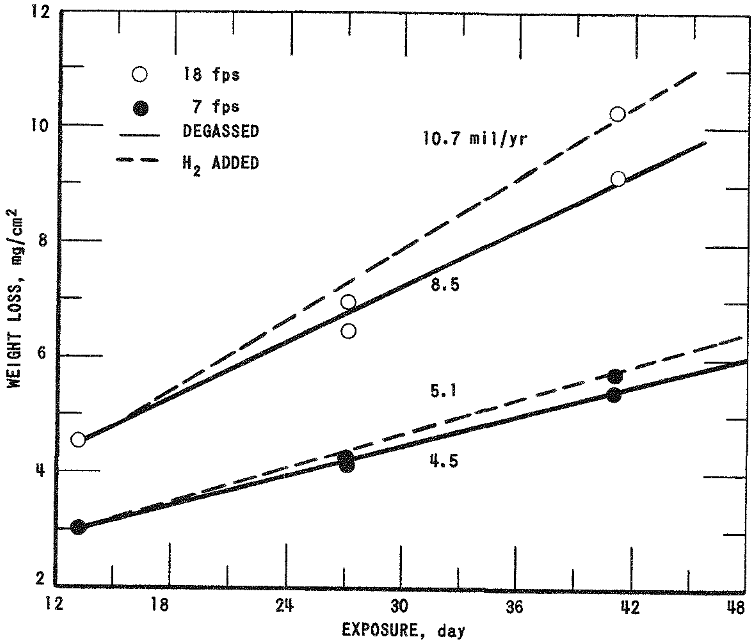


FIG. 20

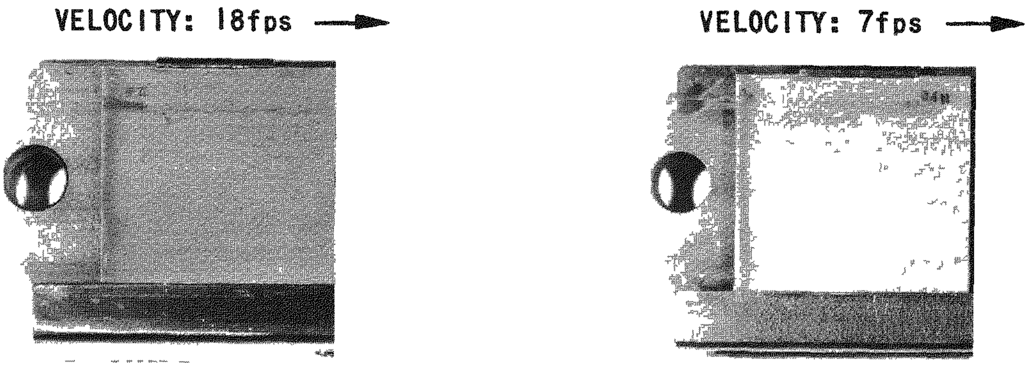
CORROSION OF M-388 ALLOY IN DEGASSED WATER AND IN HYDROGENATED WATER AT 500°F AND pH 6.8-7.0 AFTER INITIAL EXPOSURE FOR TWO WEEKS TO 500°F WATER WITH NATURAL BUILDUP OF HYDROGEN.
(LOOP NO. 3; RUN NO. 4)

H. Effect of Large Hydrogen Addition in Startup; pH 6.9

Run No. 7 in Loop No. 4 concluded the series of tests designed to reproduce the conditions that effected the low or the high corrosion rate of M-388 alloy in 500°F water.

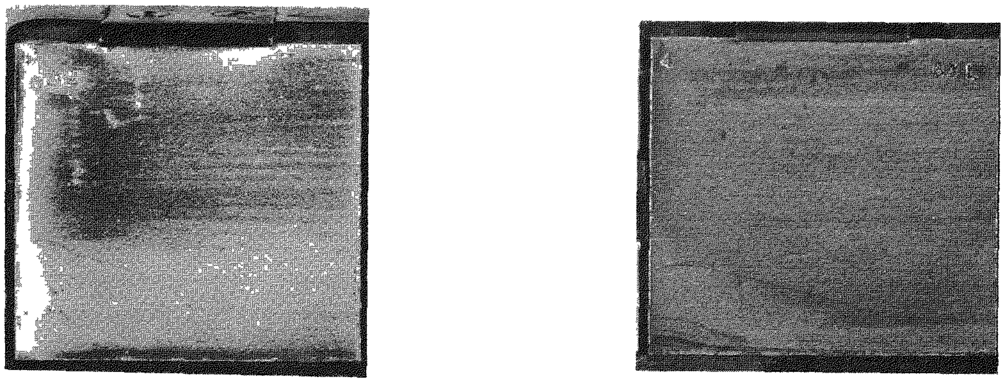
Following injection of 500 cc H_2/liter of water, Run No. 7 was operated for 346 hr, with water velocities of 16 and 22 fps through the specimen holders.

The average weight loss (9.78 mg/cm^2), combined with the poor appearances of the samples (see Fig. 22), indicate that initial addition of a large quantity of hydrogen does not give low corrosion rates.



NATURAL BUILDUP OF H_2 (240 cc/liter): 2 weeks

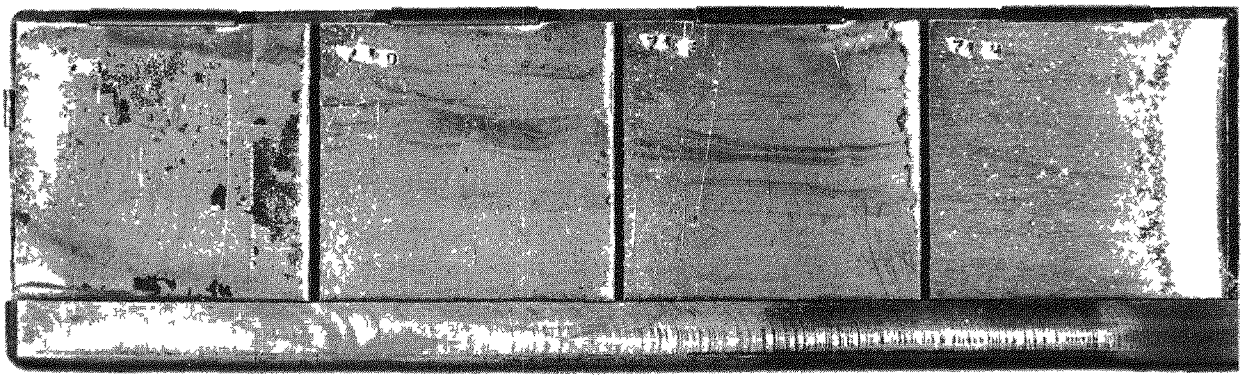
DEGASSED WATER: 4 weeks



HYDROGEN ADDED (200 cc/liter): 4 weeks

FIG. 21

TYPICAL CORROSION OF M-388 ALLOY IN DEGASSED AND IN HYDROGENATED WATER AT 500°F AND pH 6.8 - 7.0 AFTER INITIAL EXPOSURE FOR TWO WEEKS TO 500°F WATER WITH NATURAL BUILDUP OF HYDROGEN. (LOOP NO. 3; RUN NO. 4)



← FLOW

FIG. 22

M-388 ALLOY AS REMOVED AFTER 346 hr IN WATER AT 500°F. pH 7, AND 16 AND 22 fps. 500 cc H_2/liter of water ADDED AT STARTUP.

(LOOP NO. 4; RUN NO. 7)

I. Conclusions

The addition of hydrogen at startup appears to increase the degree of corrosion attack. However, the corrosion mechanism attributable to the disparity between corrosion rates of M-388 in 500°F water, with or without hydrogenation, or the manner in which it is added, remains unresolved. The wide divergence in corrosion rates is not explained by the effects of coupling variation, surface treatment, or other known changes produced during this series of tests.

VII. FURTHER CORROSION TESTS OF M-388, X-2219, AND ALUMINUM-COPPER ALLOYS

A. Loop No. 4: 600°F; pH 7.0-7.4; Degassed

Run No. 8 was operated for 10 weeks during which original and replacement specimens of M-388 and X-2219 alloys were exposed to semi-static and dynamic water at 7 and 18 fps. The purpose of the test was to compare the corrosion rates of the alloys in degassed water with the values obtained in hydrogenated water (Loop No. 3; Run No. 2).

As is made evident in the tabulation below, the corrosion rates of original samples of M-388 in degassed water were slightly higher than the values for their counter-parts in hydrogenated water. However, there were significant differences among the final appearances of the respective test specimens. The metal surfaces were fairly smooth in the case of hydrogenated water and very rough in the case of degassed water. The corrosion rates here are again too high to be attractive for reactor application.

Alloy	Corrosion Rate, mil/yr Degassed	H_2 Added
M-388 (Original)	11.6	8.5
M-388 (Replacement)	16.6	10.9
X-2219 (Replacement)	14.5	9.0

The results support previous observations that (1) pH 5 water is less corrosive than pH 7 water, and (2) the presence of some hydrogen in the water, either by addition or by natural buildup, is more favorable than degassed water or water with a large quantity of hydrogen added at startup.

B. Loop No. 3: 475°F; pH 7.1-7.5; Natural H_2 Buildup

In order to determine if a slightly lower temperature would have a noticeable effect on the corrosion rate, Run No. 5 was made at 475°F, with natural buildup of hydrogen. The original loading consisted of M-388 alloy in the static and the dynamic test sections. One specimen of Thermenol (80% Fe; 16% Al; 4% Mo) was installed in the high-velocity holder, since the material had shown some promise in independent tests. Alloys X-2219 and M-388 were used for replacements.

The final corrosion rates were as follows:

Alloy	Corrosion Rate, mil/yr 18 fps	7 fps	Semistatic
M-388 (Original)	8.7	2.7	1.2
M-388 (Replacement)	17.4	4.5	1.9
X-2219 (Replacement)	18.4	8.7	-

The rates for the samples in the high-velocity water were higher than had been expected. However, there is a possibility that the high values were occasioned by the accelerated corrosion of the Thermenol specimen. The consequent black oxide appeared to coat and/or unite with the scale on the M-388 alloy. This is evidenced in Fig. 23 by the contrast between the very dark gray scale on the dynamic specimens and the light scale on the semistatic specimens.

Although the corrosion rates are suspect (due to the Thermenol), the values still follow trends observed previously: (1) low-velocity water is more favorable than high-velocity water; (2) replacement samples suffer more corrosion attack than originally loaded samples; and (3) M-388 alloy is more resistant to corrosion than the X-2219 alloy.

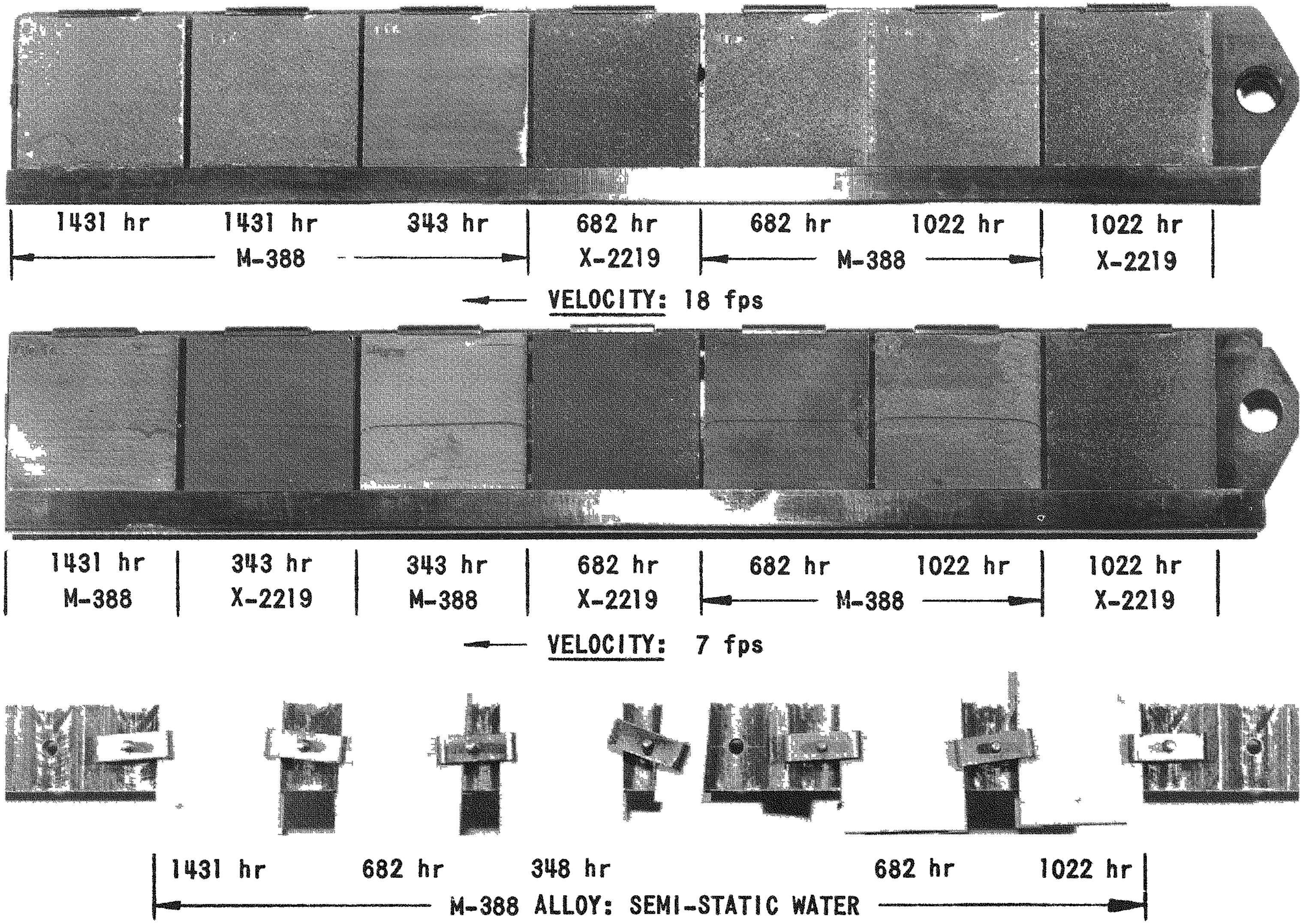


FIG. 23

M-388 AND X-2219 ALLOYS AS REMOVED FROM DYNAMIC AND SEMI-STATIC WATER AT 475°F, pH 7.1 - 7.5, WITH NATURAL BUILDUP OF HYDROGEN. (LOOP NO. 3; RUN NO. 5)

C. Loop No. 4: 600°F; pH 7.2-7.3; Degassed

Test Run No. 9 was made to evaluate the corrosion resistance of five aluminum-copper alloys made by Alcoa. The water velocity through the specimen holder was 18 fps.

The results after 63 days of exposure are summarized in Table II. Although the corrosion rates for the original samples do not vary significantly, it is unusual that, with one exception, the rates for the replacement samples are less than those of the original samples.

Table II

COMPOSITIONS AND CORROSION RATES FOR ALUMINUM-COPPER ALLOYS

	Composition, %								Corrosion Rate, mil/yr	
Alloy No.	Cu	Fe	Ni	Si	Mn	V	Zr	Co	Original	Replacement
173161	6.10	0.75	-	0.08	0.30	0.10	0.14	-	9.8	13.2
173163	6.18	0.71	0.01	0.08	0.31	0.10	0.18	0.22	12.3	7.6
173164	5.94	0.74	0.01	0.09	0.31	0.18	0.28	0.23	11.3	8.2
173165	6.08	0.74	0.01	0.08	0.16	0.18	0.27	0.23	11.3	8.5
173168	3.98	0.48	2.21	0.43	-	-	-	-	12.5	9.8

The appearance of all samples was poor. About one-half of the sample surface was bare metal; the balance was covered with scale. Removal of the scale revealed a very rough and pitted metal surface.

