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# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3333

BUSINESS AND  
TECHNICAL DEPT.

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CORROSION OF METALS OF CONSTRUCTION BY ALTERNATE  
EXPOSURE TO LIQUID AND GASEOUS FLUORINE

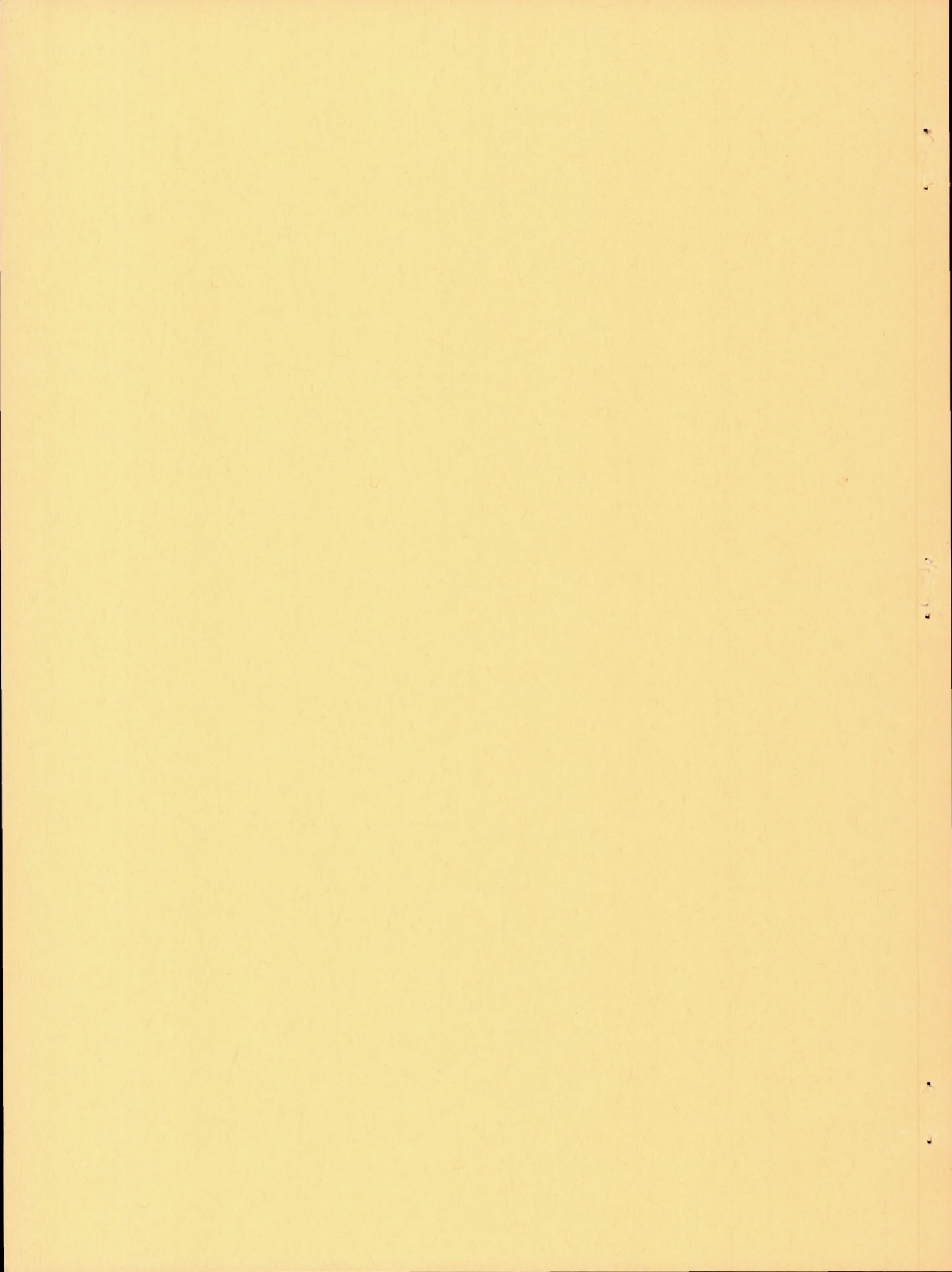
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Cleveland, Ohio



