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CORROSION OF AN ALUMINUM-NICKEL ALLOY IN A REACTOR TEST LOOP

by

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DISCLAIMER

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INTRODUCTION

For a number of years, Argonne National Laboratory has been investigating the use of aluminum or aluminum alloys as construction materials for power reactors. The advantages of aluminum over other metals are its excellent nuclear properties, abundance, and ease of fabrication.

Early research on properties of relatively pure aluminum was at relatively low temperatures (approximately 300°F or lower), where the structural and corrosion properties of aluminum are very good. Little was known, however, of the effects of elevated temperatures (say, in the range of 400°F to 600°F). With the advent of nuclear power, research was extended to include these effects.

The major disadvantages of pure aluminum at high temperatures are its high corrosion rate and low structural strength.

An alloy of aluminum which will withstand the high temperatures required for the operation of boiling water reactors is desirable. Initial studies of Draley and Ruther(4)* into the corrosion-resistant properties of aluminum alloys indicated that the most promising were the aluminum-nickel alloys.

PURPOSE OF THE STUDY

This project was started to determine the corrosion resistance of various aluminum-nickel alloys under conditions simulating reactor operation and to find the alloy with the best performance.

Up to this time there had been very little irradiation of aluminum alloy specimens under dynamic conditions. The majority of the specimens examined had been statically irradiated to determine the effects on the physical properties of aluminum.

Previous irradiations of aluminum-nickel alloys had been performed in the Argonne National Laboratory high-pressure water loop at the Materials Testing Reactor for short terms. The results of these tests were

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*Numbers in parenthesis refer to the bibliography.

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inconclusive and will be discussed later. A long-term irradiation with a close control of all variables was desirable. This long-term irradiation is the basis for the present work.

LITERATURE SURVEY AND BACKGROUND

One of the first reports on the corrosion of high-purity aluminum in water at temperatures from 200°F to 500°F was written by Draley and Ruther.(3) Their report discusses the formation of the oxide layer on the aluminum surface and presents the corrosion rates at various temperatures. Their data was substantiated by other investigators.(1,2,& 6)

In their research Draley and Ruther(4) found that aluminum-nickel alloys offered the best corrosion protection of the alloys investigated because the nickel provided local cathodic corrosion protection at grain boundaries. Huddle and Wilkins(7) corroborated the corrosion tests of Draley and Ruther on aluminum-nickel alloys, investigating varying percentages of nickel as alloying element.

An aluminum alloy containing 1% nickel has shown improved corrosion resistance over pure aluminum in static tests and therefore was selected for tests to determine its corrosion resistance under simulated reactor operating conditions.

EXPERIMENTAL APPARATUS AND PROCEDURE

Apparatus

In order to investigate the effect of irradiation on fuel elements and structural material, Argonne constructed a high-pressure water loop at the Materials Testing Reactor at the National Reactor Testing Station in Idaho. The apparatus and its operation is described in an article titled "Pressurized Water Test Loop at MTR," which appeared in the April, 1957 issue of "Nucleonics" (Vol. 15, No. 4, Pgs. 73-77).

Experimental Procedure

The purpose of this study was to determine the corrosion rate of an aluminum-nickel alloy under radiation. In order to determine the increase of corrosion with respect to time, a test section was devised which would permit the replacement of portions of the section at various intervals. The design for such a test section was taken from a previous test section which was used in this manner.

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Figure 1 is a photograph of the original test section and the two replacement sections which were inserted into the reactor tube of the high-pressure loop. The irradiation period involved nine cycles at the MTR. Sections 1, 2, and 3 constituted the original insertion. Section 4 was the first replacement, made after a three-cycle period and replacing Section 3. Section 5 was the second replacement, made after a six-cycle period and replacing Sections 2 and 4. Sections 1 and 5 were removed after the end of nine cycles.

An identical set of test sections and their replacements were inserted in the out-of-pile or external tube of the loop. These test sections were control specimens and were subjected to the same treatment except for irradiation, as the same water flowed past the reactor tube specimens and the control specimens.