D. Loop No. 1: Long-term Test; 500°F pH 5.0-6.8; Natural H_2 Buildup

Run No. 5 marked the first of a proposed series of tests to evaluate the effects of prolonged exposure of M-388 alloy to conditions prevailing in the earlier short-term (8 weeks) tests.

Accordingly, original and replacement samples of M-388 alloy were exposed for 7 months in an environment duplicating Run No. 1 in this loop: 500°F; pH 5; 200,000-ohm-cm resistivity; and flow velocities of 7 and 18 fps.

The corrosion data are plotted in Fig. 24. In general, the corrosion rates for the original samples were not as low as the values in the short-term tests, but were still quite satisfactory. However, based on periods of equal exposure, the rates for the replacement samples in 18-fps water were higher by a factor of 3 than their counterparts in the short-term test.

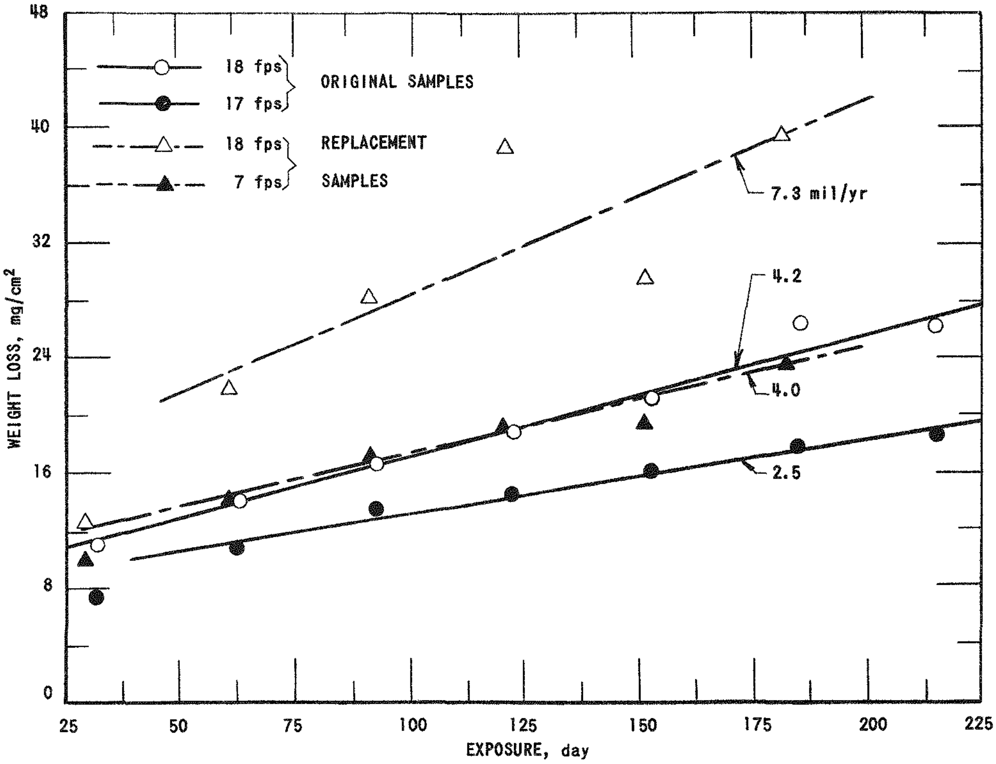


FIG. 24
CORROSION OF M-388 ALLOY IN DYNAMIC WATER AT 500°F, pH 5.0-6.8
200,000 ohm-cm RESISTIVITY, WITH NATURAL BUILDUP OF HYDROGEN
(LOOP NO. 1; RUN NO. 5)

All samples had a slight amount of loose powder over an adherent scale (see Fig. 25). Removal of the scale revealed a smooth metal surface with no pits visible at a magnification of 72X. Samples removed during the last two months of testing showed some erosion near the clamps and at the leading edges.

VIII. CORROSION-IRRADIATION TESTS IN THE MTR

Corrosion and corrosion-irradiation tests of aluminum alloys were performed in cartridges installed in the in-reactor and the out-of-reactor sections of the ANL-2 Pressurized Water Loop at MTR.

The ANL-2 facility at MTR (shown schematically in Fig. 26) is a horizontal, pressurized water loop designed to operate at 500°F, 1500 psi, with a maximum thermal flux of 2.5×10^{14} n/(cm^2) (sec). A detailed description of the loop and its operation has been reported by Martinec.(6)

Two series of tests were made. The first series included samples of 2S aluminum containing 0.5, 1.0, and 2.0 wt-% nickel, which had shown

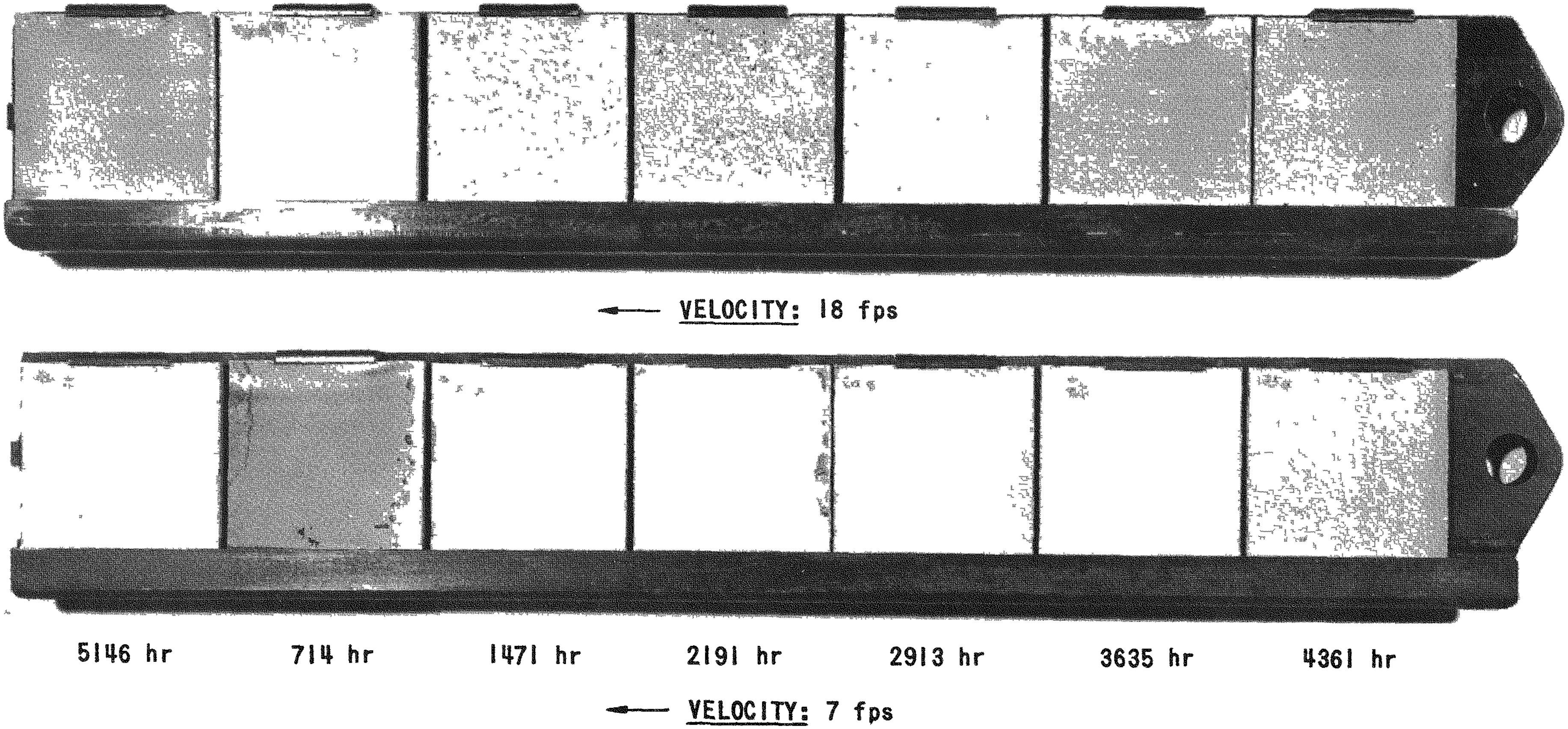
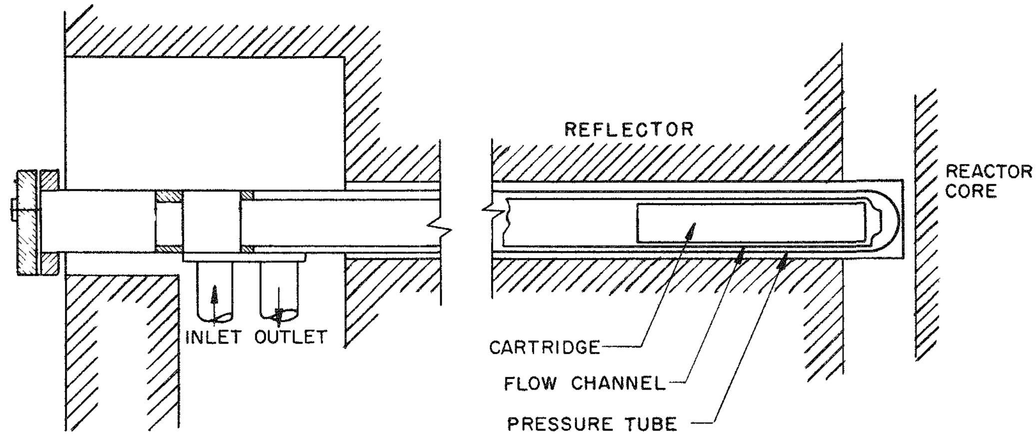
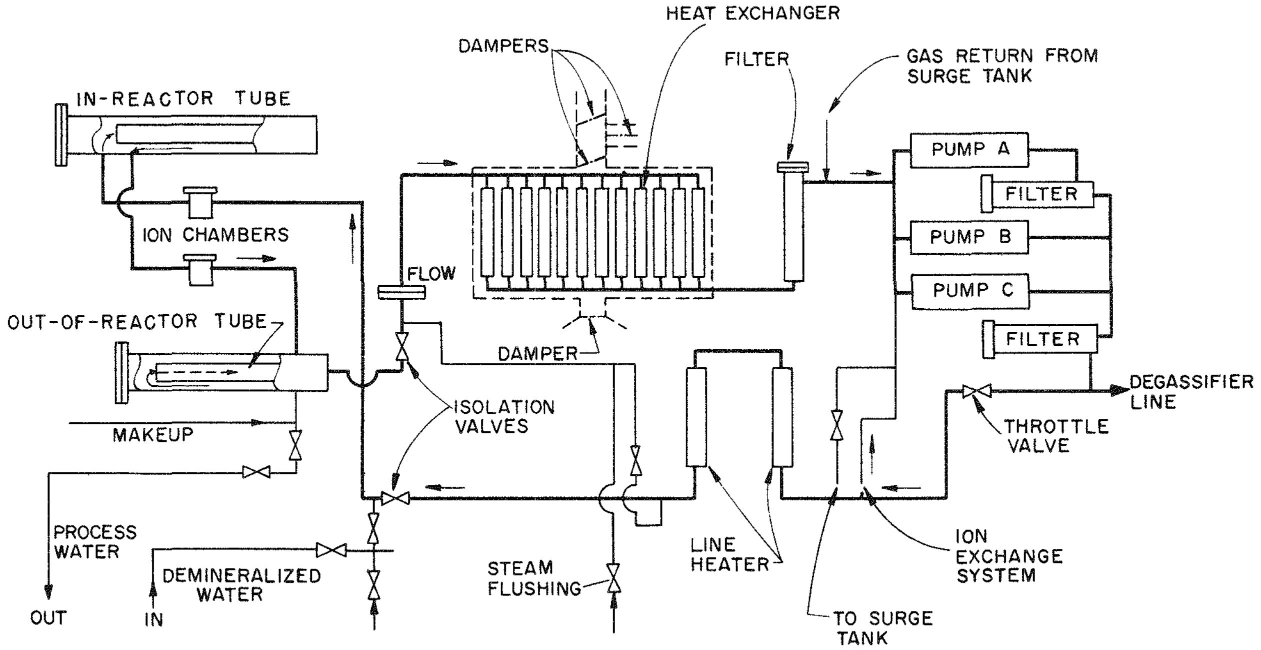


FIG. 25

M-388 ALLOY AS REMOVED FROM TESTS TOTALLING 5146 hr IN DYNAMIC WATER AT 500°F, pH 5.0 - 6.8, 200,000 ohm-cm RESISTIVITY, WITH NATURAL BUILDUP OF HYDROGEN. (LOOP NO. 1; RUN NO. 5)



IN-REACTOR TUBE



FLOW DIAGRAM

FIG. 26
ANL-2 PRESSURIZED WATER LOOP AT MTR

promise in the earlier screening tests. The second series of tests was limited to specimens of M-388 alloy.

A. 2S Aluminum-Nickel Alloys

Samples of 2S aluminum alloyed with 0.5, 1.0, and 2 wt-% nickel were installed in Cartridges MTR-W-6 (in-reactor) and MTR-W-6E (out-of-reactor). In both cartridges, the samples (7.25 in. x 1.875 in. x 0.125 in.) were arranged in two rows of three plates each, with Row No. 1 at the left end (see Fig. 27). Row No. 1 of the in-reactor cartridge was nearest the reactor core and, consequently, in the highest flux region.

Both cartridges were exposed intermittently to the following conditions during the period from March 14 to October 3, 1955:

Temp, °F	Time, hr
500	100
460-470	125
430-440	325
400-410	300

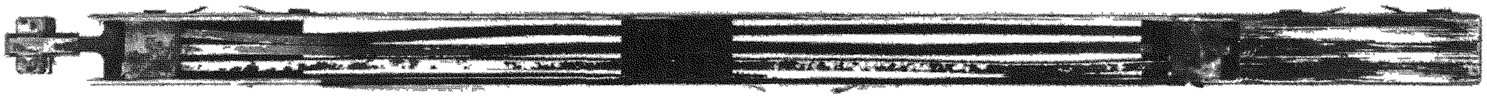
The above temperatures were steady-state conditions in deionized, degassed water. In addition, the samples were exposed to 75 hr of operation between 400 and 500°F, and 400 hr of operation below 300°F without radiation. The latter operation included some process water cooling. The velocity of the water past the plates was estimated at 30 fps. The pH ranged from 6.8 to 7.2.

The plates in the high-flux end of the cartridge received an estimated thermal flux exposure of 1×10^{21} nvt. The upper limit for fast flux exposure was less than 5×10^{19} nvt. This is equivalent to about 0.2% burnup of all core atoms in a natural uranium fuel plate.