Washington

December 1954





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CORROSION OF METALS OF CONSTRUCTION BY ALTERNATE EXPOSURE  
TO LIQUID AND GASEOUS FLUORINE

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SUMMARY

The corrosion of 3S-0 and 52S-0 aluminum, AISI 347 and 321 stainless steels, "A" nickel, and low-leaded brass has been determined from the weight change of specimens exposed alternately to liquid and gaseous fluorine. Experiments were continued for a total exposure time of up to  $3\frac{1}{2}$  months. It was found that corrosion is negligible under the conditions of the experiments. No visual differences were observed between those surfaces exposed to the gaseous phase only and those exposed to both the liquid and the gaseous phases.

INTRODUCTION

Nickel, monel, and aluminum are resistant to attack by gaseous fluorine up to  $450^{\circ}$  C, while the resistance of stainless steels is unsatisfactory above  $200^{\circ}$  to  $250^{\circ}$  C (refs. 1 to 3). No information is available in the literature, however, on the corrosion of metals by liquid fluorine at liquid nitrogen temperature or by alternate exposure to liquid and gaseous fluorine.

The experiments reported herein were undertaken to determine the corrosion of several metals alternately exposed to liquid and gaseous fluorine that would occur in applications where fluorine is repeatedly condensed. The metals studied were 3S-0 and 52S-0 aluminum, AISI 347 and 321 stainless steels, "A" nickel, and low-leaded brass. Data were obtained by alternately exposing the inner surfaces of small tubes to gaseous and liquid fluorine for a total exposure time of up to  $3\frac{1}{2}$  months. The results were evaluated by visual examination and by considering weight changes and photomicrographs of exposed specimens.

APPARATUS AND PROCEDURE

The apparatus consisted of manifolds of test specimens together with necessary valving and an insulated liquid-nitrogen bath (fig. 1).

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Test specimens. - Test specimens were tubes 1/2 inch in outside diameter, approximately 6 inches in length, and of various wall thicknesses. One end of each tube was closed by fusion welding without addition of a second material, while the other end was attached to the manifold with a brass flare-type fitting. The metals tested were 3S-0 and 52S-0 aluminum, AISI 347 and 321 stainless steels, "A" nickel, and low-leaded brass having the composition of 31.81 percent zinc, 0.96 percent lead, 0.13 percent iron, and 67.10 percent copper by difference. Stainless steels were cold-drawn and annealed. Duplicate specimens of each type were tested on each manifold.

The manifolds were constructed of 1/2-inch-outside-diameter copper tubing. Joints were soldered with no. 3 grade silver solder in the absence of flux. Test specimens, manifolds, and other equipment exposed to fluorine were degreased in carbon tetrachloride, cleaned in 10 percent nitric acid, and rinsed with water and acetone. Test specimens were desiccated for 24 hours and then weighed on an analytical balance prior to exposure.

Operating procedure. - After preparation, the parts were assembled and the system was purged and pressure-checked for leaks with helium. Approximately 0.75 pound of commercial fluorine gas (0.5 percent HF max.) at 50 pounds per square inch gage pressure was introduced into the system. The lower half of each tube was immersed in liquid nitrogen, which condensed fluorine in the tubes and lowered the pressure of the system to 20 pounds per square inch gage. This resulted in a liquid fluorine level of about  $1\frac{1}{2}$  inches. The liquid nitrogen was maintained during the working day, except on weekends, so that approximately 13 hours of each 24 consisted of exposure to liquid fluorine. Experiments were conducted for periods of  $1\frac{1}{2}$  and  $3\frac{1}{2}$  months. The experiments were concluded because of the failure of a silver-soldered joint at one of the manifolds. Prior to weighing, the fluorine was allowed to evaporate and the specimens were desiccated for 24 hours.