This method of periodically replacing portions of the test sections permits the determination of the corrosion rate over a long period of time. It also enables the determination of any difference in corrosion rate due to the irradiation of the test specimens.

The test sections consisted of rectangular, stainless steel enclosures for holding the test specimens. The test specimens were mounted in the test sections between combs or spacers of the same material as the test specimens.

There were four to six test specimens in a row in each test section. Each test specimen was one-eighth inch thick, nine-sixteenth inch wide, and two and one-half inches long, and each was made of Aluminum Company of America alloy M-388, which is 1% nickel in Type 1100 aluminum.

Constant flow (approximately sixteen feet per second) was maintained past the samples.

The acidity or pH and the resistivity of the loop water flowing past the samples were maintained by the ion-exchange system. The ion-exchange resin bed was a Rohm and Haas MB-1 monobed resin to maintain the pH of the system water between six and eight and to control the resistivity of the water to a range of one to three megohm-centimeters.

The water temperature was to be maintained between 470 and 485°F for the length of the exposure time. Difficulty was encountered in reaching this temperature range due to the lack of adequate line heater capacity. By circulating through the surge tank which maintains the system pressure, enough additional heating capacity was obtained to maintain the water temperature in the required range for a majority of the exposure time. For an analysis of the amount of time spent at each temperature range for each test section, see Table 1.

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During the reactor refueling periods the loop water temperature was reduced to 300°F due to the inability to maintain the required test temperature with the present inadequate line heater capacity and without the reactor heating. The reason for the temperature reduction is to maintain ranges at all times. Failure to reduce the loop water temperature to a stable range during a reactor shutdown would permit the oscillation of water temperature and enhance the difficulty of drawing conclusion from the data.

The amount of dissolved gases in the loop water was kept at a minimum. For the most part, the dissolved gases were either hydrogen or oxygen caused by the dissociation of water or by impure make-up water. Continual venting of the surge tank permitted the discharge of a portion of these gases from the system.

After removal from the loop, the specimens were stripped of the scale by an electrolytic process in a saturated boric acid solution. The specimens were then cleaned in a hot chromic-phosphoric acid bath with cathodic protection of the specimens. Figures 2 and 3 are typical photographs of the samples before and after the oxide film was removed from the surface of the specimen.

After cleaning, the specimens were weighed for weight loss determination.

PRESENTATION OF DATA

The data obtained during this test are given in Tables 1 to 4. Tables 1, 2, and 3 compile the data on temperature, neutron exposure, and water conditions experienced by each test section during its exposure to the test conditions. Table 4 is a compilation of the sample initial weights, final or stripped weights (the sample weight after removal of the oxide film on the surface), differences between initial and stripped weights, and the weight losses per square centimeter of specimen surface area.

Table 1 is a tabulation of the time in hours which was spent by each test section at various temperature levels during exposure. The variation in temperature throughout the exposure of the samples is due to reactor shutdown time for refueling, reactor and experiment operational difficulties, and temperature reductions required for changing the test sections in the reactor tube and out-of-pile section.

Table 2 indicates the neutron exposure received by the samples in the reactor tube and the per cent of the exposure time spent in the temperature range of 470°F to 485°F. The only reason for not maintaining a higher percentage of time at the required temperature range was the lack of sufficient line heater capacity.

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Table 3 summarizes the water conditions which prevailed during the exposure of each test section. Approximately 90% of the exposure time was spent with a water resistivity above one megohm-centimeter. The lower values of resistivity occurred only at times when the test sections were changed, which required the draining and refilling of the reactor tube and out-of-pile sections with fresh water.

As stated previously, the pH of the system was maintained at a range of six to eight by a monobed ion-exchange system. Minor variations above and below these limits were encountered, but the average value of the pH was consistently close to a neutral value of seven.