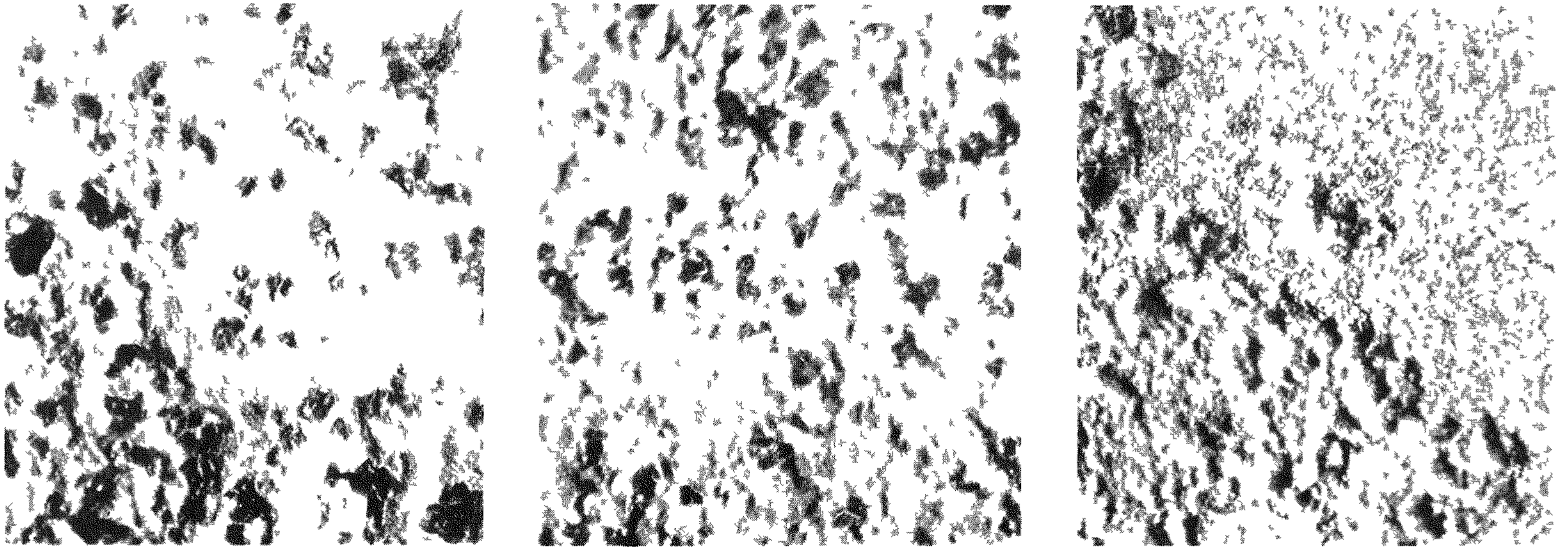
Upon completion of the irradiation period, the samples were removed and shipped to ANL. At Argonne the samples were stripped of the scale and cleaned electrolytically in a saturated boric acid solution. All operations were performed in high-level caves.

The results are summarized in Table III. The corrosion rate increased with distance from the core. This is made evident by the appearances (Figs. 27 and 28) and the stripped weight losses of the samples. The samples in the out-of-reactor cartridge showed a large increase in corrosion as compared to their counterparts in the in-reactor cartridge. The relative roughness of the surfaces correlates with the weight loss of the respective specimens and test location. The warpage of the plates (see Fig. 27) is attributed to the linear expansion differential between the aluminum-nickel samples and the stainless steel clamps at either end of the specimens. The maximum warpage occurred in plates located in the high-flux region of the in-reactor cartridge.

CARTRIDGE NO. MTR-W-6-E (OUT-OF-REACTOR)



CARTRIDGE NO. MTR-W-6 (IN-REACTOR)



2S Al - 2% Ni
(X7)

2S Al - 1% Ni
(X7)

2S Al - 0.5% Ni
(X7)

FIG. 27

LOADING ARRANGEMENT OF IN-REACTOR AND OUT-OF REACTOR CARTRIDGES AND GENERAL SURFACE APPEARANCE OF OUT-OF-REACTOR SPECIMENS OF 2S ALUMINUM-NICKEL ALLOYS.

Table III

SUMMARY OF MTR CORROSION-IRRADIATION
OF ALUMINUM-NICKEL ALLOYS

Composition % Ni	Row*	Position*	Weight Loss, mg/cm^2
	In-Reactor Cartridge MTR-W-6		
0.5	1	Top	4.71
0.5	2	Top	5.02
1.0	1	Center	3.61
1.0	2	Center	5.28
2.0	1	Bottom	3.11
2.0	2	Bottom	5.58
	Out-of-Reactor Cartridge MTR-W-6-E		
0.5	2	Top	16.15
0.5	1	Center	15.40
1.0	1	Top	19.30
1.0	1	Bottom	19.65
2.0	2	Center	14.71
2.0	2	Bottom	15.00

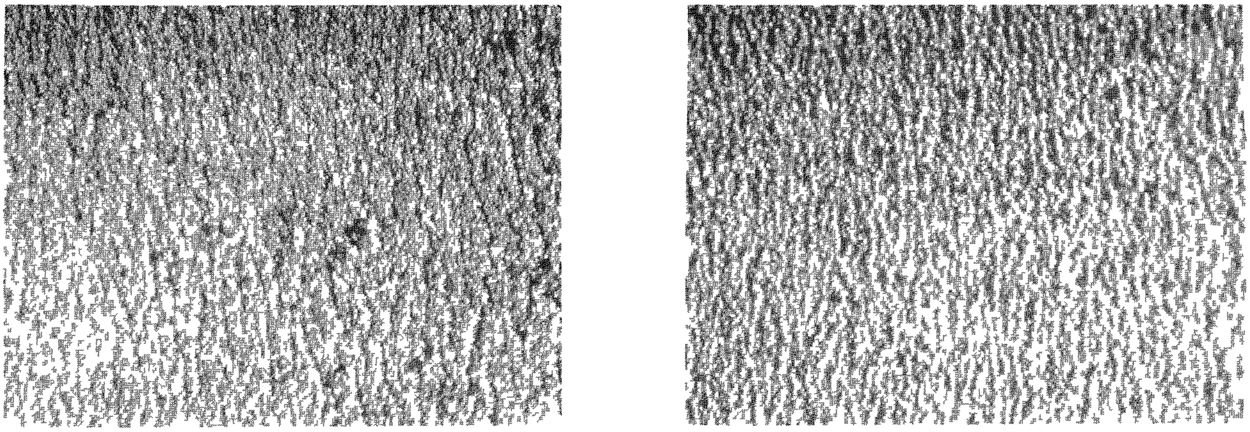
*See Fig. 27

A comparison ot the MTR test results with those of the loop tests at ANL show: (1) the samples in the out-of-reactor cartridge exhibit corrosion rates similar to loop tests with degassed, neutral water at 500°F; and (2) the weight losses of the in-reactor samples approximate the values of samples exposed in loops containing neutral water at 500°F, with natural buildup of hydrogen ranging from 200 to 300 cc H_2/liter of water.

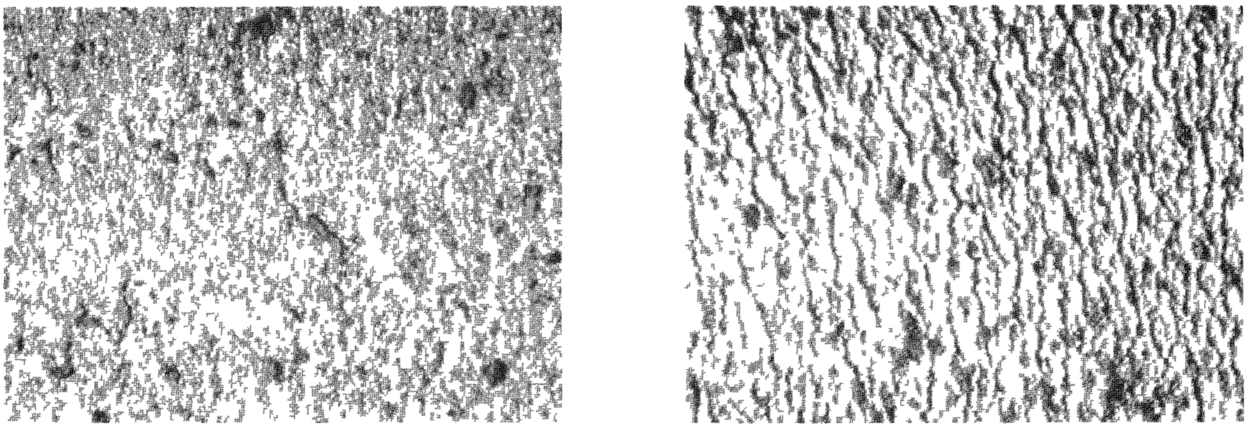
B. M-388 Alloy

1. Cartridge MTR-W-7

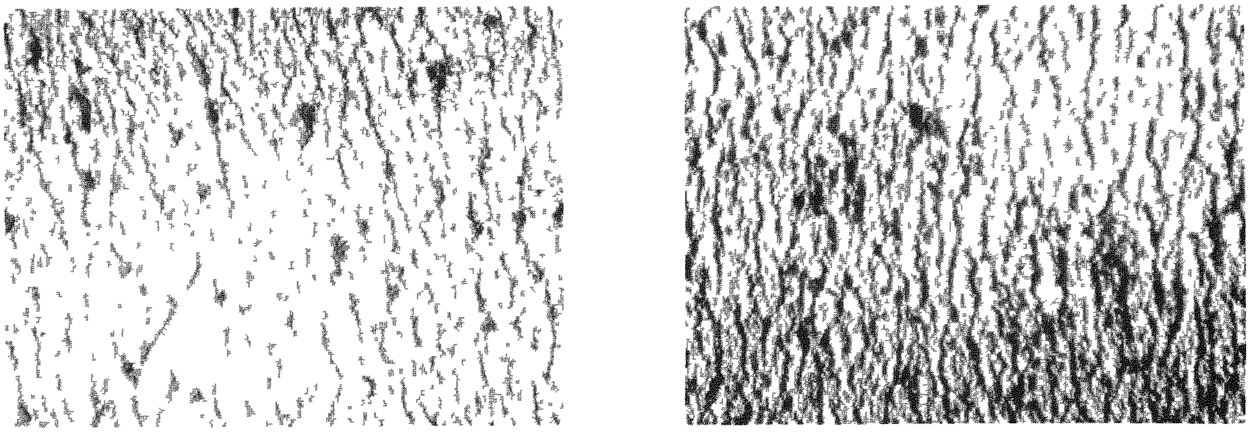
The loading of M-388 samples (2.500 in. x 0.562 in. x 0.125 in.) in the in-reactor and the out-of-reactor cartridges was designed to permit three withdrawals for comparison of corrosion rates of specimens in the respective cartridges. All specimens were held in combs made of M-388 alloy. With reference to the illustration, each cartridge consisted of five sections: three for the original samples (Secs. 1, 2, 3), and two for replacement samples (Secs. 4, 5).



2S Al - 0.5% Ni



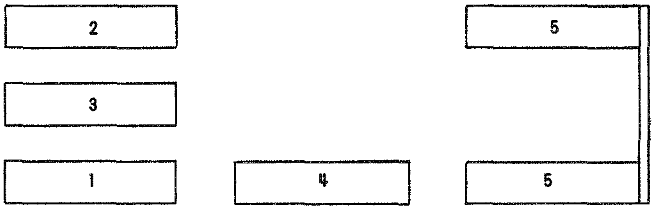
2S Al - 1% Ni



2S Al - 2% Ni

FIG. 28

REPRESENTATIVE SURFACE AREAS OF 2S ALUMINUM-NICKEL ALLOYS FROM IN-REACTOR CARTRIDGE MTR-W-6. (X7)



At the end of the first test period, samples in Section 1 were withdrawn and replaced with coupons from Section 4. At the end of the second period, samples from Sections 2 and 4 were withdrawn and replaced with specimens from Section 5. Thus, samples in Sections 3 and 5 were available for weight loss determinations at the end of the third period.

Owing to refueling and operational difficulties, the temperature varied considerably during the three exposure periods as follows.

	Time, hr		
Temp, °F	Period 1	Period 2	Period 3
<200	24	120	218
300	-	-	16
400	-	20	30
485-500	200	340	300

Further, due to operational errors, the ion exchange column was not placed in operation during the second period and a portion of the third period (see Table IV). The consequent low purity of the water had an adverse effect on the in-reactor replacement samples, as compared with the out-of-reactor replacements (see Fig. 29).

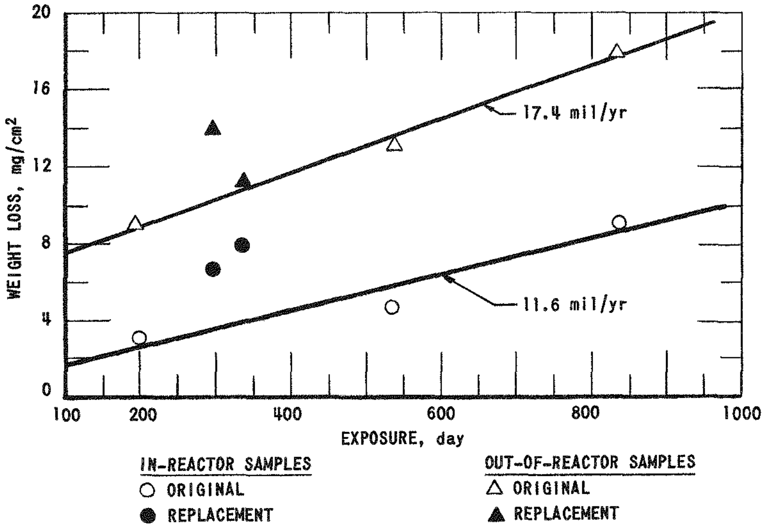


FIG. 29

CORROSION-IRRADIATION OF M-388 ALLOY IN WATER AT 485-500°F AND 16 fps.
(CARTRIDGE MTR-W-7)

Table IV

SUMMARY OF TESTS ON M-388 ALLOY IN CARTRIDGE MTR-W-7

Cartridge Section	Hours at 485-500°F	Water Conditions[a]		Total Neutron Exposure		% of Exposure at 485-500°F	Weight Loss (mg/cm²)	
		pH	Resistivity (megohm-cm)	Fast x 10^{19} nvt	Thermal x 10^{20} nvt		In-Reactor	Out-of-Reactor
1	200	6.2-7.8	0.5-3.0	2.0	2.0	80	1.82; 3.22; 3.14; 3.98	6.86; 7.98; 9.40; 11.40
4 (Replacement)	340	7.4-8.5 [c]	Very Low [b]	3.0	3.0	75	8.56; 7.48; 7.52; 7.78	11.39; 10.73; 11.43; 11.25
2	540	-	-	5.0	5.0	77	4.64; 4.95; 4.56	13.63; 13.36; 13.15; 12.76
5-6 (Replacement)	300	7.3-8.5 [c]	0.25-2.5 [d]	4.8	4.8	50	6.96; 6.59; 6.46; 6.82; 7.30; 6.70; 6.56; 5.78	14.1; 13.7; 13.9; 14.0; 13.7; 13.7; 14.0; 14.1
3	840	-	-	9.8	9.8	64	7.86; 8.54; 10.9	17.8

---

[a] Water velocity: 16 fps.

[b] Ion exchanger not placed in operation due to oversight.

[c] Only sporadic pH readings were taken

[d] Ion exchanger in operation

In general, the appearances of all samples were not good. All were covered partially with a loose black scale. Specimens exposed for two or more periods showed areas of bare metal. The appearance of the 340-hr replacement sample in Fig. 30 is typical of the corrosion attack around the clamp area that was observed on all out-of-reactor samples. The corrosion attack was not as pronounced on the in-reactor samples. The balance of the photographs show that the surface roughness of the out-of-reactor samples was enhanced by continued exposure, while that of the in-reactor samples remained about the same. The 840-hr specimens showed some signs of erosion attack. However, the increase in corrosion with distance from the core was not as noticeable in this experiment as it was in the MTR-W-6 exposure.

2. Cartridge MTR-W-9

Exposure of M-388 alloy in MTR-W-9 differed from the previous exposure (MTR-W-7) in two respects: (1) each withdrawal was made at the end of three cycles instead of one cycle; and (2) the water conditions were improved considerably. The test conditions are summarized in Table V.

The increase in exposure time gave rise to another variable-erosion. The samples were clamped in a manner such that a high-velocity area (~24 fps) existed for one-third the length of the samples between clamps. This velocity-accelerated corrosion, coupled with increased test time, resulted in the formation of grooves in the surface of the samples. Since the sample was small (2.500 in. x 0.562 in. x 0.125 in.), localized accelerated corrosion was an important factor in the weight loss determination.