## RESULTS AND DISCUSSION

The corrosion data obtained are given in table I. Table II gives the average change in weight per square inch of internal surface area of each metal after alternate exposure to liquid and gaseous fluorine. The data in table II represent maximum values which could be expected under these conditions, since at least part of the weight change may have been due to atmospheric corrosion on the outer surfaces. Since the estimated maximum error is 1 milligram, the lowest weight gains may have an error of as much as 100 percent while the largest weight gains may have an error of as much as 10 percent. Nevertheless, the data are considered reliable as to order of magnitude because good precision was obtained for most duplicate experiments. For every metal tested, a gain in weight was observed even after 2730 hours of exposure.



Penetration rates. - On the assumption that the gain in weight is due entirely to the addition of fluorine to form metal fluorides, it is possible to calculate the weight of metal consumed by assuming a composition for each fluoride. Penetration rates were calculated from the weight of metal consumed and are given in table III. Since the amount of metal which reacted was small, it was assumed that the film was non-protective and the rate was linear. The fluorides assumed were  $AlF_3$ ,  $NiF_2$ ,  $FeF_3$ , and  $CuF_2$ . These data indicate that corrosion of these metals by fluorine is practically negligible under conditions of the experiments. The rates for the stainless steels are lower than those reported at  $70^\circ F$  in reference 4, which may be a result of the lower average temperature in this investigation and of differences in types of stainless steel.

Surface appearance. - Metallurgical examination of the specimens, as shown by the photomicrographs in figure 2, did not reveal any pitting or intergranular corrosion except in the case of nickel (fig. 2(e)) in which slight intergranular corrosion was observed; however, this is considered negligible over the time period involved. The physical appearance of specimens after 2730 hours of exposure is compared with that of unexposed specimens in figure 2. The scratches in the surface of the specimens were a result of handling or were introduced intentionally to determine the degree of adherence of the scale. Except for nickel, the most noticeable change was in the color of the metal surface or in the presence of films. For nickel (fig. 2(e)) both exposed and unexposed surfaces appeared identical. Both aluminums (figs. 2(a) and (b)) appeared considerably lighter in color than original samples but otherwise were unchanged. The stainless steels (figs. 2(c) and (d)) had areas in which slight iridescence appeared, indicating the presence of a thin film. This seemed to be more prevalent with 347, but was not general for either type. Low-leaded brass (fig. 2(f)) was lightly covered with a reddish film which was not continuous but generally covered the entire surface. There was no visual difference between portions of the specimens exposed to the gaseous phase only and those exposed to both the liquid and the gaseous phase, nor was the liquid-gas interface detectable.

On the basis of the data obtained, it is concluded that any of the materials investigated are suitable for use with fluorine under the conditions of these experiments.

#### SUMMARY OF RESULTS

A quantitative investigation was conducted of the corrosion of 3S-0 and 52S-0 aluminum, AISI 347 and 321 stainless steels, "A" nickel, and low-leaded brass by alternate exposure to liquid and gaseous fluorine for periods of up to  $3\frac{1}{2}$  months. The results of the investigation may be summarized as follows:

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1. For storage and handling purposes, the change in weight of each of the metals investigated was negligible under conditions of the experiments.

2. No difference was observed between portions of specimens exposed to gaseous fluorine only and those exposed alternately to liquid and gaseous fluorine.

Lewis Flight Propulsion Laboratory  
National Advisory Committee for Aeronautics  
Cleveland, Ohio, September 28, 1954

