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REACTOR TECHNOLOGY DIVISION
Section IV - Engineering Materials

THE CORROSION OF MINIATURE FUEL
PLATES IN SIMULATED REACTOR
COOLING WATER

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TABLE OF CONTENTS

	Page
1.0 INTRODUCTION	5
2.0 ABSTRACT	5
3.0 TEST MATERIALS	6
4.0 TEST CONDITIONS	7
5.0 CORROSION DATA	7
6.0 DISCUSSION OF DATA	13
7.0 CONCLUSION	19
8.0 ACKNOWLEDGEMENTS	19

LIST OF TABLES AND FIGURES

		Page
I	Number of Pits Observed on Fuel Plates Exposed to 0.005M Hydrogen Peroxide at 85°C.	8
II	Maximum Pit Depths Observed on Fuel Plates Exposed to 0.005M Hydrogen Peroxide at 85°C.	9
III	Maximum Pit Diameters Observed on Fuel Plates Exposed to 0.005M Hydrogen Peroxide at 85°C.	10
IV	Incremental Weight Changes on Fuel Plates Exposed to 0.005M Hydrogen Peroxide at 85°C.	11
V	Cumulative Weight Changes and Corrosion Rates on Fuel Plates Exposed to 0.005M Hydrogen Peroxide at 85°C.	12
VI	The Percent Increase in the Average Number of Pits Formed on Fuel Plates as a Function of Exposure Time.	14
VII	Average Maximum and Actual Maximum Pit Depths Observed on Fuel Plates in 0.005M Hydrogen Peroxide at 85°C.	16
VIII	Average Incremental Weight Changes Observed on Fuel Plates Exposed to 0.005M Hydrogen Peroxide at 85°C.	17
IX	Average Cumulative Weight Changes Observed on Fuel Plates Exposed to 0.005M Hydrogen Peroxide at 85°C.	18
X-1,2	Photographs of Fuel Plates Prior to Corrosion Test.	20-21
XI-1,2	Photographs of Fuel Plates After 1 Month's Exposure to 0.005M Hydrogen Peroxide at 85°C.	22-23
XII-1,2	Photographs of Fuel Plates After 2 Month's Exposure to 0.005M Hydrogen Peroxide at 85°C.	24-25
XIII-1,2	Photographs of Fuel Plates After 3 Month's Exposure to 0.005M Hydrogen Peroxide at 85°C.	26-27

1.0 INTRODUCTION

This report is issued as one of a series of reports concerned with corrosion studies for the Materials Testing Reactor. The corrosion resistance of miniature fuel plates in simulated reactor cooling water was investigated and the results are included herewith. The fuel plate samples were prepared by C. D. Smith of the Metallurgy Division at Oak Ridge National Laboratory. The purpose of this investigation was twofold; 1) to determine the effect of various practices for fuel plate fabrication on corrosion resistance, and 2) to determine the extent of penetration of the fuel plates by localized corrosion attack.

2.0 ABSTRACT

The corrosion resistance of miniature fuel plates was evaluated in 0.005M hydrogen peroxide at 85°C. The individual plates consisted of an uranium-aluminum core clad with a layer of 2S aluminum and 72S aluminum. The fuel plate samples were in four groups, each of which represented a different processing practice in the fabrication of fuel plate assemblies. The corrosion test was conducted for 3 months with monthly sample inspections. All four groups of samples exhibited good corrosion resistance during the first month of exposure, but localized corrosion attack became prominent on several groups during the last two months of the test. Corrosion rates, calculated on the assumption that corrosion was of a uniform nature, were 0.18 mil/year and less on all groups at the end of 3 months. Of major significance, however, was the formation and development of pitting attack. Test results and data indicate that penetration of the protective aluminum cladding to the uranium-aluminum core occurred in one instance. Specimens prepared by hot rolling followed by cold rolling exhibited the best resistance to localized corrosion attack of the four groups. These samples were designated as Group 1. The maximum pit depth observed on the samples after 3 months was 8.4 mils. Samples in Group 4 showed the next best corrosion resistance; maximum pit penetration on these specimens was 10.0 mils after 3 months. The most severe penetration, 17.6 mils, was observed on specimens in Groups 2 and 3 after 3 months of exposure.