In the present test, the erosion problem was enhanced by the fact that the loop pump operated almost continuously, even when the loop water temperature decreased as a result of reactor shutdown. In this case, the pump was in operation for 4,002 hr even though the loop temperature ranged between 470 and 485°F for only 2,360 hr. (The loop temperature seldom drops below 300°F when the pump is operating, due to the heat generated by the pump.)

The weight losses for the samples in the in-reactor and out-of-reactor cartridges are listed in Table VI. The corrosion rates, plotted in Fig. 31, are excessively high and show only to a slight degree the apparently reduced corrosion under irradiation that was observed in the earlier cartridges.

Photomicrographs of uniformly corroded areas at 20X magnification (see Fig. 32) showed little difference in surface roughness due to irradiation. In Fig. 33 the in-reactor samples show at lower magnification (2X) considerably less attack than the out-of-reactor samples; furthermore, the attack is emphasized only in the velocity-accelerated corrosion region described above.

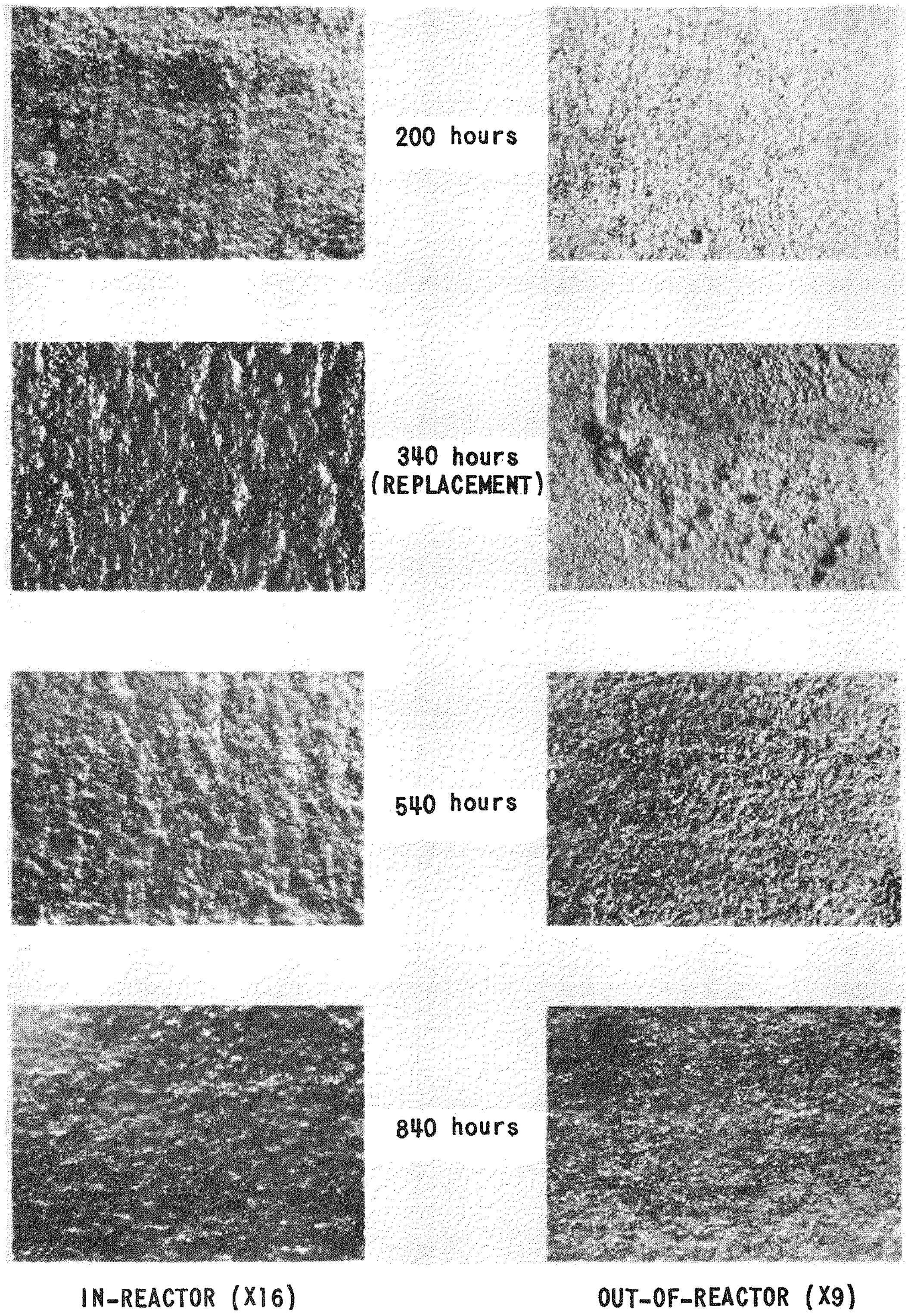


FIG. 30

REPRESENTATIVE AREAS OF M-388 SAMPLES EXPOSED IN CARTRIDGE MTR-W-7.

Table V

SUMMARY OF OPERATING CONDITIONS FOR CARTRIDGE MTR-W-9

		Hours at Temperature °F				Water Conditions				Thermal* Neutron Exposure x 10^{20} nvt
						Resistivity, megohm-cm	pH		Oxygen ppm	
Period	Cycle	300-400	400-470	470-485	300-485		Range	Average		
1	75	123	102	178	403	0.2-3.0	6.1-8.6	7.2	0.17-0.05	2.75
	76	87	69	257	413	1.5-3.0	5.6-8.2	6.6	0.60-0.00	2.90
	77	193	106	219	518	1.5-3.0	5.9-7.2	6.5	1.52-0.33	2.55
2	78	24	89	249	362	0.9-3.0	4.8-7.5	6.2	1.4 -0.6	2.91
	79	167	90	232	489	1.5-3.0	6.4-9.2	7.2	0.6	2.84
	80	140	23	312	475	1.5-3.0	6.6-9.6	7.3	not measured	3.01
3	81	90	62	266	418	1.5-3.0	6.1-8.5	7.5	0.8	2.90
	82	143	36	327	506	1.5-3.0	6.2-8.5	7.3	2.1 -1.3	3.22
	83	71	27	320	418	0.5-3.5	6.3-8.8	7.5	3.2	3.10

---

*Fast neutron flux was lower by a factor of 10.

Table VI

WEIGHT LOSSES OF M-388 ALLOY EXPOSED IN CARTRIDGE MTR-W-9

Cartridge Section	Hours at Temperature		Weight Loss, mg/cm²			
			In-Reactor		Out-of-Reactor	
	470-485°F	300-485°F	Individual	Average	Individual	Average
1	654	1334	13.0; 11.9; 12.1; 13.3; 10.5; 9.7	11.8	21.0; 21.0; 20.9; 21.4; 19.5; 18.1	20.3
4 (Repl.)	793	1326	15.1; 16.3; 14.2 14.5; 13.6; 12.4	14.4	12.7; 12.5; 12.7; 13.3; 12.6	12.8
2	1447	2660	28.7; 28.2; 26.6; 23.1; 21.0	25.5	29.0; 29.8; 29.8; 31.5; 29.5	29.9
5 (Repl.)	913	1342	14.6; 10.8; 9.9; 10.8; 11.9; 10.9; 10.2; 10.3; 11.5;	11.2	16.2; 15.9; 16.2; 15.9; 16.3; 16.0; 15.9; 16.0; 15.6	16.0
3	2360	4002	35.6; 36.4; 32.5; 30.4	33.7	43.6; 43.4; 43.0; 46.5	44.1

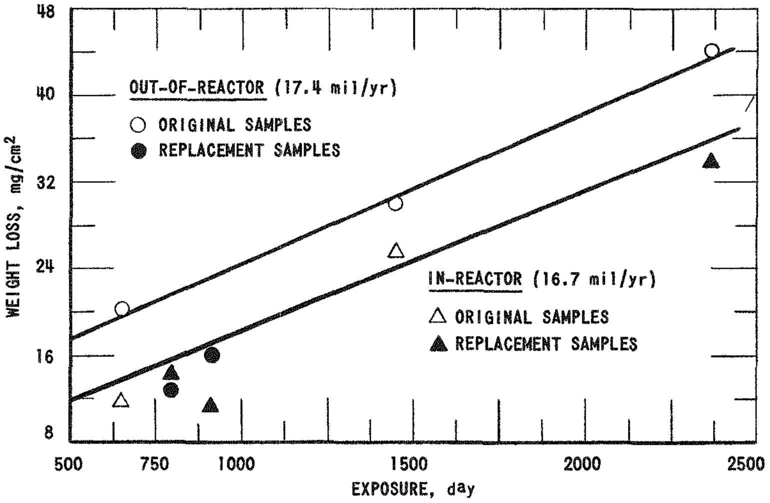
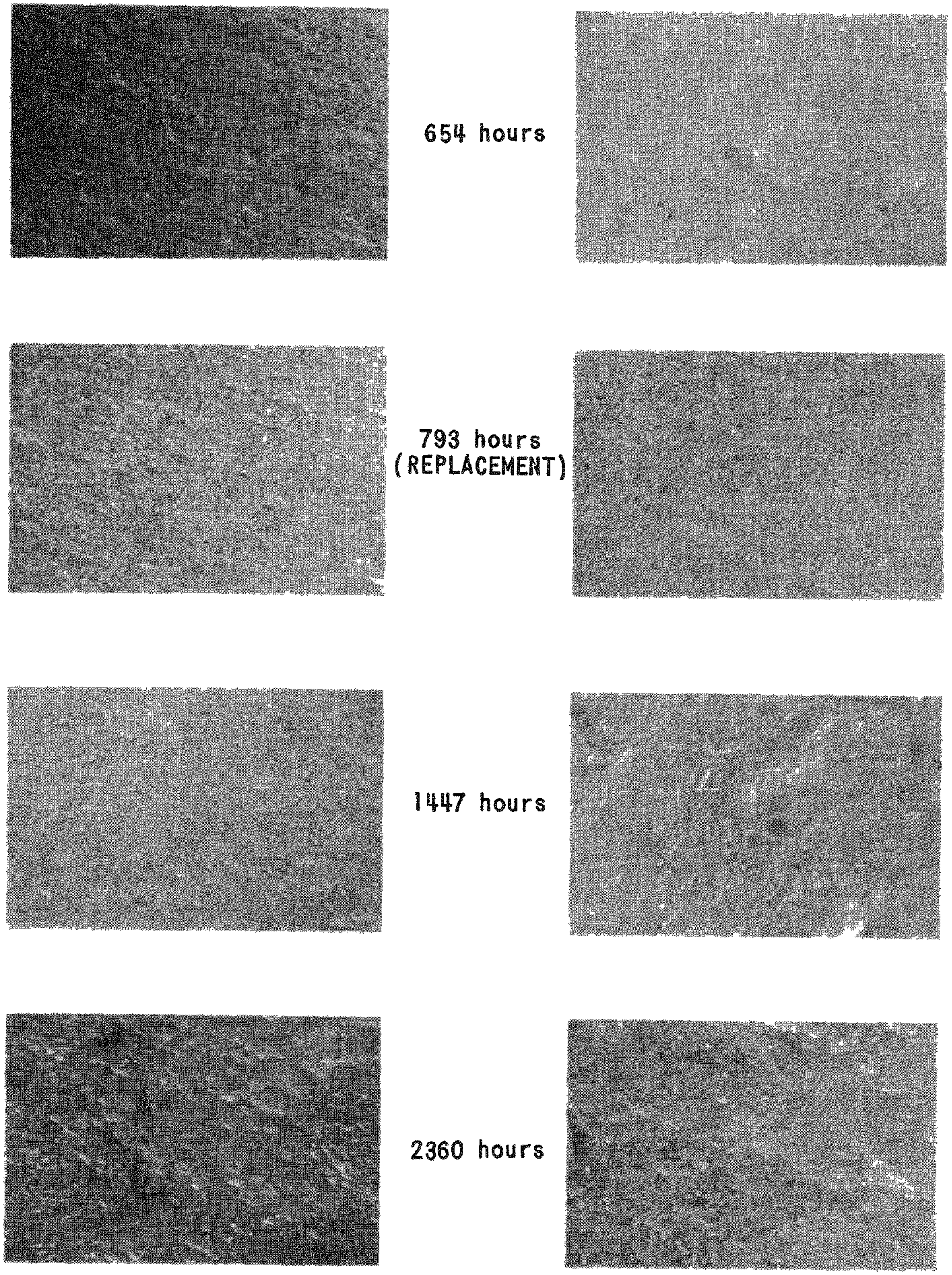


FIG. 31

CORROSION-IRRADIATION OF M-388 ALLOY IN WATER AT 470-480°F AND 16 fps. (CARTRIDGE MTR-W-9)



654 hours

793 hours
(REPLACEMENT)

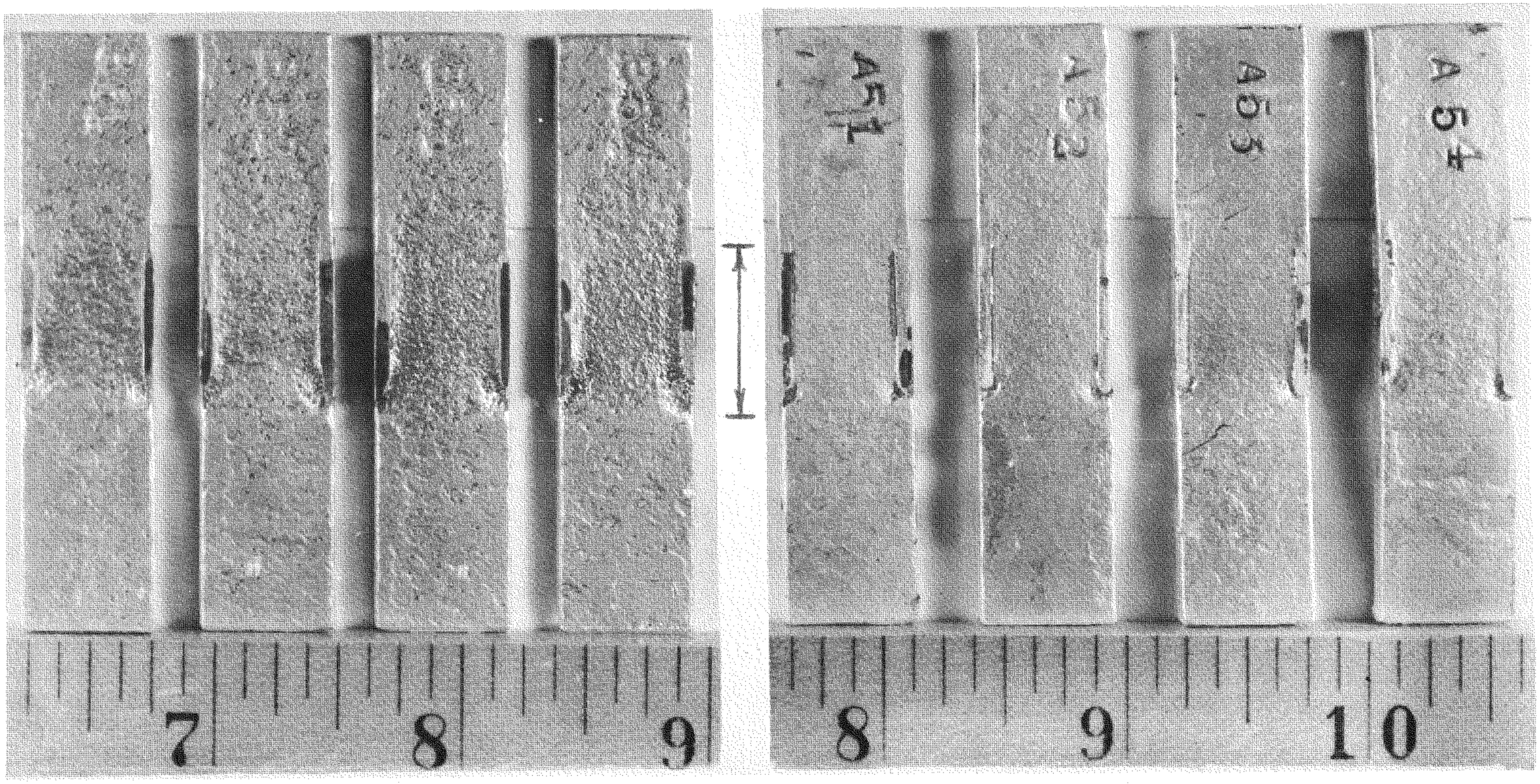
1447 hours

2360 hours

IN-REACTOR

OUT-OF-REACTOR

FIG. 32
REPRESENTATIVE AREAS OF M-388 SAMPLES EXPOSED IN CARTRIDGE MTR-W-9. (X20)



OUT-OF-REACTOR

IN-REACTOR

FIG. 33

COMPARISON OF IN-REACTOR WITH OUT-OF-REACTOR SAMPLES OF M-388 ALLOY EXPOSED IN CARTRIDGE MTR-W-9. ARROWS INDICATE REGION OF VELOCITY-ACCELERATED CORROSION. (X2)

IX. CORROSION OF M-388 ALLOY UNDER BOILING WATER HEAT TRANSFER CONDITIONS

The possibility of using M-388 alloy as fuel cladding in a boiling water reactor justified a study of its corrosion behavior under heat transfer conditions in boiling water.