#### REFERENCES

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TABLE I. - CORROSION DATA

Metal	Weight, g			Internal area, sq in.	Time, hr
	Before exposure	After exposure	Weight change		
3S-0 Aluminum	18.9033	18.9033	0	7.20	1055 <sup>a</sup>
	18.6296	18.6322	.0026	7.12	1055
	16.4636	16.4744	.0108	5.83	2730 <sup>b</sup>
	16.3856	16.3962	.0106	5.83	2730
	18.8299	18.8313	.0014	7.20	2730
	18.6457	18.6563	.0106	7.20	2730
52S-0 Aluminum	28.6731	28.6750	0.0019	8.36	1055
	27.8926	27.9019	.0093	8.21	1055
	27.7912	27.8075	.0163	8.06	2730
	27.9204	27.9041	-.0163	8.06	2730
	28.1495	28.1594	.0099	8.36	2730
	26.5484	26.5579	.0095	7.77	2730
AISI 347	42.2858	42.2870	0.0012	7.29	1055
	41.8131	41.8132	.0001	7.12	1055
	35.4984	35.5015	.0031	5.83	2730
	35.6087	35.6121	.0034	5.91	2730
	42.1893	42.1932	.0039	7.12	2730
	42.6253	42.6275	.0022	7.20	2730
AISI 321	27.3230	27.3249	0.0019	7.20	1055
	26.9847	26.9865	.0018	7.03	1055
	23.4952	23.4980	.0028	5.91	2730
	23.5475	23.5523	.0048	5.83	2730
	27.2577	27.2587	.0010	7.12	2730
	27.7913	27.7934	.0021	7.20	2730
"A" nickel	43.5582	43.5587	0.0005	7.20	1055
	43.6383	43.6387	.0004	7.20	1055
	36.3945	36.4005	.0060	5.74	2730
	41.4378	43.4404	.0026	7.12	2730
	38.8173	38.8203	.0030	6.34	2730
Low-leaded brass	57.7751	57.7800	0.0049	6.58	1055
	59.2956	59.2993	.0037	6.82	1055
	48.5486	48.5662	.0176	5.39	2730
	48.4982	48.5133	.0151	5.39	2730
	58.6092	58.6168	.0076	6.66	2730
	59.0067	59.0116	.0049	6.66	2730

<sup>a</sup>Exposed 783 hr to gas; 272 hr to liquid.

<sup>b</sup>Exposed 1714 hr to gas; 1016 hr to liquid.

TABLE II. - AVERAGE WEIGHT CHANGE OF SPECIMENS FOR  
ALTERNATE EXPOSURE TO LIQUID AND GASEOUS FLUORINE

Metal	Weight change, mg/sq in. (internal area)	
	<sup>a</sup> <sub>1055 hr</sub>	<sup>b</sup> <sub>2730 hr</sub>
3S-O Aluminum	0.18	1.33
52S-O Aluminum	.68	<sup>c</sup> 1.48
AISI 347 stainless steel	.09	.49
AISI 321 stainless steel	.26	.43
"A" nickel	.06	.63
Low-leaded brass	.64	1.99

<sup>a</sup>Exposed 783 hr to gas; 272 hr to liquid.

<sup>b</sup>Exposed 1714 hr to gas; 1016 hr to liquid.

<sup>c</sup>Negative value excluded.

TABLE III. - CALCULATED AVERAGE PENETRATION RATES

Metal	Inches per month	
	<sup>a</sup> <sub>1055 hr</sub>	<sup>b</sup> <sub>2730 hr</sub>
3S-O Aluminum	$2.6 \times 10^{-6}$	$7.4 \times 10^{-6}$
52S-O Aluminum	10.0	<sup>c</sup> 8.5
AISI 347 stainless steel	1.0	1.9
AISI 321 stainless steel	2.7	1.7
"A" nickel	.4	1.7
Low-leaded brass	5.2	6.3

<sup>a</sup>Exposed 783 hr to gas; 272 hr to liquid.

<sup>b</sup>Exposed 1714 hr to gas; 1016 hr to liquid.

<sup>c</sup>Negative value excluded.