3.0 TEST MATERIALS

Twelve samples of miniature fuel plates were received representing four fabrication practices. Triplicate specimens for each practice were subjected to corrosion tests. The individual samples were approximately 1 inch wide x 4.3 inches long x 0.053-0.064 inch thick. The core of each specimen contained a 13% uranium-aluminum alloy which was clad on all sides with layers of 2S aluminum and 72S aluminum, respectively. The inner core alloy was at least 1/4 inch from the edges on all sides of the specimen.

Four methods for preparation of the samples were used. These were as follows:

- 1) Group 1 - Regular Practice
  - a) Hot rolled to 0.070 inch
  - b) Cold rolled to 0.064 inch
- 2) Group 2 - Modified Practice
  - a) Hot rolled to 0.070 inch
  - b) Cold rolled to 0.064 inch
  - c) Fluxed; heated at 1100°F
- 3) Group 3 - Modified Practice Plus Cold Roll
  - a) Hot rolled to 0.070 inch
  - b) Cold rolled to 0.064 inch
  - c) Fluxed; heated at 1100°F
  - d) Cleaned
  - e) Cold rolled to 0.053 inch
- 4) Group 4 - Modified Practice Plus Cold Roll and Brazing
  - a) Hot rolled to 0.070 inch
  - b) Cold rolled to 0.064 inch
  - c) Fluxed; heated at 1100°F; cleaned
  - d) Cold rolled to 0.053 inch
  - e) Annealed 2 hours at 1100°F
  - f) Edges fluxed
  - g) Subjected to regular brazing cycle
  - h) Cleaned

In each group of specimens, the core alloy was one-third of the total thickness of the plates. The thickness ratio of 72S aluminum to 2S aluminum claddings was 1:2. Approximate thicknesses for the component layers of the fuel plates were:

Groups 1 and 2: Total thickness - 0.064 inch

Uranium-aluminum core	0.021 inch
2S aluminum (each side)	0.014 "
72S aluminum (each side)	0.007 "

Groups 3 and 4: Total thickness - 0.053 inch

Uranium-aluminum core	0.018 inch
2S aluminum (each side)	0.012 "
72S aluminum (each side)	0.006 "

4.0 TEST CONDITIONS

Demineralized water containing 0.005M hydrogen peroxide was used as the corrosion test medium. The water pH was adjusted regularly between 5.5 and 6.5. The temperature of the water was maintained at $85^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Hydrogen peroxide was added at 4 hour intervals during the course of the test in order to keep the concentration near 0.005M. Daily peroxide and pH determinations were made. Solution agitation was accomplished by means of an electrically operated stirrer.

The samples were inspected prior to test for measurement of pit depths and diameters. The samples were then degreased, washed in acetone and alcohol, dried at 110°C , and weighed.

The total time of the test was 3 months. Samples were removed at monthly intervals for measurement of corrosion damage.

5.0 CORROSION DATA

Photographs of the four groups of specimens were made prior to the corrosion test and at each monthly inspection period. Pit counts, maximum pit depths and diameters, and weight changes on the specimens were determined at one month intervals. These data appear in the following tables.

TABLE 1

NUMBER OF PITS OBSERVED ON FUEL PLATES EXPOSED
TO 0.005M HYDROGEN PEROXIDE AT 85°C

<u>Group</u>	<u>Sample</u>	<u>Initial</u>	<u>1st Month</u>	<u>2nd Month</u>	<u>3rd Month</u>
1	1	Nil	Nil	38	38
	2	39	39	42	48
	3	4	4	4	60
2	1	Num.*	Num.	7	18
	2	2	2	15	21
	3	Num.	Num.	8	16
3	1	3	3	16	110
	2	Num.	Num.	7	24
	3	Num.	Num.	3	8
4	1	Num.	Num.	Num.	Num.
	2	Num.	Num.	Num.	Num.
	3	Num.	Num.	Num.	Num.

*Numerous, extremely shallow pits; not countable by naked eye.