A. Boiling Corrosion Heat Transfer Facility No. 2

Test Facility No. 2 was designed to evaluate the combined effects of boiling water corrosion and heat transfer on a single M-388-clad stainless steel Type 304 tube.

The test section is shown schematically in Fig. 34. The M-388-clad tube was jacketed by a pressure vessel and sealed at the inlet and outlet ends with a Swagelok fitting and a Teflon-packed gland. The test section was installed between companion pipe flanges in a 550°F, 1800-psi heat transfer loop which served as the heat source on the inside of the specimen tube. The pressure, temperature (422°F), and heat flux within the pressure vessel were controlled by a pressure controller adjusted to maintain 300 psig by regulating the flow of coolant through a closed condenser coil inside the vessel. Thus, boiling occurred on the clad surface and the steam liberated was condensed by the cooling coil and returned to the water phase.

The average heat flux desired was 25,000 Btu/(hr)(ft^2). However, it is estimated that the heat flux varied from 40,000 at the bottom to 15,000 at the top of the sample tube.

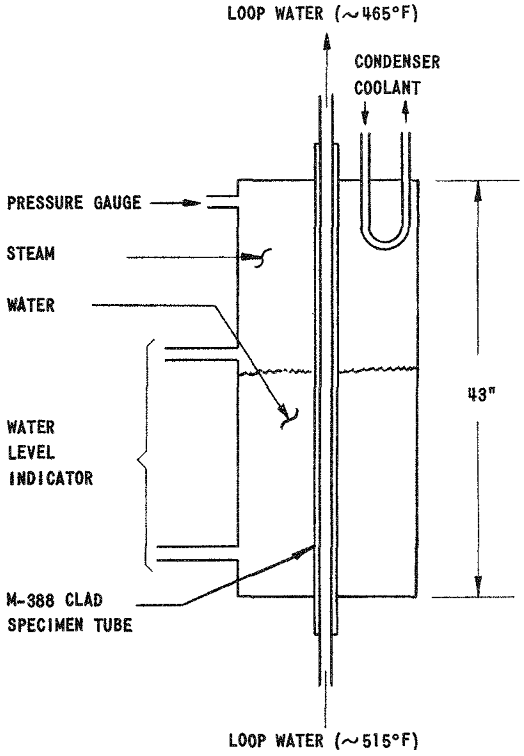


FIG. 34
SCHEMATIC OF TEST SECTION IN BOILING WATER CORROSION-HEAT TRANSFER TEST FACILITY NO. 2

1. Tube No. 1

The initial test was made on a Type 304 tube (0.375 in. OD), with an M-388-clad thickness of 1/16 in. The test was operated for 1612 hr at 422°F, with an average heat flux of 25,000 Btu/(hr)(ft^2). The water conditions, and temperature drops through the tube are summarized in Table VII. The variation in pH after 177 hr was occasioned by attempts to maintain a low pH value. Each day, a portion of the loop water was bypassed through a cation resin bed. As a consequence, the pH would drop initially to the lower value and then rise to the higher value during the next 24-hour period (or 72-hour period during weekends).

Table VII

OPERATING CONDITIONS - TUBE NO. 1

Time, hr	Mean Avg ΔT at Heat Flux, of 25,000 Btu/(hr)(ft^2) °F	Water Conditions	
		pH	Resistivity, ohm-cm
0	40	6.5	500,000
3	42	6.9	130,000
7	59	6.8	130,000
9.5	69	-	-
12.5	69	7.2	300,000
15.5	60	-	-
17	58	-	-
177	58	6.5-7.0	130,000
388	60	6.5-7.5	200,000
1031	61	6.5-7.3	300,000
1343	62	6.5-7.2	400,000
1612	63	6.5-7.2	400,000

The observations made at the end of each test period are listed in Table VIII. The weight gains or losses were based on the surface area in contact with the water, since this area exhibited almost all of the corrosion attack. The weight gain at 170 hr may be in error, as the inside of the tube was not cleaned. Subsequent examination revealed that loose scale from the loop heat source had deposited on the inside wall of the specimen tube. At the end of each successive period, the walls were cleaned with acetone prior to calculations of weight changes. The red coloring observed on the tube surface in the steam phase was probably iron oxide entrained from the vessel wall by the boiling, splashing water. Since aluminum alloys have a high initial corrosion rate which levels off after a few hours, it is not possible to determine a true overall corrosion rate based on the single stripped weight loss listed in Table VIII. However, based on this value, the apparent overall corrosion rate is 2.9 mil/yr.

Figure 35 shows the stripped appearance of the tube after exposure for 1000 hr in the steam-water region. The scratches were incurred during removal for periodic examination. At the conclusion of the test, microscopic examination revealed small shallow pits at various places along the scratches. The tube was bowed slightly, probably due to the different coefficients of expansion for the stainless steel and the aluminum-nickel clad.

Table VIII

SUMMARY OF BOILING WATER CORROSION-HEAT TRANSFER TEST ON ALUMINUM-NICKEL CLAD TUBE NO. 1

Test Period	Time, hr	Weight Change, mg/cm^2		Outside Diameter of Tube, in.			Appearance
		Gain	Loss	Water Phase	Steam-Water Phase	Steam Phase	
Start	0			0.5002	0.5002	0.5002	Metallic.
1	170	2.22		0.5008	0.5014	0.5004	Water phase: Adherent grey coating typical of M-388 alloy. Steam-water phase: Slight reddish coloring, probably iron oxide. Steam phase: Adherent dull white-grey coating.
2	1083	1.61		0.5012	0.5014	0.5003	Water phase: Adherent red coating with a few, very small spots of bare metal along scratches in tube. Steam-water phase: Adherent red coating. Steam phase: Adherent dull white-grey coating with a little red coloring near steam-water phase.
3	1702 (Before strip)	1.98		0.5012	0.5014	0.5005	Water phase: Adherent red coating with more of the very small spots of bare metal showing. Steam-water phase: A band of darker red coating. Steam phase: Adherent dull white-grey coating with a little red coloring near steam-water phase.
	(After strip)		3.95	0.4996	0.5000	0.5002	Dull metallic appearance.

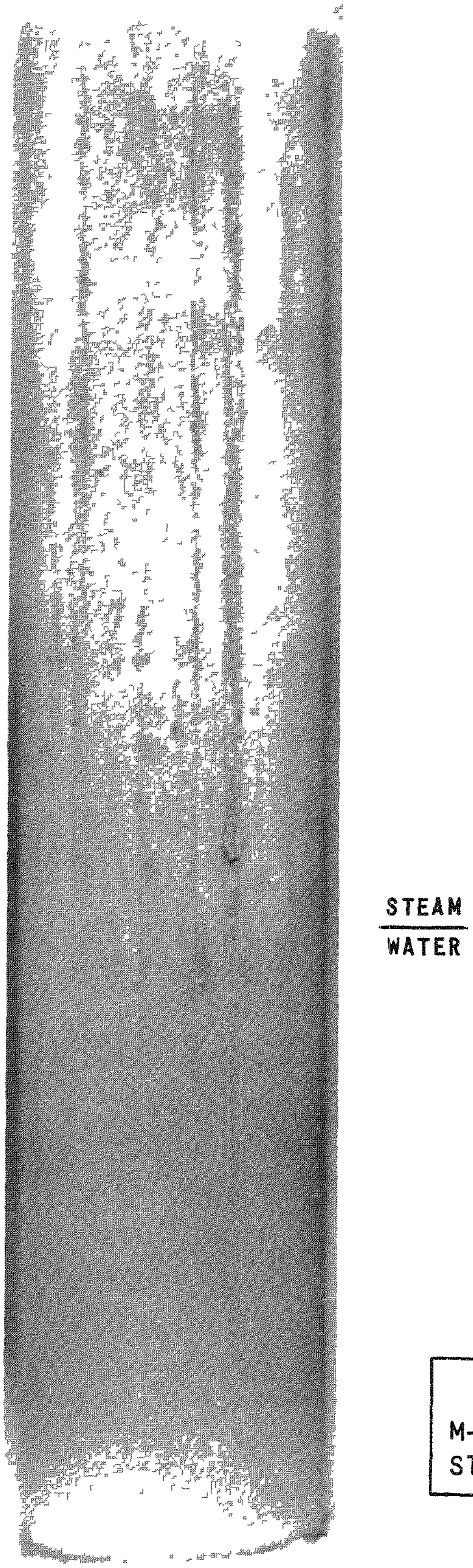


FIG. 35

M-388 CLADDING AFTER 1000 hr IN STEAM-WATER REGION (TUBE NO. 1)

2. Tube No. 2

Tube No. 2 was a duplicate of Tube No. 1. The original intent was to evaluate the corrosion behavior of the cladding under long-term (3,000 hr) exposure to the test environment for Tube No. 1. However, the test was terminated at the end of the first period (661 hr). Examination showed accelerated corrosion attack had occurred in two areas containing known defects (inclusions). One area was located between two weld beads near the top of the steam phase [see Fig. 36 (A)]. The other area was located in the parent metal in the steam-water phase [see Fig. 36 (B)]. Except for these two areas the tube surface looked very good.

Prior to removal of the scale deposit, the tube registered a weight gain of 1.7 mg/cm^2. The stripped weight loss was 1.26 mg/cm^2. When latter was combined with that for Tube No. 1, weight loss rate of 2.8 mil/yr. was obtained. Micrometer measurements showed no significant change in the diameter of the tube.

3. Tube No. 3

Tube No. 3 was made from Tube No. 1 by grinding and polishing off about 10 mils of M-388 clad.

After 3689 hr of exposure to conditions (see Table VII), the tube as-removed showed a weight gain of 4.56 mg/cm^2. The stripped weight loss was 9.11 mg/cm^2. Examination revealed slightly increased corrosion attack around surface scratches incurred during removal for inspection.

A plot (Fig. 37) of the individual weight losses for Tubes No. 1, 2, and 3 shows very consistent results, yielding a final corrosion rate of 3.3 mil/yr.

B. Boiling Corrosion Heat Transfer Facility No. 3

Test Facility No. 3 differed from Test Facility No. 2 in two respects: (1) a total of 25 samples could be tested simultaneously; and (2) electric resistant heating was used instead of high-temperature water.

Each sample (Fig. 38) was a stainless steel-clad resistance heater (0.625 in. OD x 20 in. long) jacketed with M-388 alloy (0.040 in. thick). Figure 39 shows the test apparatus with the heaters installed in the pressure vessel. The temperature and pressure in the vessel were maintained equal to the conditions in the previous tube tests.

During the course of the test, 0, 375, 750, and 1500 watts of electrical energy were applied, respectively, to four sets of specimen tubes. The heat flux at 1500 watts corresponds to about 22,000 Btu/(hr)(ft^2).

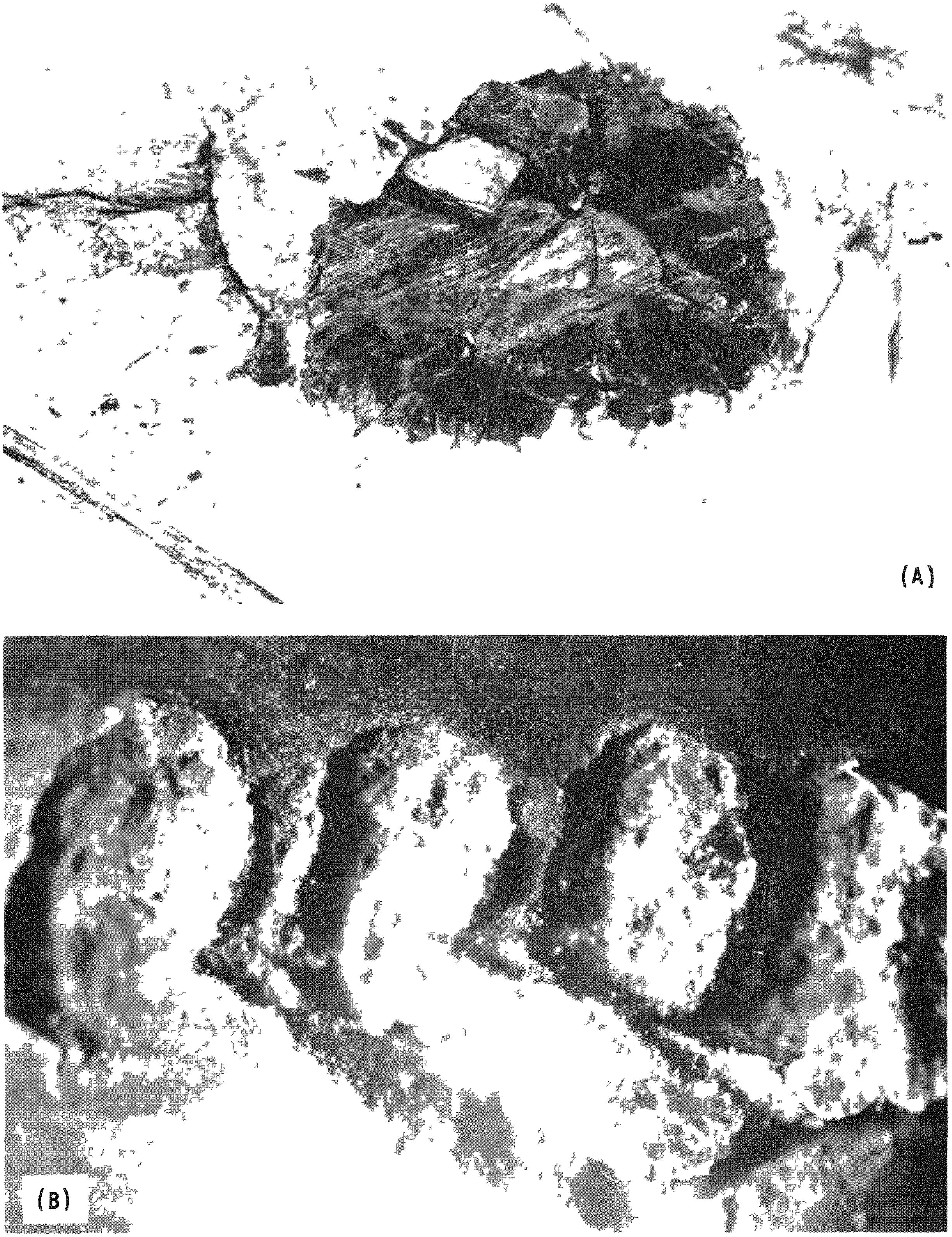


FIG. 36

ACCELERATED CORROSION ATTACK AT SURFACE INCLUSIONS IN M-388 CLAD TUBE NO. 2 (A) BETWEEN WELD BEADS IN STEAM PHASE AND (B) IN PARENT METAL IN STEAM-WATER PHASE. (X50)