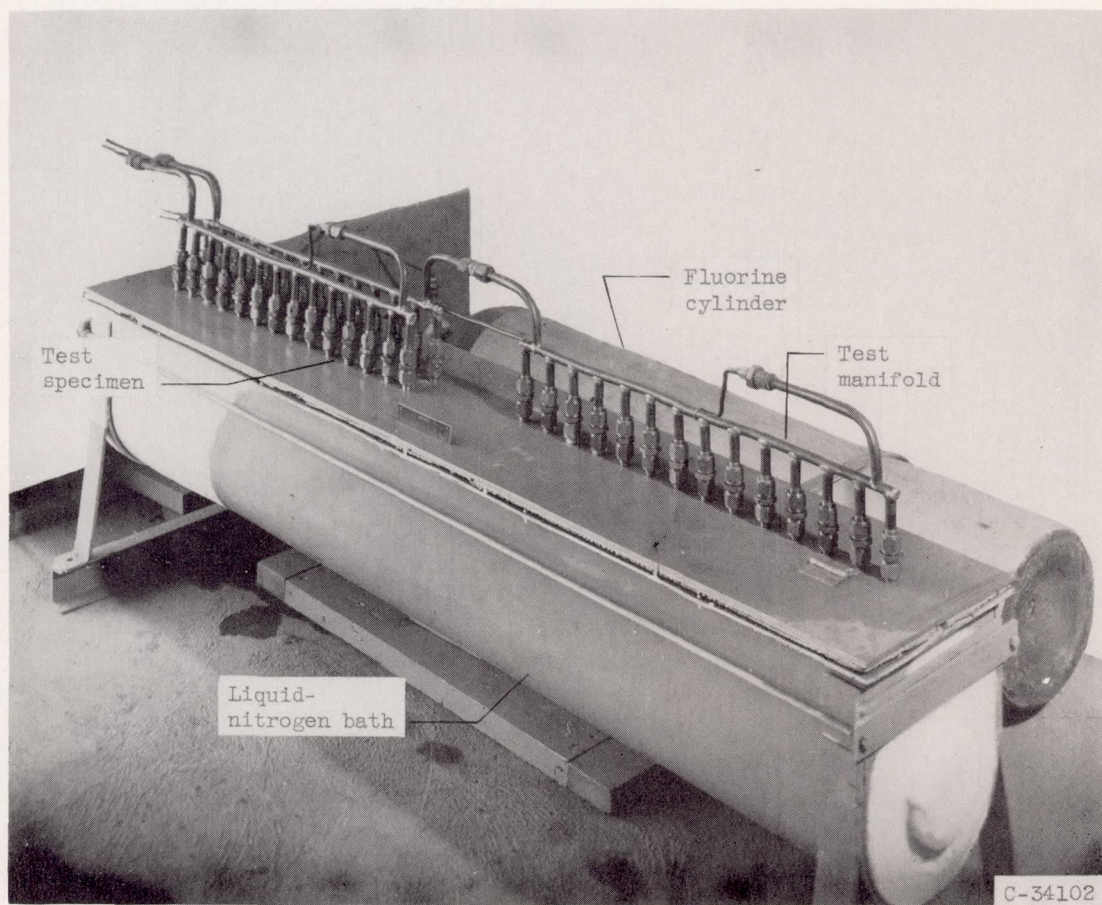
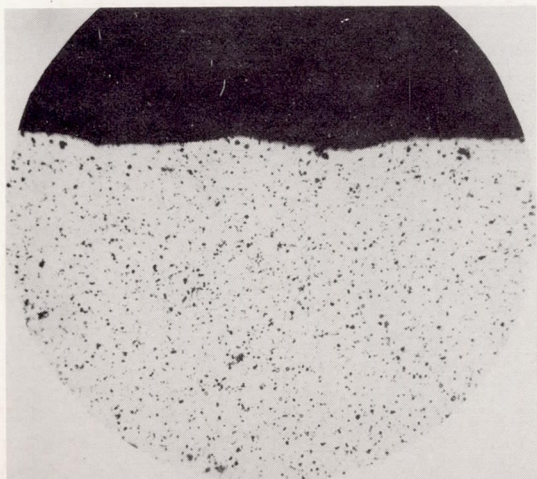