The concentration of dissolved oxygen in the water was kept as low as possible. The water was continually circulated through the surge tank to purge any gases from the water, and the surge tank was vented to the atmosphere periodically. All make-up water was de-oxygenated by passage through a sulfite de-oxygenating resin. Evidently the resin deteriorated, because, as make-up water was added during a cycle, the amount of dissolved oxygen in the water increased The resin was almost completely spent toward the end of the cycles, when the dissolved oxygen content of the water reached a peak of three and two-tenths parts per million. This high oxygen concentration was not detrimental. Draley and Ruther(3) had previously found in earlier research that oxygen-saturated water actually reduced the corrosion of aluminum. As the water was far from being oxygen saturated, it is believed that this fact had little effect upon the results of the experiment.

Table 4 indicates the weight loss of each sample. In the in-pile samples, the last numeral in the sample number indicates the relationship of the sample to the reactor core. Number one is the sample closest to the reactor core.

DISCUSSION AND CONCLUSIONS

The results of the corrosion study are illustrated in Figure 4, which is a plot of the weight loss of the aluminum-nickel samples with respect to the time at test temperatures of 470°F to 485°F. The corrosion rate determined by this test indicates that the weight loss per unit time is the same for both the in-pile irradiated specimens and the out-of-pile control specimens which did not have any neutron exposure, except that the out-of-pile specimens had a higher initial rate of corrosion which elevated the curve above that of the in-pile specimens.

This corroborates, to some extent, the results of N. R. Grant(5) in his previous short-term study of the corrosion of aluminum-nickel alloys. Grant's test was inconclusive due to poor operating conditions during the test, but is useful in explaining some of the results obtained from this test.

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The average corrosion rate of Grant's out-of-pile specimens is identical with that of the out-of-pile specimens in this test. The in-pile specimens of both Grant and this test had a lower corrosion rate. The variation in the position of the corrosion curves on the graph is due to the difference in initial rates of corrosion. A possible reason for this difference in initial corrosion rates is the prevalence of different water conditions during this corrosion period. The slightly lower pH average of the water during the initial corrosion period of Grant's test could account for this difference.

The difference in water conditions, which govern the initial corrosion rate, would also account for different weight losses of the replacement specimens. The high pH and low resistivity of the water during the initial corrosion period of the replacement specimens in Grant's test would account for the increased weight losses of those specimens above the original specimens. The difference in pH of the water at the time of insertion of the replacement specimens for this test would also account for the variation in weight losses.

It is evident that the variation of water purity, after completion of the initial corrosion and establishment of the relatively impervious layer of corrosion product, has little effect upon the corrosion rate of aluminum. It is another matter whether this supposition will also hold true for the variation of pH after the initial corrosion is completed.

It would be interesting to determine whether much variation in corrosion rate would be found if the pH of the water were raised, after the establishment of the initial corrosion product at pH 6.

Another interesting item which should be noted is the decrease in weight loss of the in-pile specimens with increase of distance from the reactor core. This was not noted in the out-of-pile specimens and could be attributed only to an effect of exposure to radiation. The same effect was noted by N. R. Grant in previous tests of this nature. No cause for this effect has been determined.

The corrosion rate obtained from the samples is greater than that obtained by similar tests but may be due to erosion. Inspection of the samples after stripping of the corrosion product indicated that more metal loss occurred in the area of the retaining clamps than was observed in any other area. There is an increased velocity in these areas which may cause a greater breakdown of the protective corrosion product than normally found under lower flow velocity conditions.

In conclusion, it may be stated that the alloy of 1% nickel in Type 1100 aluminum has shown fairly good corrosion resistance in this test with water conditions of high temperature (470°F to 485°F), high

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purity (over one megohm-centimeter resistivity), and neutral pH. Perhaps better corrosion resistance could be demonstrated if the water could be maintained at a slightly acid condition.

Although this alloy exhibits better corrosion resistance than 2S aluminum at high temperatures, it does not exhibit any increased structural strength, which is also a matter to be considered in reactor construction.

The confirmed ability of this alloy to resist corrosion at higher water temperatures than have ever been used before on an aluminum alloy should be taken into consideration by nuclear engineers when designing reactor components and fuel element claddings for use in low-power-producing reactors. Its light weight makes it suitable for the construction of reactor components for the package type reactors that are to be transported into remote regions.