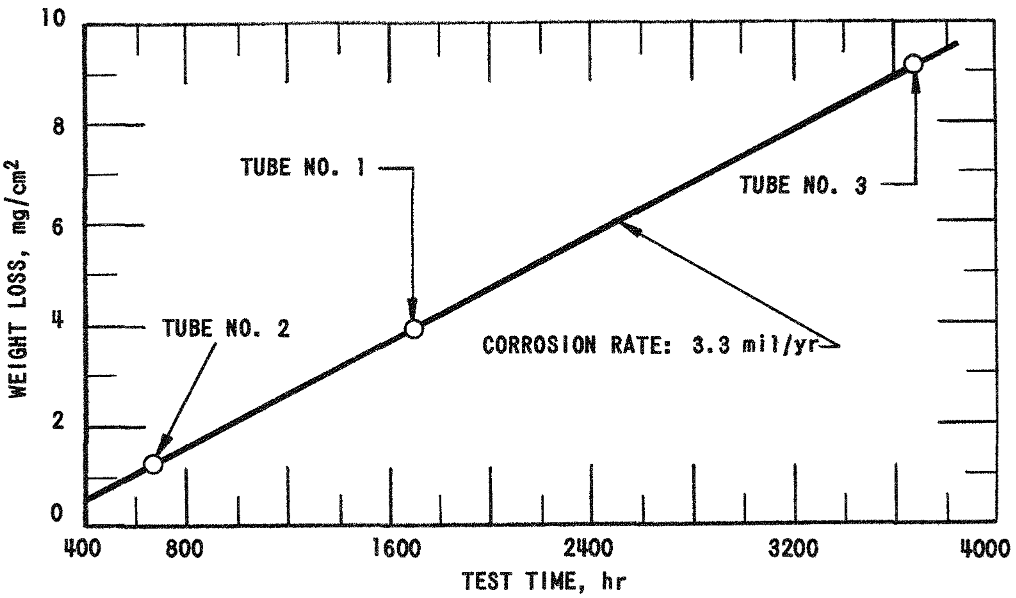


FIG. 37

SUMMARY OF BOILING CORROSION-HEAT TRANSFER TESTS ON M-388 CLAD STAINLESS STEEL TYPE 304 TUBES IN WATER AT 422°F AND 300 psig. (TEST FACILITY NO. 2)

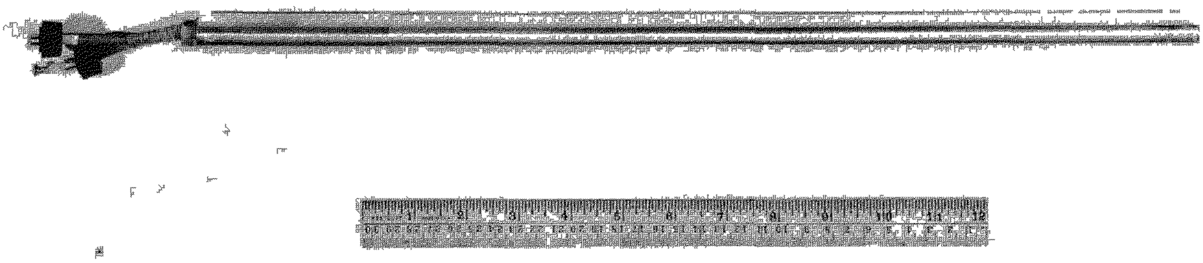


FIG. 38

M-388 CLAD STAINLESS STEEL RESISTANCE HEATER TUBE USED IN BOILING CORROSION HEAT TRANSFER TEST FACILITY NO. 3.

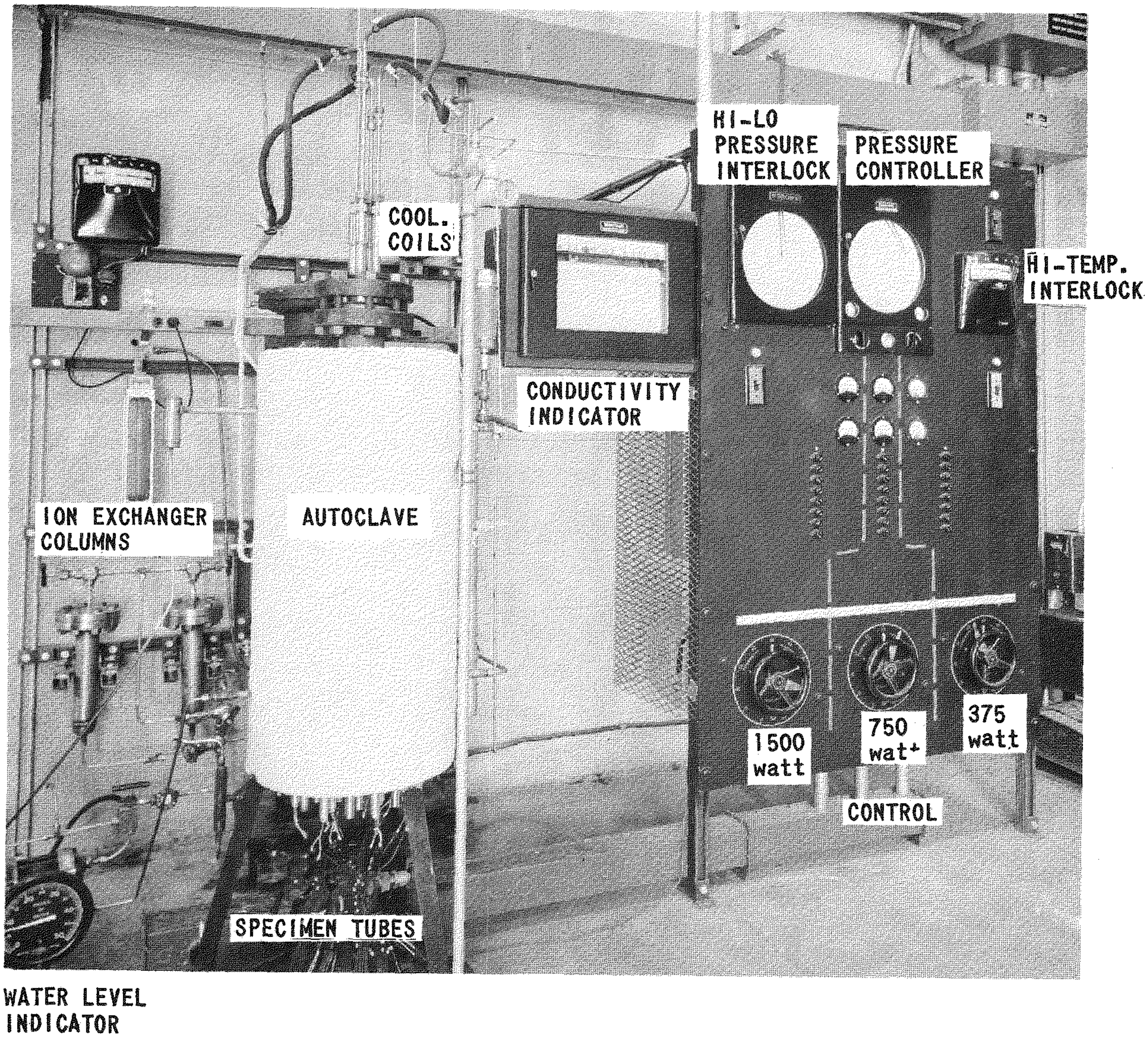


FIG. 39
BOILING CORROSION-HEAT TRANSFER TEST FACILITY NO. 3

Periodically, certain heaters were removed for inspection and determinations of weight changes; replacement tubes were installed and the test was resumed.

The test results are summarized in Table IX and Fig. 40. Owing to the scatter of data in Fig. 40, the rate values could vary ±0.2 mil/yr. Most of the differences in rates between the power levels are believed due to differences in surface temperature.

Table IX

SUMMARY OF BOILING CORROSION HEAT TRANSFER TESTS IN FACILITY NO. 3

Sample No.	Power, watts	Time, hr	As-removed Weight Gain, mg/cm^2	Stripped Weight Loss, mg/cm^2
6	0	721	1.57	1.62
15		2194	2.36	3.41
14		4356	3.85	4.88
29		5315	4.90	7.36
21		5775	5.76	5.32
23	0	8930	6.85	6.26
2	375	721	1.72	2.05
3		1462	2.05	2.10
16		4356	4.46	5.96
30		5315	5.72	9.07
17		5775	5.78	7.56
25		7446	6.02	7.95
28	375	8930	8.36	10.11
1	750	721	1.85	2.30
4		1462	2.13	2.67
9		2915	3.38	4.17
13		4356	4.23	7.15
31		5315	5.01	11.05
18		5775	5.59	8.56
24		7446	6.18	10.05
26	750	8930	5.62	10.77
7	1500	721	1.95	3.19
5		1462	2.61	3.68
12		4356	4.55	8.74
32		5315	5.64	12.95
19		5775	5.76	10.91
20		7446	5.62	11.37
22	1500	8930	5.52	15.25

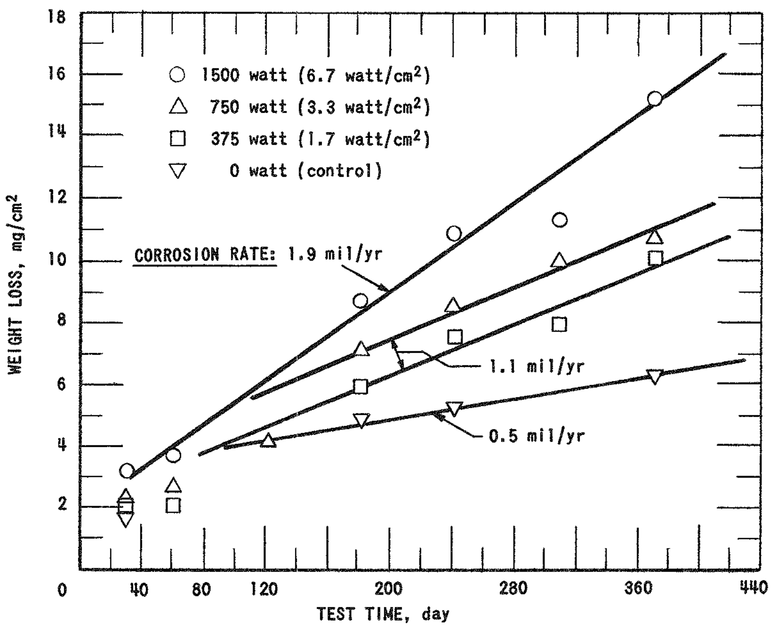


FIG. 40

SUMMARY OF BOILING CORROSION-HEAT TRANSFER TESTS ON M-388 CLAD ELECTRIC RESISTANCE HEATERS IN WATER AT 422°F AND 300 psig. (TEST FACILITY NO. 3)

C. Conclusions

The corrosion rate of M-388 is acceptable for the specified test conditions: (1) absence of radiation; (2) demineralized water at 422°F; and (3) heat transfer rates not exceeding 40,000 Btu/ft^2. There is no accelerated corrosion attack due to boiling heat transfer, and no significant buildup of corrosion products on heat transfer surfaces.

X. COMPATIBILITY OF M-388 ALLOY WITH STAINLESS STEEL

Assuming that M-388 alloy can be used as fuel cladding in reactor systems at moderate temperatures, information was desired as to the compatibility of the M-388 with basic core structural materials. More specifically, the behavior of M-388 in combination with stainless steels Type 304 and Type 405 under water conditions is of immediate interest to the test program.

A. Static Corrosion Tests

Accidental exposure of a riveted couple of M-388 alloy and Type 304 stainless steel to tap water at room temperature resulted in accelerated corrosion of the aluminum-nickel alloy. The same results were obtained in a subsequent test for two weeks at the same conditions. Figure 41 shows the accelerated attack on the aluminum sample in the region of contact with the Type 304 specimen.

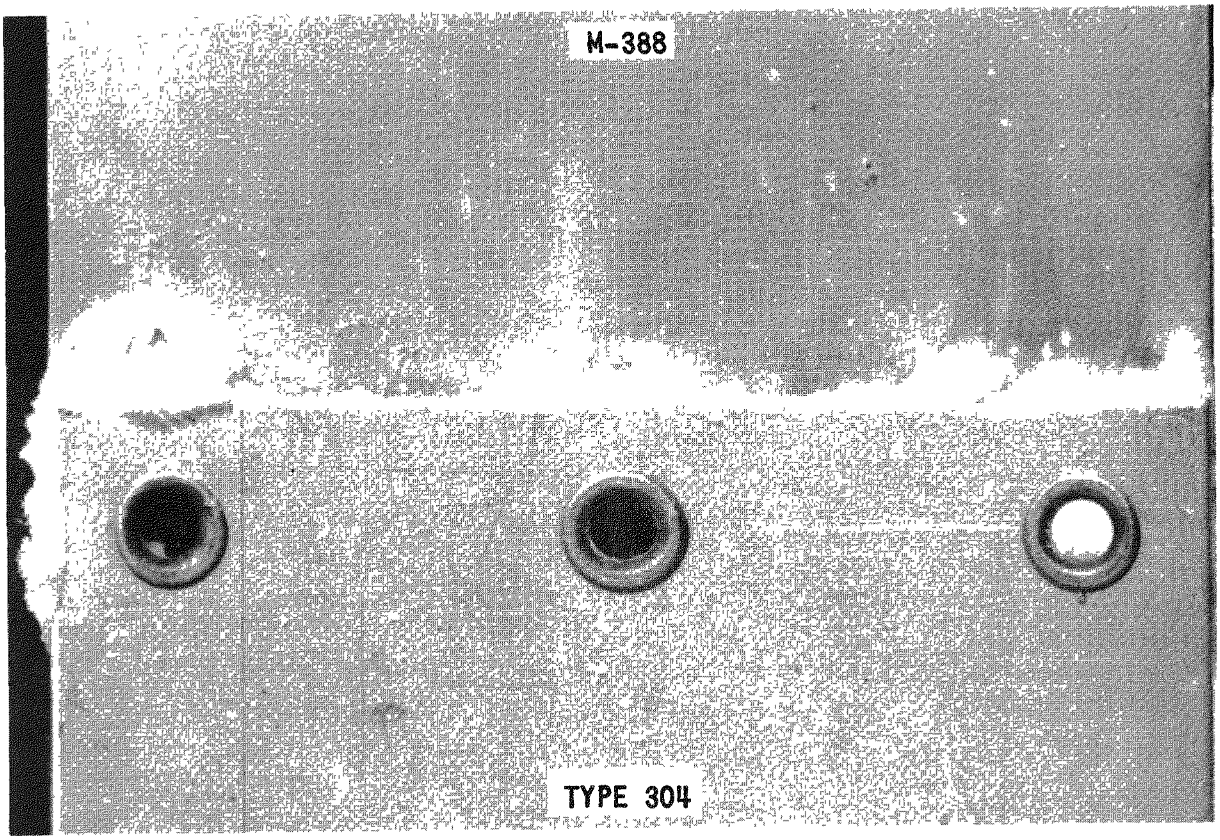
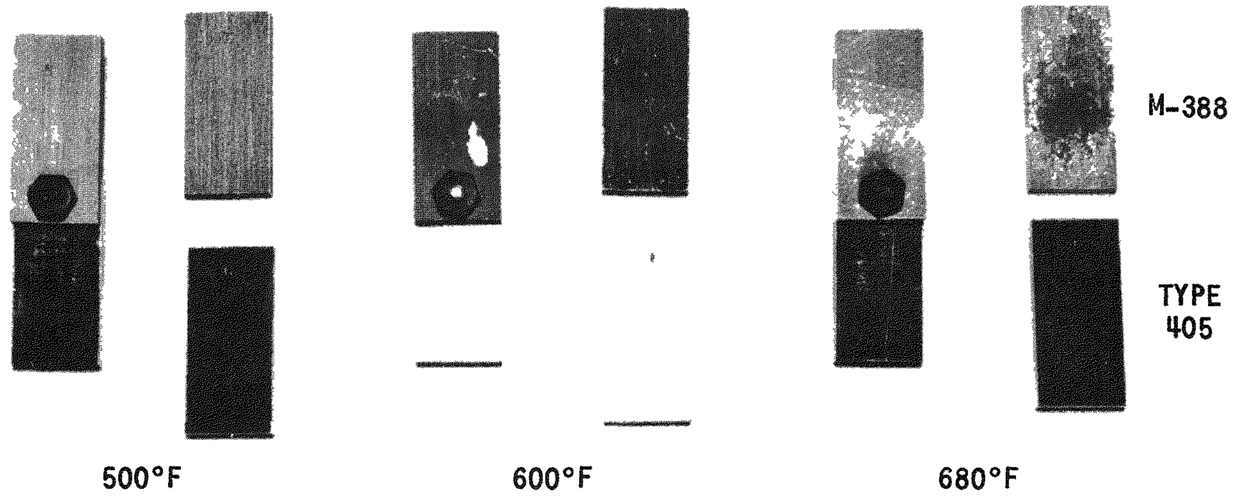