TABLE II

MAXIMUM PIT DEPTHS (MILS) OBSERVED ON FUEL PLATES
EXPOSED TO 0.005M HYDROGEN PEROXIDE AT 85°C

<u>Group</u>	<u>Sample</u>	<u>Initial</u>	<u>1st Month</u>	<u>2nd Month</u>	<u>3rd Month</u>
1	1	N11	N11	8.4	8.4
	2	1.4	1.4	4.0	6.4
	3	<u>1.2</u>	<u>1.2</u>	<u>1.2</u>	<u>1.2</u>
	Average	0.9	0.9	4.5	5.3
2	1	1.6	1.6	8.8	12.0
	2	2.8	2.8	9.6	17.6
	3	<u>1.3</u>	<u>1.3</u>	<u>7.2</u>	<u>9.2</u>
	Average	1.9	1.9	8.5	12.9
3	1	2.4	2.4	8.0	14.0
	2	0.9	0.9	7.2	8.8
	3	<u>0.8</u>	<u>0.8</u>	<u>8.2</u>	<u>17.6</u>
	Average	1.4	1.4	7.8	13.5
4	1	2.4	2.4	2.4	2.6
	2	2.0	2.0	2.0	10.0
	3	<u>3.2</u>	<u>3.2</u>	<u>3.2</u>	<u>4.8</u>
	Average	2.5	2.5	2.5	5.8

Note: Approximately 5-10 percent of total number of pits were selected for greatest depth; above figures represent the average maximum pit depth for this 5-10 percent selected.

TABLE III

MAXIMUM PIT DIAMETERS (MILS) OBSERVED ON FUEL PLATES
EXPOSED TO 0.005M HYDROGEN PEROXIDE AT 85°C

<u>Group</u>	<u>Sample</u>	<u>Initial</u>	<u>1st Month</u>	<u>2nd Month</u>	<u>3rd Month</u>
1	1	Nil	Nil	40	40
	2	28	28	28	28
	3	20	20	20	20
2	1	16	50	60	28
	2	20	20	40	40
	3	10	20	20	40
3	1	50	50	60	60
	2	20	20	40	40
	3	20	20	20	20
4	1	10	10	10	10
	2	10	10	20	20
	3	10	10	20	20

TABLE IV

INCREMENTAL WEIGHT CHANGES (MG./DM²) ON FUEL PLATES
EXPOSED TO 0.005M HYDROGEN PEROXIDE AT 85°C

<u>Group</u>	<u>Sample</u>	<u>1st Month</u>	<u>2nd Month</u>	<u>3rd Month</u>
1	1	- 1.5	- 3.1	+ 13.0
	2	- 2.0	- 0.8	+ 13.6
	3	- 0.4	- 2.3	+ 12.1
	Average	- 1.3	- 2.1	+ 12.9
2	1	+ 7.5	- 0.9	+ 0.6
	2	+ 4.8	- 1.5	+ 5.7
	3	+ 4.6	- 0.4	+ 1.5
	Average	+ 5.6	- 0.9	+ 2.6
3	1	+ 5.8	- 1.8	+ 5.5
	2	+14.4	- 0.7	- 2.7
	3	+12.2	- 0.3	+ 0.3
	Average	+10.8	- 0.9	+ 1.0
4	1	+ 4.6	- 0.9	+ 6.5
	2	+12.1	+ 0.9	- 1.2
	3	+ 9.3	+ 0.2	- 1.0
	Average	+ 8.7	+ 0.07	+ 1.4

TABLE V

CUMULATIVE WEIGHT CHANGES AND CORROSION RATES ON FUEL PLATES
EXPOSED TO 0.005M HYDROGEN PEROXIDE AT 85°C FOR 3 MONTHS

Group	Sample	As Removed		Defilmed	
		Mdm*	Mpy**	Mdm	Mpy
1	1	+2.8	--	N11	N11
	2	+2.8	--	-2.7	0.05
	3	+3.1	--	-1.3	0.02
	Average	+2.9		-1.3	0.02
2	1	+2.4	--	-8.2	0.14
	2	+3.0	--	-9.9	0.17
	3	+1.9	--	-7.8	0.14
	Average	+2.4		-8.6	0.15
3	1	+3.2	--	-10.0	0.18
	2	+3.7	--	-10.0	0.18
	3	+4.1	--	-6.0	0.11
	Average	+3.7		-8.7	0.15
4	1	+3.4	--	-5.0	0.09
	2	+3.9	--	-0.9	0.02
	3	+2.8	--	-0.9	0.02
	Average	+3.4		-2.3	0.04

Notes: Corrosion rates based on defilmed and corrected weight loss and represent a corrosion rate for the outer layer of 72S aluminum.