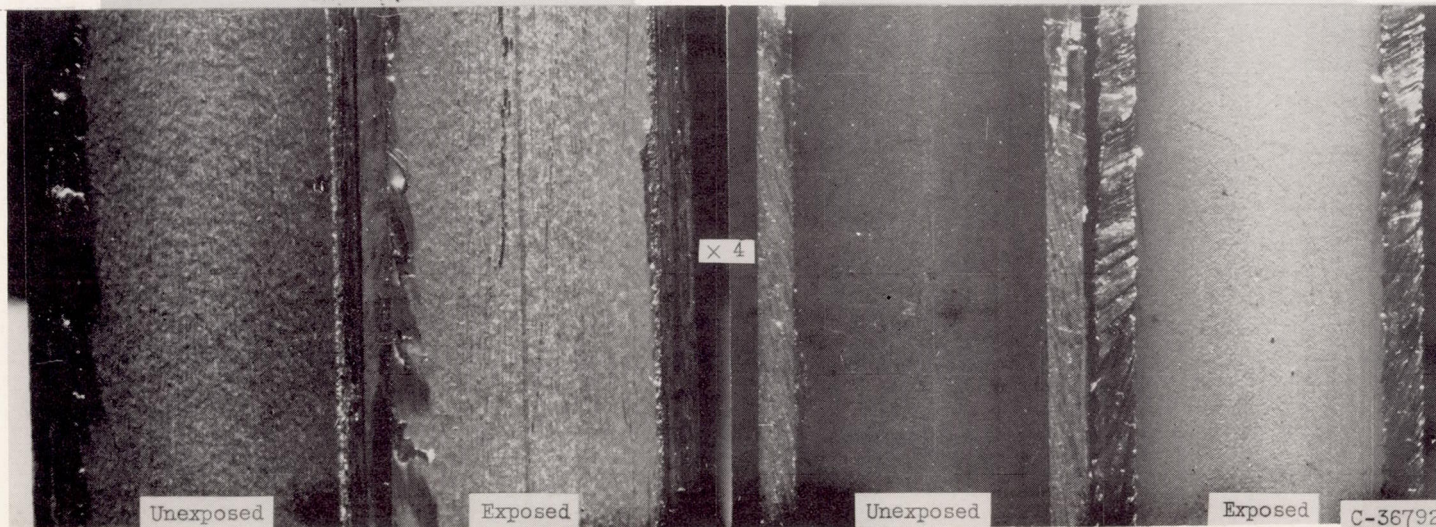
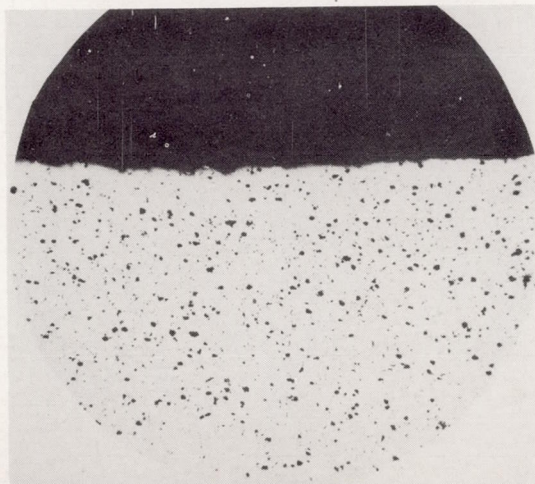