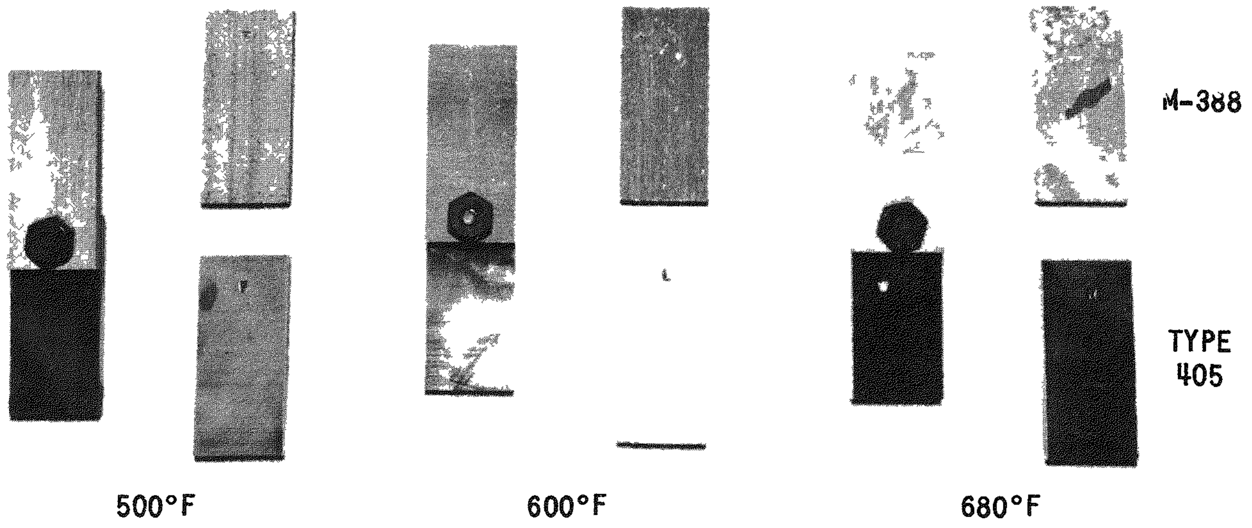
FIG. 41

ACCELERATED CORROSION OF M-388 ALLOY AT RIVETED JUNCTURE WITH TYPE 304 STAINLESS STEEL AFTER TWO WEEKS IN TAP WATER AT ROOM TEMPERATURE.

In subsequent experiments, individual and coupled specimens of M-388 and Type 405 stainless steel were exposed for 1449 hr to static degassed water and to air-saturated, demineralized water at 500, 600, and 680°F As shown in Fig. 42, accelerated corrosion attack occurred only on the specimens in air-saturated water at 680°F.



DEGASSED WATER



AIR-SATURATED WATER

FIG. 42

SINGLE AND COUPLED SPECIMENS OF M-388 ALLOY AND TYPE 405 STAINLESS STEEL AFTER EXPOSURE FOR 1449 hr TO STATIC WATER AT CONDITIONS NOTED.

Figure 43 shows the results of tests designed to evaluate the effect of surface area differential on the corrosion of coupled specimens of M-388 and Type 304 stainless steel. The specimens were exposed for 2500 hr in air-saturated water and in degassed, demineralized water at 550°F. Accelerated attack occurred only in air-saturated water and on a relatively small M-388 component of a relatively large Type 304 specimen couple.

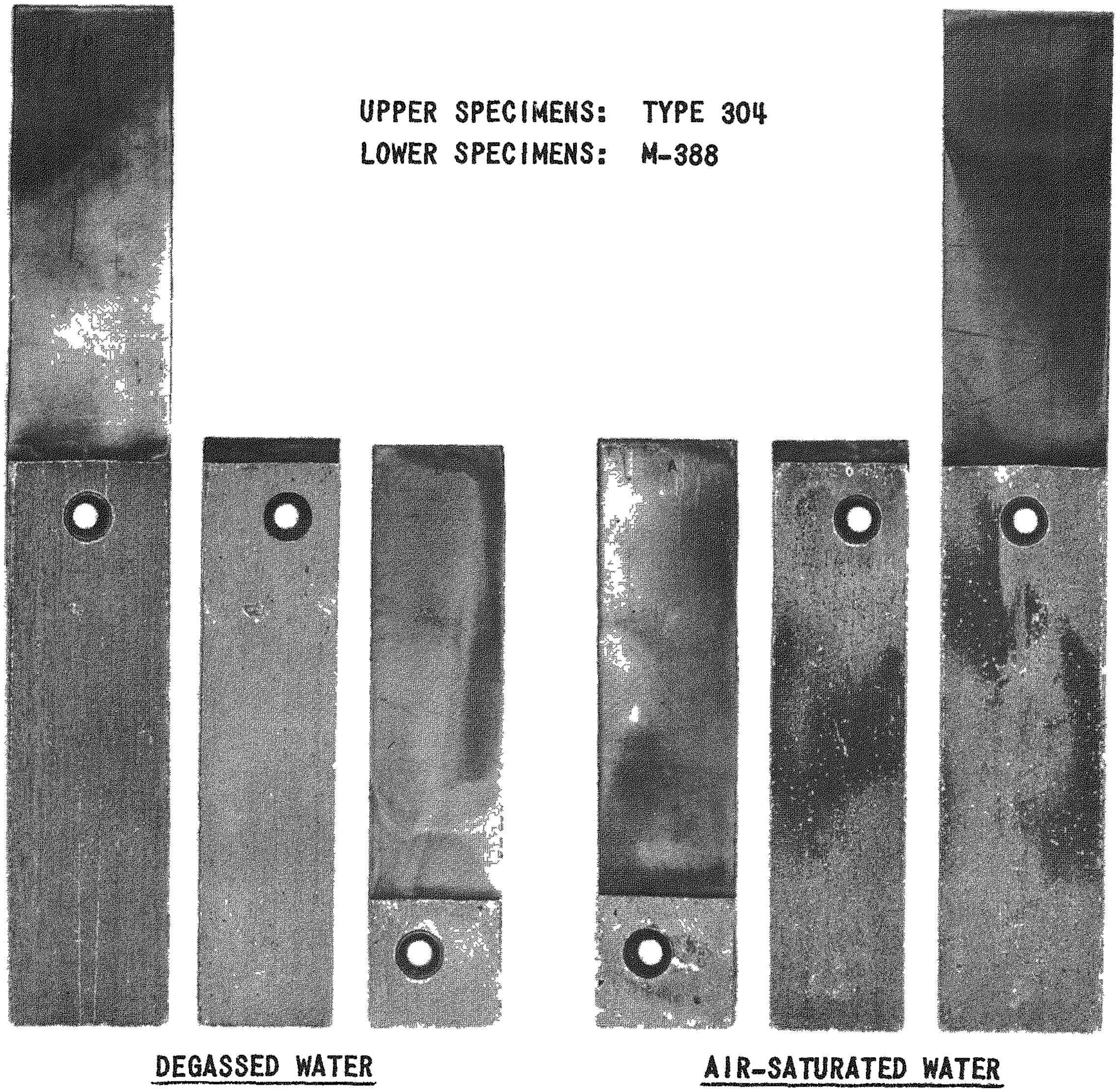


FIG. 43

EFFECT OF SURFACE AREA DIFFERENTIAL ON CORROSION OF COUPLES OF M-388 ALLOY AND TYPE 304 STAINLESS STEEL AUTOCLAVED FOR 2500 hr IN DEGASSED WATER AND IN AIR-SATURATED WATER AT 550°F.

B. Dynamic Corrosion Tests

The dynamic corrosion test loops and the specimen holders at ANL were fabricated from Type 347 and/or 304 stainless steel. The results in the dynamic section revealed no evidence of accelerated corrosion attack that could be attributed to a coupling effect. In the semistatic water section (at low pH) there was slightly greater pitting attack in areas in contact with the holder than on the balance of the specimen surfaces. However, it is believed that pitting stemmed from a crevice rather than a galvanic couple effect.

Samples of Type 347 stainless steel were tested in dynamic water at 500 and 600°F, pH 5 and 7, with natural hydrogen buildup, and with manual injection of hydrogen gas. At both temperatures the samples and the holders in pH 5 water were cleaner (less deposit of magnetite) than the specimens in pH 7 water. The corrosion rates in 500°F water (see Fig. 44) were equal but opposite in sign; in 600°F water the rates were equal but less than the values at 500°F (see Fig. 45).

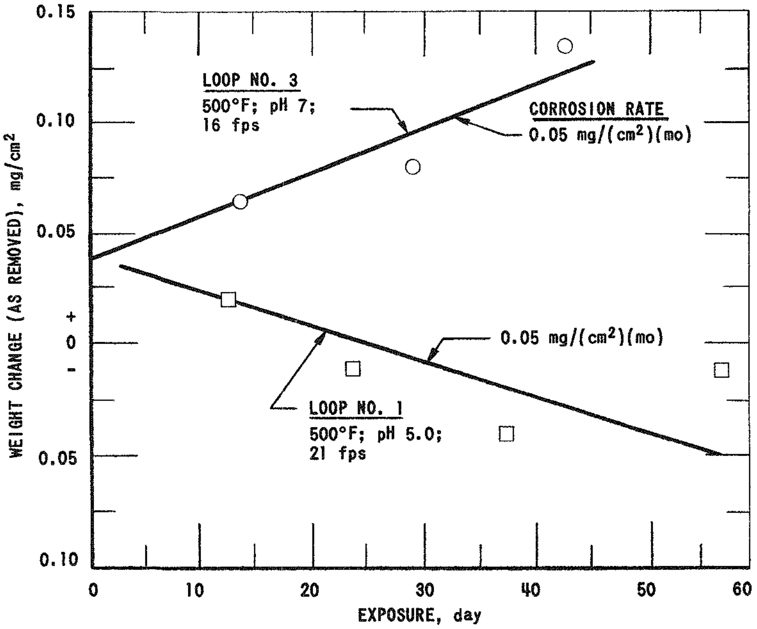


FIG. 44
CORROSION OF TYPE 347 STAINLESS STEEL IN DYNAMIC WATER AT 500°F AND pH 5-7.

C. Conclusions

Accelerated corrosion of M-388 alloy occurs when coupled with Type 304 stainless steel and exposed to tap water at room temperature, or in air-saturated, demineralized water at 680°F. In the latter environment the attack is magnified if the surface area of M-388 is small compared to that of the stainless steel.

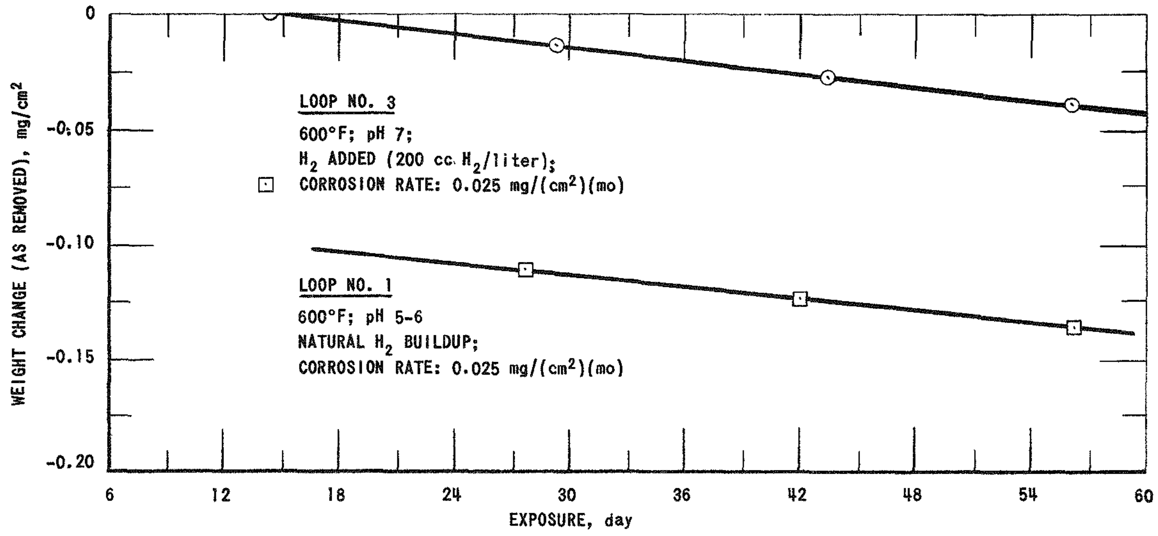


FIG. 45
CORROSION OF TYPE 347 STAINLESS STEEL IN DYNAMIC WATER AT 600°F AND pH 5-7, WITH NATURAL HYDROGEN BUILDUP AND WITH MANUAL INJECTION OF HYDROGEN GAS

Crevices or contacts between M-388 and stainless steel are to be avoided (1) in static water or in regions of low flow velocity, and (2) in water of poor quality or water which is prone to air saturation.

XI. DISCUSSION

The development of aluminum-nickel alloy M-388 has eliminated the catastrophic disintegration experienced by 2S aluminum and other commercial aluminum alloys in high-temperature water. However, the corrosion behavior of M-388, in particular the wide variation in corrosion rates in 500°F water, poses an enigma.

On the basis of the foregoing test results, the disparity between corrosion rates at 500°F cannot be attributed solely to the absence or to the presence of hydrogen in the water, or to the manner in which it is added. That hydrogen does exercise some influence on the corrosion behavior of M-388 is evidenced by the higher intercept and the roughened surface appearance observed in certain instances. Other test parameters - surface treatment, coupling, pH, temperature, nuclear radiation, and heat transfer - also do not account singly for the magnitude of variation in corrosion rates.