It is believed that further research in aluminum alloys will bring forth an alloy which will be highly competitive with other materials in corrosion resistance and strength in high temperature water-cooled nuclear reactors.

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BIBLIOGRAPHY

(1) Boyer, M. H., Litz, L. M., and Strom, P. O., Aqueous Static Corrosion of Aluminum Alloys Coupled to Stainless Steel and Zirconium at 350°F. LRL-74 (January, 1954).

(2) Boyer, M. H., Litz, L.M., and Strom, P. O., Reproducibility of 480°F Static Aqueous Corrosion of Pure Aluminum. LRL-112 (March, 1954).

(3) Draley, J. E., and Ruther, W. E., Aqueous Corrosion of 2S Aluminum at Elevated Temperatures. ANL-5001 (February 1, 1953).

(4) Draley, J. E., and Ruther, W. E., Corrosion Resistant Aluminum above 200°F. ANL-5430 (July 15, 1953).

(5) Grant, N. R., Aluminum Alloy Corrosion Irradiation Tests. ANL-5601 (December, 1956).

(6) Huddle, R. A. U., and Wilkins, N. J. M., The Corrosion of Commercially Available Pure Aluminum in Demineralized Water between 125°F and 300°F. AERE M/R 1669 (May 15, 1955).

(7) Huddle, R. A. U., and Wilkins, N. J. M., The Resistance of Binary Aluminum Alloys to Corrosion by Water at High Temperatures and Pressures. AERE M/R 1669A (May 2, 1956).

Table 1

TIME AT VARIOUS TEMPERATURES

Section	Time, Hours			
	Below 200°F	300°F - 320°F	400°F - 470°F	470°F - 485°F
1	410	760	529	2362
2	230	527	429	1439
3	121	260	240	657
4	109	267	189	782
5	180	233	100	923

Table 2

NEUTRON EXPOSURE

Section	Time at Temperature of 470°F - 485°F (hr)	Per Cent of Neutron Exp. Time at 470°F - 485°F	Neutron Exposure	
			Fast, nv x 10^{-19}	Thermal, nv x 10^{-20}
1	2362	78	26.2	26.2
2	1439	72.8	17	17
3	637	69	8.21	8.21
4	782	77.3	8.76	8.76
5	923	86.6	9.28	9.28

Table 3

WATER CONDITIONS

Section	Resistivity, megohm-cm	pH Range	Avg. pH	Oxygen Concentration, ppm
1	0.2 - 3.5	4.8 - 9.6	7.03	0.05 - 3.2
2	0.2 - 3.0	4.8 - 9.6	6.84	0.05 - 1.95
3	0.2 - 3.0	5.6 - 8.6	6.78	0.05 - 1.95
4	0.25- 3.0	4.8 - 9.6	6.9	0.6 - 1.4
5	0.25- 3.5	6.1 - 8.5	7.43	0.8 - 3.2