*Mg/dm²/day

**Mil/year

6.0 DISCUSSION OF DATA

In general, the distribution and frequency of pits remained fairly constant on all groups of specimens during the first month of exposure. However, during the second and third months, a definite increase in pit frequencies on all groups was observed with the greatest increase occurring during the third or final month of exposure. Inspection of the four groups prior to exposure disclosed the samples contained in Group 1 to have the best appearance and surface condition. Sample 2 of this group did show 39 pits, but these were extremely shallow and barely detectable as pits. The remaining three groups showed numerous tiny pits which were not of a nature to be counted accurately. The greatest increase in pit frequency was observed on the samples in Group 3 during the third month of exposure. The average percent increase in the number of pits for each group compared to the original number of pits is shown below:

PER CENT INCREASE IN NUMBER OF PITS

<u>Group</u>	<u>Avg. Initial No. of Pits</u>	<u>1st Month</u>	<u>2nd Month</u>	<u>3rd Month</u>
1	14	0%	100%	250%
2	0.7	0	1333	2430
3	1.0	0	800	4600
4	---	---	---	---

*Pits too small and numerous to count

The above results for the first three groups are shown graphically in Figure VI as a function of exposure time.

Maximum pit depth measurements were determined microscopically on each specimen in each group. These results are tabulated in Table II. Samples in Group 1 showed the smallest average maximum pit depth, 5.3 mils, after 3 months exposure; samples in Group 3 showed the largest average maximum pit depth, 13.5 mils, for the same period of time. The average maximum pit depth for Group 2 was 12.9 mils; for Group 4 it was 5.8 mils. In Group 1, the greatest pit depth measured was 8.4 mils. Since the thickness of the 28 aluminum-72S aluminum cladding was 21 mils this indicates a safety factor of two and one-half times before penetration of the inner uranium-aluminum core could occur. In Group 2, the deepest pit penetration was 17.6 mils which allowed an additional thickness of only 3.4 mils before the inner core would be reached. This maximum pit depth was measured after an exposure period of 3 months. In Group 3, a maximum pit depth of 17.6 mils was observed also after 3 months of exposure. This penetration is extremely close to the combined cladding thickness of 18 mils for this group of specimens. During the last month of test.

FIG. VI THE PER CENT INCREASE IN THE AVERAGE NUMBER OF PITS FORMED ON FUEL PLATES AS A FUNCTION OF EXPOSURE TIME

6.0 DISCUSSION OF DATA (CONT'D)

a small trace of uranium, 0.001 gm/liter, was detected in the water, indicating that actual penetration of the uranium-aluminum core had occurred. Indications were that the penetration had taken place on one or more specimens in Group 3. True microscopic observations of maximum pit depths were somewhat obscured by the accumulation of corrosion products at the base of the developed pits. Cleaning the specimens to remove these accumulations was not always completely successful. Maximum pit penetration observed on the Group 4 specimens was 10 mils after an exposure of 3 months, thus leaving a thickness of 8 mils which had not been penetrated. Summarizing, it should be noted that the maximum pit depths, on all groups, were observed after the third month of exposure. There were no serious pit depths found during the first two months of test. Results of these tests are plotted in Figure VII.

Maximum pit diameters are reported in Table III. These data show that no severe progression in the observed diameters occurred during the 3 months exposure. The diameter of the pits, when one had started, remained fairly constant throughout the course of the test.

The average incremental weight changes on the samples are included in Table IV and Figures VIII. The trend for weight changes in Groups 2, 3, and 4 was similar; an initial weight gain during the first month, a decrease in weight during the second month, and, finally, a gradual gain in weight during the third and final month of exposure. In Group 1, the specimens exhibited a gradual weight decrease during the first two months followed by an abrupt weight increase. Figure IX presents a comparison of the average cumulative weight changes on the four groups of specimens. In no case was the loss in weight on any of the fuel plate samples of more than minor significance. It should be stated, however, that the weight losses are not a direct result of uniform corrosion attack, but represent in general, the weight loss due to the metal removed from pits. Then, too, metal loss as a result of pitting is obscured by the weight gains on the samples due to the formation of the protective hydrated aluminum oxide film. Each sample of the four groups exhibited a weight gain at the end of 3 months exposure. In order to determine the equivalent amount of aluminum that entered into combination with oxygen to form the oxide layer, the samples were cleaned in a mixture of 2% chromic acid - 5% phosphoric acid for 20 minutes at 60-70°C. The equivalent thickness loss of aluminum, mils/year, on the 12 specimens is shown in the last column of Table V. These values are extremely low, 0.18 mil/year and less, and do not represent any significant thickness loss due to normal corrosion attack.