Figure 1. - Apparatus for fluorine-corrosion experiments.





x 250



Unexposed

Exposed

x 4

Unexposed

Exposed

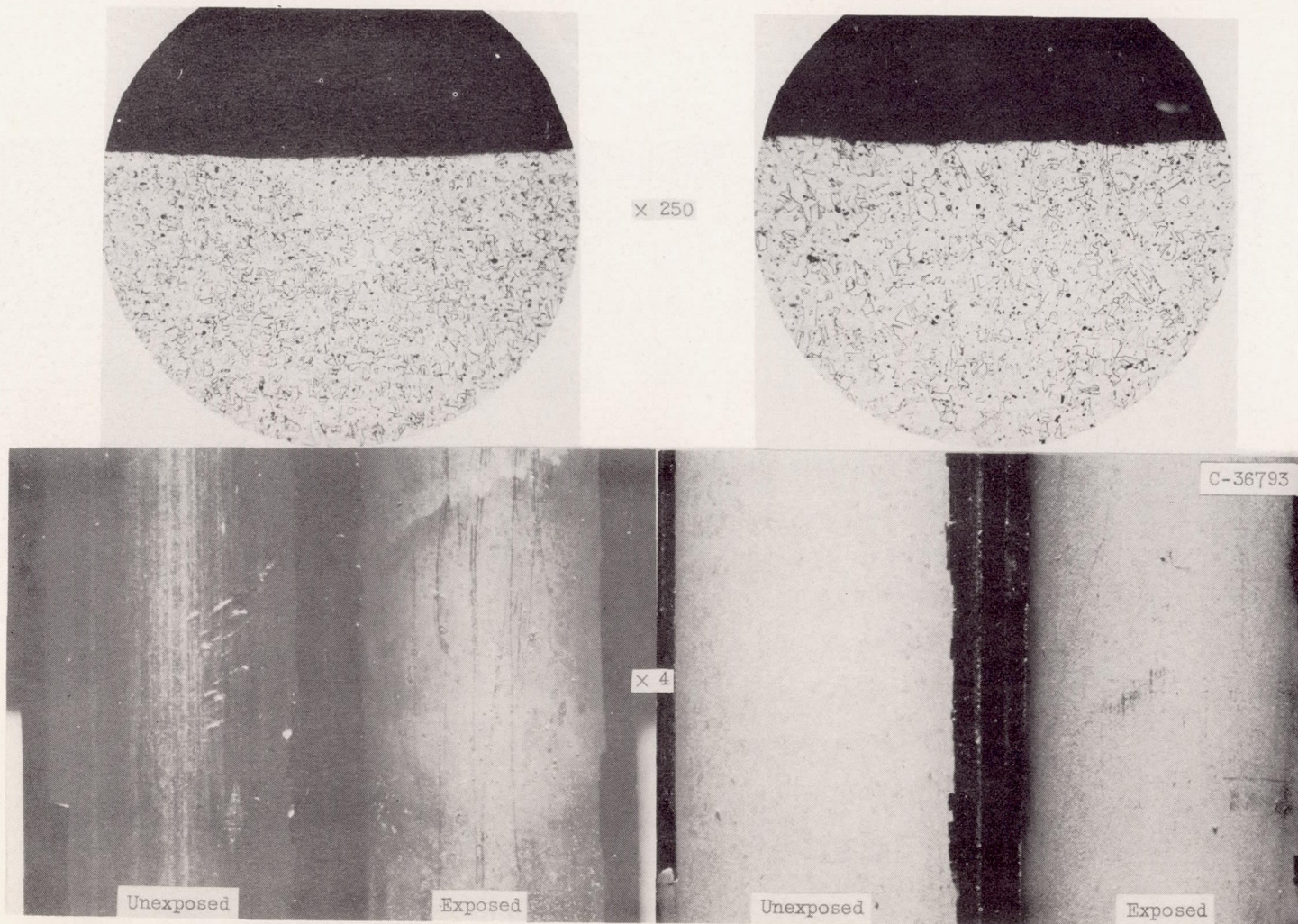
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(a) 3S-0 Aluminum.

(b) 52S-0 Aluminum.

Figure 2. - Comparison of metals before and after 2730 hours total exposure to liquid and gaseous fluorine. Photomicrographs of cross section of exposed metal.



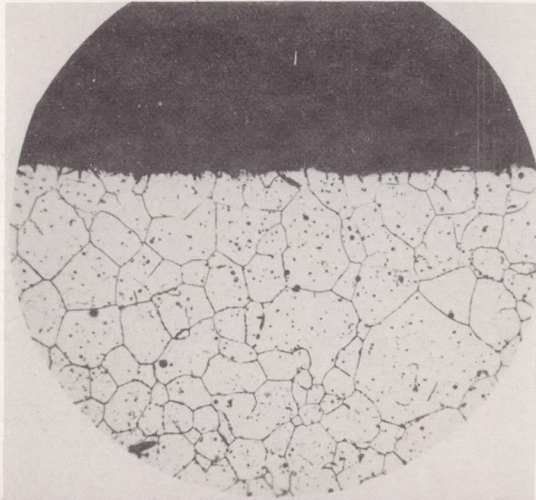


(c) AISI 347 stainless steel.