Table 4 13

SAMPLE WEIGHT LOSS

IN-PILE SAMPLES

Sample Number	Original Weight (gm)	Stripped Weight (gm)	Difference (gm)	Wt. loss, mg/cm^2
A51	7.9677	7.1449	0.8228	35.6
A52	7.8778	7.0359	0.8419	36.4
A53	7.8376	7.0973	0.7503	32.5
A54	7.9735	7.2717	0.7018	30.4
A31	7.8844	7.2223	0.6621	28.7
A32	7.8727	7.2208	0.6519	28.2
A33	7.8888	7.2739	0.6149	26.6
A34	7.8916	7.3578	0.5338	23.1
A35	7.8763	7.3901	0.4862	21.0
A11	7.8919	7.5914	0.3005	13.0
A12	7.8970	7.6212	0.2758	11.9
A13	7.8805	7.5998	0.2807	12.1
A14	7.9027	7.5954	0.3073	13.3
A15	7.8875	7.6276	0.2429	10.5
A16	7.8959	7.6708	0.2251	9.7
A21	7.8776	7.5296	0.3480	15.1
A22	7.8954	7.5187	0.3767	16.3
A23	7.8801	7.5519	0.3282	14.2
A24	7.8687	7.5330	0.3357	14.5
A25	7.9004	7.5861	0.3143	13.6
A26	7.9050	7.6197	0.2853	12.4
A1	7.8934	7.4984	0.3950	17.1
A2	7.8834	7.6310	0.2524	10.9
A3	7.8949	7.6601	0.2348	10.2
A4	7.8350	7.5969	0.2381	10.3
A5	7.8731	7.6080	0.2651	11.5
A41	7.8997	7.5625	0.3372	14.6
A42	7.8903	7.6407	0.2496	10.8
A43	7.8747	7.6464	0.2283	9.9
A44	7.8754	7.6264	0.2490	10.8
A45	7.8840	7.6093	0.2747	11.9

Table 4

SAMPLE WEIGHT LOSS

OUT-OF-PILE SAMPLES

Sample Number	Original Weight (gm)	Stripped Weight (gm)	Difference (gm)	Wt. loss, mg/cm^2
B51	7.8939	6.8871	1.0068	43.6
B52	7.9406	6.9371	1.0035	43.4
B53	7.8869	6.9047	0.9922	43.0
B54	7.9690	6.8943	1.0747	46.5
B31	7.9532	7.2843	0.6689	29.0
B32	7.8485	7.1604	0.6881	29.8
B33	7.9483	7.2597	0.6886	29.8
B34	7.9482	7.2209	0.7273	31.5
B35	7.8771	7.1954	0.6817	29.5
B11	7.9017	7.4168	0.4849	21.0
B12	7.8404	7.3560	0.4844	21.0
B13	7.8892	7.4068	0.4824	20.9
B14	7.8912	7.3975	0.4937	21.4
B15	7.8848	7.4353	0.4495	19.5
B16	7.8765	7.4586	0.4179	18.1
B21	7.8795	7.5856	0.2939	12.7
B22	7.8564	7.5670	0.2894	12.5
B23	7.8394	7.5448	0.2946	12.7
B24	7.8477	7.5398	0.3079	13.3
B25	7.8885	Lost		
B26	7.8382	7.5467	0.2915	12.6
B1	7.8803	7.5109	0.3694	16.0
B2	7.8776	7.5111	0.3665	15.9
B3	7.8829	7.5128	0.3701	16.0
B4	7.8812	Lost		
B5	7.8915	7.5311	0.3604	15.6
B41	7.9489	7.5744	0.3745	16.2
B42	7.8722	7.5056	0.3666	15.9
B43	7.8686	7.4949	0.3737	16.2
B44	7.9455	7.5791	0.3664	15.9
B45	7.8940	7.5185	0.3755	16.3