There is evidence that the corrosion rate is affected strongly by the ratio of exposed sample surface area to the volume of circulating water, and by the velocity of the water. The mechanism of corrosion associated with the theory of surface area-to-water volume ratio is still a subject of controversy. The original hypothesis(7) was that as the aluminum oxide corrosion product dissolved, it tended to saturate the water. This, in turn, served to inhibit further dissolution of the corrosion product and, hence, to retard further corrosion attack. The hypothesis is supported by the needle-like oxide crystals deposited throughout the test loops. Such formations are typical of the growth of crystals in a saturated or supersaturated solution.

When test results at Argonne and at other laboratories were examined from this standpoint, many previously unexplained discrepancies were resolved. In Table X the corrosion data are correlated with the sample area-to-water volume ratios prevailing in the respective tests described in this report. For example, the ratios for the corrosion-irradiation tests at MTR were 3.5 cm^2/liter for Cartridge MTR-W-7, and 4.4 cm^2/liter for Cartridge MTR-W-9. Thus the higher corrosion rates at MTR are explained partially by a comparison with the ratios 60-90 cm^2/liter in the loop tests at Argonne, wherein lower corrosion rates were obtained.

It has been recognized subsequently that the volume of water per se is not the important factor, but rather the volume of refreshed or purified water. Assuming that the corrosion rate is controlled by the rate of solution of Al_2O_3 from the specimen surface, then the corrosion rate should be less in a saturated solution than in a less concentrated solution. This is illustrated by the accelerated corrosion of replacement samples as compared to the originally loaded specimens. In the process of loading replacement samples, the saturated solution is drained and replaced with fresh water. The buildup of dissolved Al_2O_3 from the saturated solution in the initial test period may serve to retard corrosion of the original samples in the ensuing test period in a less concentrated solution. The replacement samples, minus the protection afforded their originally loaded counterparts, suffer accelerated attack in the fresh or partially diluted solution.

Assuming that a corrosion rate of 5 mil/yr for M-388 alloy is acceptable for use as fuel element cladding, then a surface area-to-water volume ratio of 60 cm^2/liter of water is the lower limit for water at 422-500°F. The corrosion at 600°F is too high regardless of the surface area-to-water ratio. There is no significant advantage between water at pH 5 or pH 7.

The effect of water velocity on corrosion of M-388 is evidenced by the difference in rates exhibited by specimens in semistatic and in boiling water, and corrosion rates registered by samples exposed to water flowing at 7, 16, and 18 fps. The accelerated corrosion attack at the leading edges of the samples (high-velocity region) indicates that flow velocities of 16-18 fps approach the maximum that can be tolerated by the alloy under the water conditions employed.

Table X

CORROSION RATES AS A FUNCTION OF TEST PARAMETERS AND SPECIMEN SURFACE AREA-TO-WATER VOLUME RATIOS

Loop No.	Run No.	Temp, °F	pH	Ratio Area/Water, cm²/liter	Velocity, fps	Corr. Rate, mil/yr	Velocity, fps	Corr. Rate, mil/yr	Velocity, fps	Corr. Rate, mil/yr	Comments
					TEST LOOPS AT ANL						
1	1	500	4.9-5.1(H_2SO_4)	92	20	2.0	7	1.4	Semistatic	1.2	Natural H_2 Buildup
	2	600	5.3-5.9(H_2SO_4)	84	18	6.0	7	4.7	Semistatic	2.8	Natural H_2 Buildup
	4	500	5.8-6.1(H_2SO_4)	25	18	10.3					Regular Samples
						6.9					Pretreated samples
3	1	500	6.5-6.9	73	16	2.0	6	1.5	Semistatic	1.5	Natural H_2 Buildup
	2	600	6.8-7.0	76	16	8.5	6	6.5	Semistatic	5.5	Hydrogen added
	4	500	6.8-7.0	49	18	10.7	7	5.1			Hydrogen added
						8.5	7	4.5			Degassed
	5	475	7.1-7.5	59	18	8.7	7	2.7	Semistatic	1.2	Natural buildup
4	2	500	6.3-6.9	12	18	11.0					Degassed
	3	500	6.4-6.7	8	18	11.0					Hydrogen added
	5	500	6.8	71	18	8.7					
	8	600	7.0-7.4	16	18	11.6					Degassed
	9	600	7.2-7.3	30	18	9.8-12.5					Degassed
					ANL-2 PRESSURIZED WATER LOOP AT MTR						
Cartridge	MTR-W-7	485	6.2-6.8	3.5	16	17.4					Out-of-reactor samples
						11.6					In-reactor samples
Cartridge	MTR-W-9	485	5.6-9.5	4.4	16	17.4					Out-of-reactor samples
						16.7					In-reactor samples
					BOILING CORROSION-HEAT TRANSFER TEST LOOPS						
2	1-3	422	6.5-7.5	92	Natural Convection	3.3					
3	1	422	6.5-7.5[a]	57-131	Natural Convection	1.8 (1500 watt heat through-put)					
						0.93 (750)					
						0.93 (375)					
						0.36 (0 watt heat through-put)					

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[a] Estimated from resistivity values.

It is difficult to predict the maximum temperature for cladding applications of M-388 alloy, since a great deal depends on the expected fuel element lifetime, cladding thickness, and the water conditions to be employed in the reactor. For example, the experience gained to date indicates that the alloy could be used for a relatively long-life core in high-purity water at a bulk water temperature of 420°F. However, the life expectancy will decrease as the temperature is increased to 500°F, or higher.

In summation, it is evident that there are still many unresolved problems pertinent to the successful application of aluminum-nickel alloys in high-temperature, water-cooled reactor systems. For example, the dependence on a high ratio of alloy surface area to water volume to prevent excessive corrosion is, at best, a very haphazard method of corrosion inhibition. If inhibition is to be accomplished by maintaining a high concentration of dissolved Al_2O_3 in the water, the corrosion resistance could be affected adversely by any factor tending to dilute the prescribed concentration. This could include precipitation and deposition in cold sections or on heat transfer surfaces, pickup by cleanup systems, or dilution as a result of leakage and subsequent replenishment with makeup water. The tendency for the oxide to dissolve and then crystallize and deposit elsewhere in the system poses a two-fold problem in reactor systems: a barrier to heat transfer and interference with moving parts. That it did not cause difficulties in tests at 422°F and heat fluxes averaging 25,000 $Btu/(hr)(ft^2)$ does not necessarily infer that difficulties will not be encountered at higher temperatures and heat transfer rates.

A more reliable method of corrosion inhibition is desirable. Alternate measures are being explored. One method that holds exceptional promise is the addition of phosphoric acid to the system water.

The sequel to this report will include (1) evaluations of phosphoric acid additions as well as of other additives designed to improve the corrosion resistance of M-388; and (2) the results of long-term corrosion tests which were prefaced by Run No. 5 in Loop No. 1 (see page 34).

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APPENDIX

TECHNIQUE FOR STRIPPING CORROSION FILM FROM ALUMINUM AND ALUMINUM-NICKEL ALLOYS

as evolved by

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The following procedures will successfully strip the corrosion product film from aluminum-nickel alloys formed at temperatures up to 315°C. Films formed at temperatures above 315°C will give some trouble because of their more adherent nature, and the technique may have to be varied somewhat to achieve good stripping.

I. BORIC ACID ROUGH STRIP (Fig. 46)

1. Immerse the sample to be stripped in the boric acid bath for about one minute of soaking.
2. Control the temperature of the stirring boric acid at 20-30°C.
3. Pass a current (ac) density of 0.02 amp-cm^2 of sample area by means of a controlling powerstat. Voltage will vary as the sample strips, but hold the current constant. Pass current for one-half to one minute only.
4. Invert sample and pass the same current density for an additional one-half to one minute.
5. Brush sample in distilled water with a bristle brush.
6. Sample is now ready for phosphoric acid and chromic acid stripping.

Notes on Boric Strip

a. Boric acid should be saturated at room temperature and prepared from recrystallized pure boric acid if possible. If not, purify the saturated boric acid by passing dc current at 120 volts or higher, using an aluminum-foil anode. This will require several anodes. In stripping some more difficult films, it may be necessary to follow the saturated boric acid strip with a nonsaturated boric strip at higher voltage.

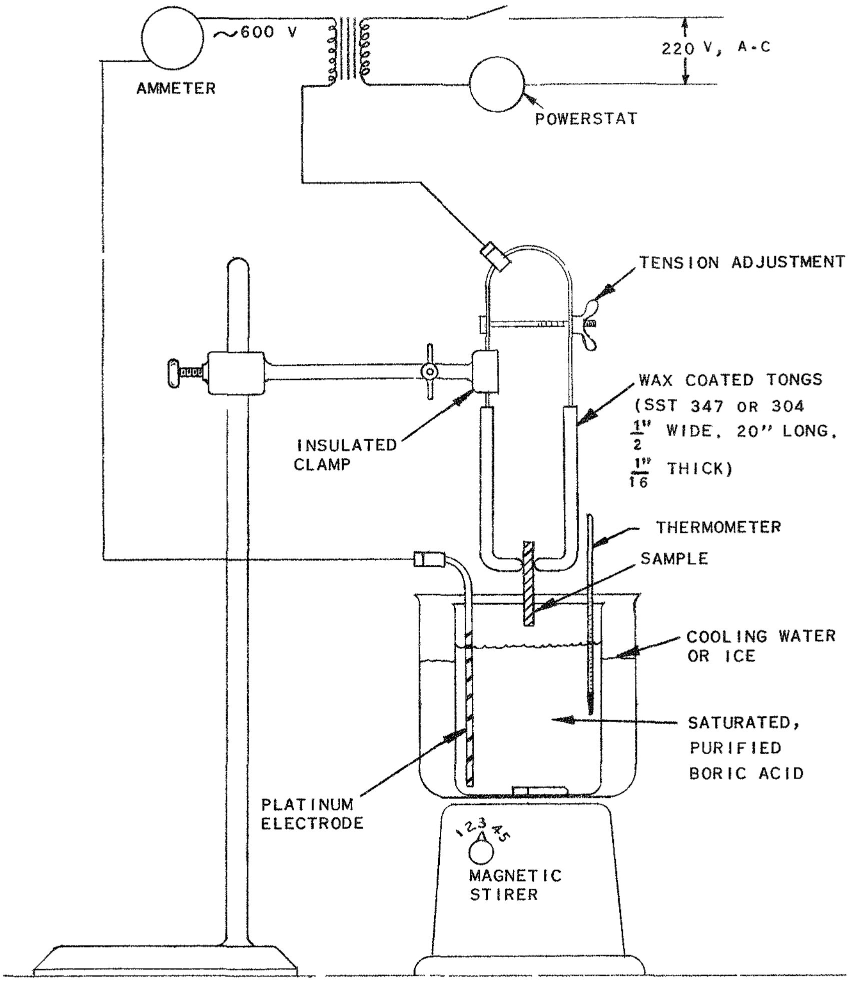

FIG. 46
APPARATUS FOR ROUGH STRIP

b. The wax used to coat the tongs is Unichrome Stop-Off Compound No. 330, manufactured by the United Chromium, Inc., 100 East 42nd Street, New York 17, New York.

II. CHROMIC-PHOSPHORIC FINISH STRIP (Fig. 47)

1. Immerse one to four samples in the chromic-phosphoric bath, using insulated tongs and a platinum anode.

2. Bath temperature should be about 85 to 95°C.

3. Using a dc supply, pass a 200-mamp current at about 20 volts through one or more samples in series.

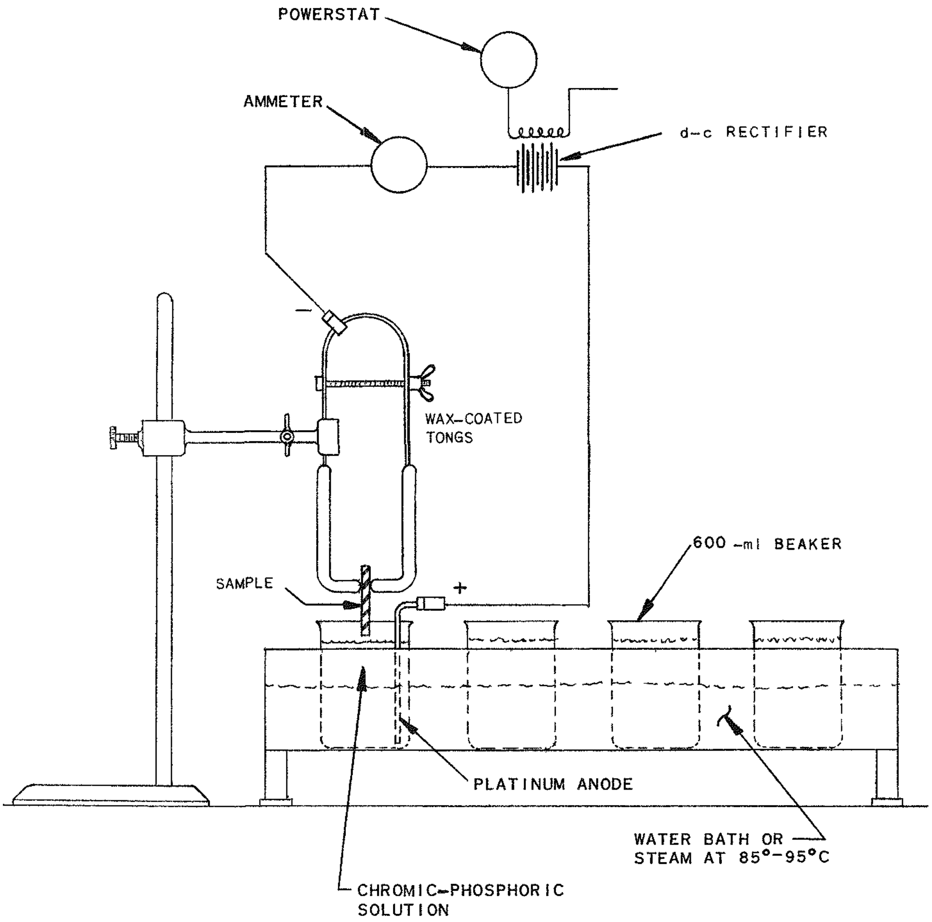

FIG. 47
APPARATUS FOR FINISH STRIP

4. Strip samples for 30 min, then invert and strip for an additional 30 min.

5. It will be necessary to add distilled water to the chromic-phosphoric bath as the solution evaporates.

Notes on Finish Strip

a. Chromic-phosphoric strip solution is constituted of 162.4 gm CrO_3 and 200 cc H_3PO_4 in 2 liters of distilled water.

b. A blank sample should be run to check the correction on the stripping process. Argonne blanks have shown a final weight loss of -0.06 to -0.08 mg/cm^2.

III. MATERIALS

A. Boric Acid Strip

1. One transformer - Electron Type H-1804 or similar, capable of taking 115 volts on primary and giving 440 volts on secondary - roughly 0.75 to 1.0 kva rating, 50-60 cycle ac. With a 220-volt input the transformer will give a 880-volt output. Although this exceeds the rating of the transformer, it should not be damaged, since operation is for short periods only.
2. One Powerstat - 240-volt, 5-amp capacity, or more.
3. One Ammeter - ac; 0.0-3.0 amp.
4. One platinum sheet, 5 in. by 4 in. and about 0.010 in. to 0.020 in. thick.
5. One magnetic stirrer.
6. One 1000-ml beaker.
7. One single-throw switch - 230-volt, ac.
8. Wax-coated tongs.

B. Chromic-Phosphoric Acid Strip

1. One Powerstat - 115-volt, 1-amp capacity.
2. One ac/dc, 115-volt rectifier of 1-amp capacity, or less.
3. One 4-hole steam bath tray.
4. Two dc ammeters - 0-500 mamp.
5. One platinum sheet, 6 in. by 12 in., and approximately 0.020 in. thick.
6. Four 600-ml beakers.
7. Four wax-coated tongs.
8. Miscellaneous ring stands and clamps.