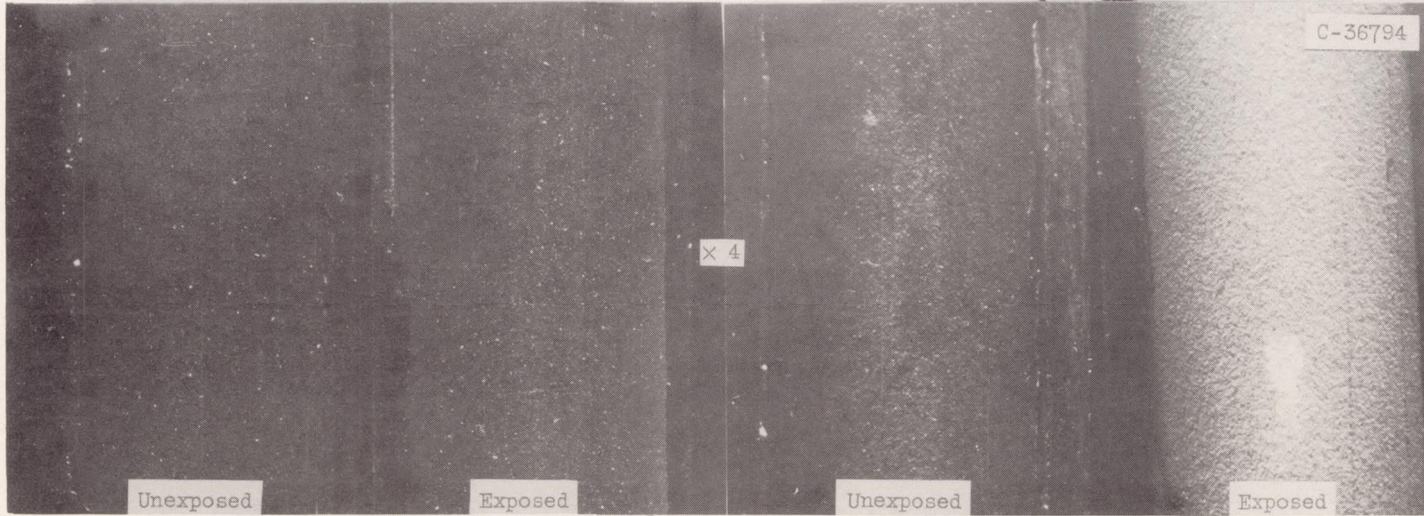
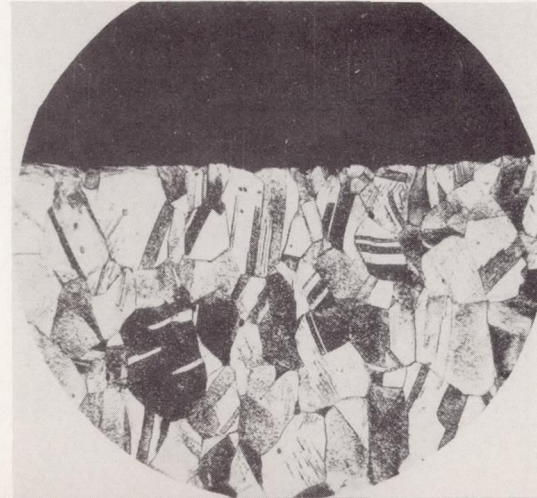
(d) AISI 321 stainless steel.

Figure 2. - Continued. Comparison of metals before and after 2730 hours total exposure to liquid and gaseous fluorine. Photomicrographs of cross section of exposed metal.





x 250



(e) "A" nickel.

(f) Low-leaded brass.

Figure 2. - Concluded. Comparison of metals before and after 2730 hours total exposure to liquid and gaseous fluorine. Photomicrographs of cross section of exposed metal.