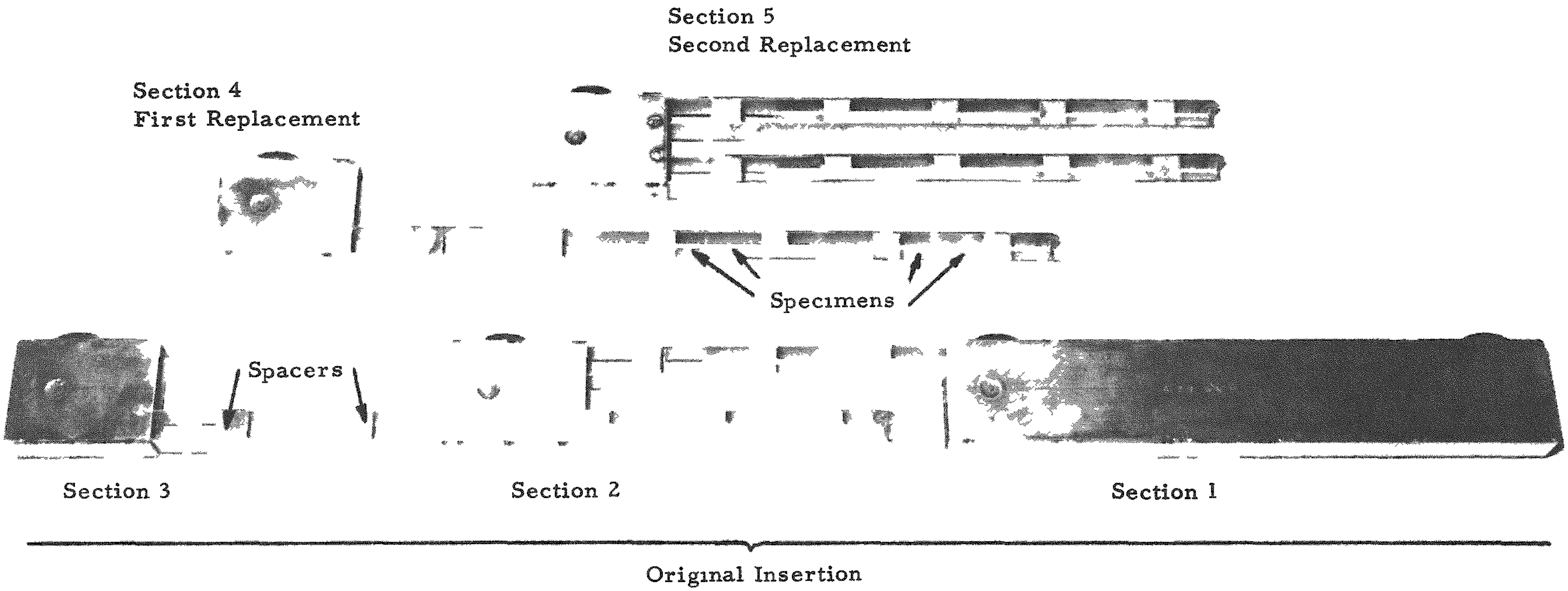
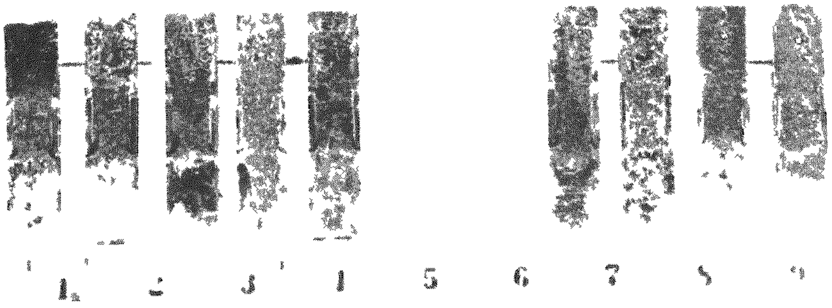


Figure 1

TEST SECTIONS AND SPECIMENS

Figure 2

IN-PILE SPECIMENS A51 TO A54 AND A31 TO A35
BEFORE AND AFTER REMOVAL OF OXIDE FILM



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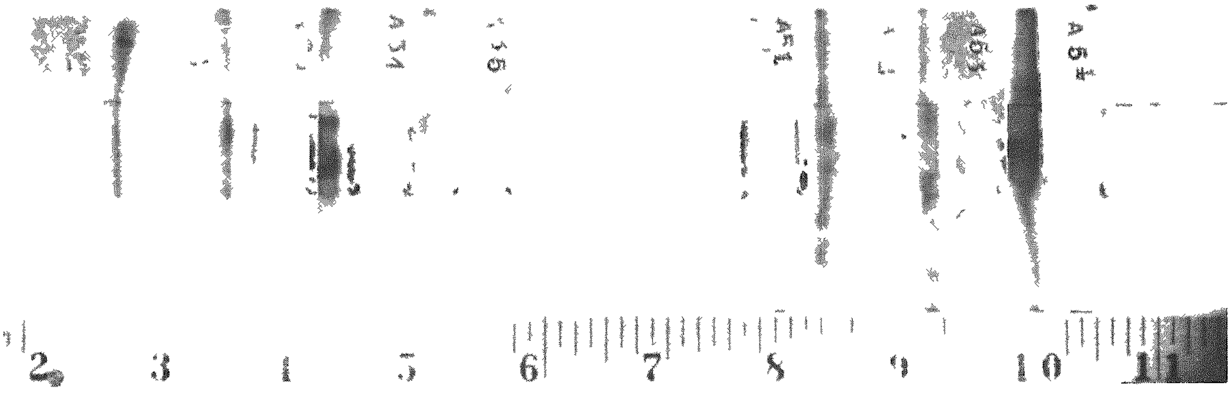