A. GROUP 1

B. GROUP 2

C. GROUP 3

D. GROUP 4

FIG. VII AVERAGE MAXIMUM AND ACTUAL MAXIMUM PIT DEPTHS OBSERVED ON FUEL PLATES IN 0.005M HYDROGEN PEROXIDE AT 85°C

DWG. 9964

FIG. VII AVERAGE INCREMENTAL WEIGHT CHANGES OBSERVED ON FUEL PLATES EXPOSED TO 0.005M HYDROGEN PEROXIDE AT 85°C

7.0 CONCLUSION

The results of these tests indicate that failure of fuel plates is more apt to occur from the formation and development of localized corrosion (pits) than by normal corrosion attack. Such localized corrosion attack may penetrate through the outer protective cladding of 2S and 72S aluminum and into the inner uranium-aluminum core material. This penetration can result in the contamination of the cooling water with active material. Contamination of the test medium did occur in this investigation with samples in Group 3 after an exposure period of two months.

Based on overall corrosion performance, samples treated in Groups 1 and 4 exhibited the most satisfactory behavior. Samples in Group 1 exhibited slightly superior behavior to those of Group 4, indicating that the method of processing for Group 1 was the most successful of the four techniques employed. Samples treated by methods used in Groups 2 and 3 were not satisfactory and pit penetration to the core material was evidenced by the presence of uranium in the test water after 2 months exposure.

Photographs of the test specimens appear in Figure X-XIII and show the initial sample condition, and the effects of corrosion after 1, 2, and 3 months exposure in 0.005M hydrogen peroxide at 85°C.

8.0 ACKNOWLEDGEMENTS

The writer wishes to express his appreciation to Miss H. Barker, Mr. S. Wheeler, and Mr. J. Brown, of the Engineering Materials Section, for their assistance in handling of test specimens and preparing photographs and graphs for this corrosion investigation.

GROUP 1

GROUP 2

FIGURE X-1 PHOTOGRAPHS OF MINIATURE FUEL
PLATES PRIOR TO EXPOSURE IN SIMULATED
COOLING WATER (MAG IX)

GROUP 3

GROUP 4

FIGURE X-2 PHOTOGRAPHS OF MINIATURE FUEL
PLATES PRIOR TO EXPOSURE IN SIMULATED
COOLING WATER (MAG IX)

GROUP 1

GROUP 2

FIGURE XI-1 PHOTOGRAPHS OF MINIATURE FUEL
PLATES AFTER 1 MONTH'S EXPOSURE IN 0005M
HYDROGEN PEROXIDE AT 85° (MAG IX)

GROUP 3

GROUP 4

FIGURE XI-2 PHOTOGRAPHS OF MINIATURE FUEL
PLATES AFTER 1 MONTH'S EXPOSURE IN 0.005M
HYDROGEN PEROXIDE AT 85°C (MAG IX)

GROUP 1

GROUP 2

FIGURE XII-1 PHOTOGRAPHS OF MINIATURE
FUEL PLATES AFTER 2 MONTH'S EXPOSURE
IN 0.005 M HYDROGEN PEROXIDE AT 85° C
(MAG IX)

PHOTO NO
- 10317

GROUP 3

GROUP 4

FIGURE XII-2 PHOTOGRAPHS OF MINIATURE
FUEL PLATES AFTER 2 MONTH'S EXPOSURE
IN 0.005 M HYDROGEN PEROXIDE AT 85°C
(MAG IX)

GROUP 1

GROUP 2

FIGURE XIII-1 PHOTOGRAPHS OF MINIATURE FUEL
PLATES AFTER 3 MONTH'S EXPOSURE IN 0.005
M HYDROGEN PEROXIDE AT 85°C (MAG IX)

PHOTO NO.
10319

GROUP 3

GROUP 4

FIGURE XIII-2 PHOTOGRAPHS OF MINIATURE
FUEL PLATES AFTER 3 MONTH'S EXPOSURE IN
0.005 M HYDROGEN PEROXIDE AT 85°C (MAG IX)

END