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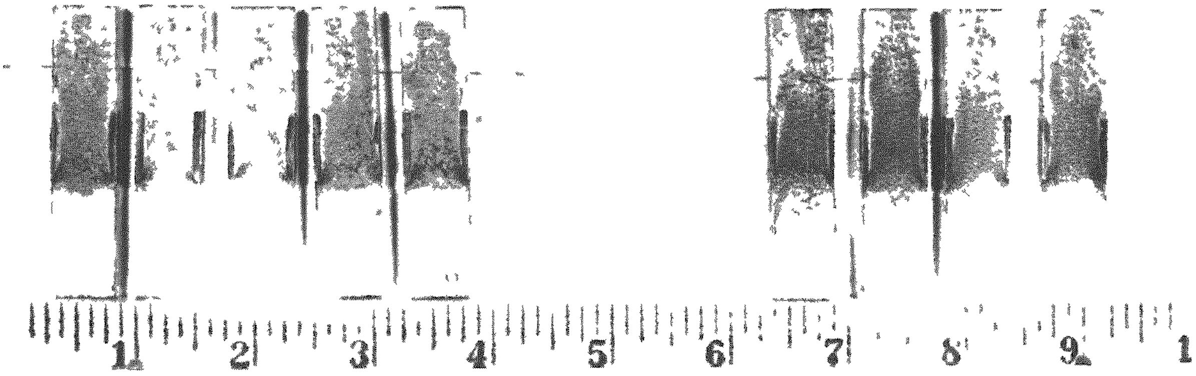
Figure 3

OUT-OF-PILE SPECIMENS B51 TO B54 AND B31 TO B35
BEFORE AND AFTER REMOVAL OF OXIDE FILM



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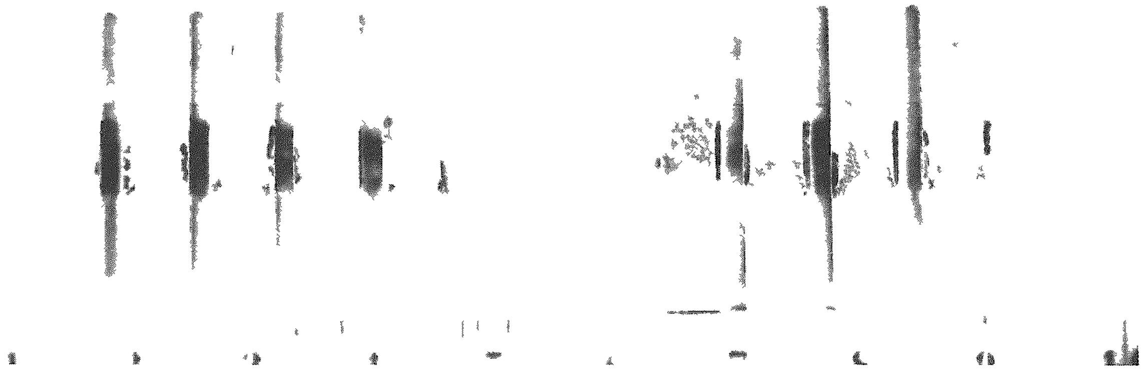

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FIGURE 4

CORROSION RATE OF ALUMINUM ALLOY M-388
IN HIGH-TEMPERATURE WATER