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ACCENT ON VALUE

GENERAL AND STRESS CORROSION OF HIGH NICKEL ALLOYS IN SIMULATED SUPERHEAT REACTOR ENVIRONMENT

By
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U.S. ATOMIC ENERGY COMMISSION
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VALLECITOS ATOMIC LABORATORY
GENERAL ELECTRIC
ATOMIC POWER EQUIPMENT DEPARTMENT
SAN JOSE, CALIFORNIA

DISCLAIMER

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GENERAL AND STRESS CORROSION OF HIGH NICKEL ALLOYS IN SIMULATED SUPERHEAT REACTOR ENVIRONMENT

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W. L. Pearl and G. G. Gaul

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INTRODUCTION

The 300 series stainless steels had been selected originally as the reference fuel cladding material for utilization in several superheat reactor (SHR) systems being designed and built. Fuel jacket failures that occurred in Type 304 stainless clad fuel elements exposed in the Vallecitos boiling water reactor (BWR) superheated steam loop (SADE) (1, 2) and subsequent out-of-pile stress corrosion tests (3) indicated the questionable dependability of such stainless steels for this SHR fuel cladding application.

A literature survey was carried out (4) to determine what commercially available materials might possibly withstand the type of attack noted (1, 2, 3) with adequate high temperature physical, mechanical and chemical properties to be applicable for the proposed SHR fuel cladding. Of the materials indicated, several high nickel alloys were of significant promise to justify a major evaluation program.

The out-of-pile general and stress corrosion testing methods previously utilized for evaluating Type 304 stainless steel (3, 5) are serving again as major tools for the out-of-pile evaluation of the high nickel alloys.

It is the purpose of this report to summarize the results of the evaluation program carried out to-date on the high nickel alloys Inconel, Incoloy and Hastelloy-X in the out-of-pile superheat facilities as part of Task E of the Atomic Energy Commission sponsored Superheat Program, Contract AT(04-3)-189, Project Agreement No. 13.

CONCLUSIONS

The following conclusions are based on the out-of-pile general and stress corrosion studies completed to-date on Type 304 stainless steel, Inconel, Incoloy and Hastelloy-X:

1. The performance of Inconel, Incoloy and Hastelloy-X was acceptable under conditions that caused failures with previously tested Type 304 stainless steel.
2. The cycle test as utilized to date has produced a type failure that can occur in a superheat reactor system but has not reproduced the most general type failure experienced in the fuel cladding exposures in the SADE facility.
3. Under certain conditions that may exist in a superheat reactor system, oxidizing chlorides (e.g. cupric chloride and ferric chloride) will attack the materials tested to varying degrees with or without the presence of stress.
4. Further testing of the Inconel, Incoloy and Hastelloy-X alloys is advisable in a cycle type test utilizing oxidizing chlorides as they may occur in a reactor system.

MATERIALS

The heat transfer specimens consisted of tubes, either welded or seamless, cold drawn, annealed and pickled. Each test sheath was 36-3/4-inches long by 9/16-inch OD by 0.500-inch ID. The ends of the sheaths were machined to 0.560-inch OD and the last 1/4 inch on each end threaded. Two mils were centerless ground from the OD of the Incoloy sheaths to remove a layer of unknown composition believed to be caused by the annealing environment. The Inconel and Hastelloy-X were used as received. The sheaths were marked, degreased in acetone, pickled for 10 minutes in a 130 F, 20-percent, nitric acid bath, washed, dried and weighed.

For the localized corrosion tests (cycle tests) the sheaths were preheated for 4 hours at 1200 F. The Inconel and Incoloy were preheated in an air atmosphere and the Hastelloy-X in dry hydrogen. The preheated sheaths were descaled in a solution of 20-percent sodium hydroxide and 3-percent potassium permanganate, scrubbed with soap and water, rinsed and acetone dried prior to pickling procedure.

The coupons for isothermal testing were sheared from sheet and all edges were machined. They were given a uniform surface with "O" grade paper and then were washed with soap, rinsed and acetone dried.

The chemical composition and mechanical properties of the test materials are listed in Table I.

After test and prior to descaling, the tubes and test coupons were weighed and examined at magnifications up to 40× by means of a stereo-microscope. Descaling, as required, was performed in a solution of 20-percent sodium hydroxide and 3-percent potassium permanganate operated at 210 F up to 1-1/2 hours. Nylon brushes and nylon wool were used to remove the rotted scale. Control pieces gave less than two mg/dm^2 loss of base metal in the same time. The specimens were weighed as required. For some tests, the sheaths were examined by ultrasonics for flaw indications greater than the normal level present in incoming tubing. The sheaths and coupons were sectioned in selected areas for microscopic examination.

TABLE I

Composition and Mechanical Properties of High Nickel Alloys

Chemical Composition	Inconel		Incoloy		Hastelloy-X	
	Sheaths	Coupons	Sheaths	Coupons	Sheaths	Coupons
C	0.02	0.05	0.05	0.05	0.09	0.10
Mn	0.23	0.18	0.97	0.89	0.54	0.60
Fe	6.22	6.91	44.44	45.10	17.30	18.70
S	0.007	0.007	0.007	0.008	0.006	0.006
P	-	-	-	-	0.018	0.015
Si	0.09	0.18	0.66	0.43	0.55	0.85
Ni	77.57	76.22	32.10	32.56	49.7	46.6
Co					1.55	1.87
Cr	15.44	15.88	21.33	20.61	20.85	21.68
Cu	0.01	0.05	0.42	0.33	-	-
Mo	-	-	-	-	8.90	9.17
D	-	-	-	-	0.001	-
W	-	-	-	-	0.46	0.44

Mechanical Properties

	Inconel Sheaths	Inconel Coupons	Incoloy Sheaths	Incoloy Coupons	Hastelloy-X Sheaths	Hastelloy-X Coupons
Ultimate Strength, psi	94,700	96,000			112,100	116,200
Elongation in 2 inches, %	46	43			47	40

METHOD

A. General Corrosion

The general corrosion tests were carried out in the CL-1 superheat corrosion facility, shown in schematic diagram in Figure 1 and previously described elsewhere (5, 6). The tests with heat transfer were performed with longitudinal stresses applied as described for stress testing of Type 304 stainless steel (3). The runs for each material approximated 1000 hours. The facility water was maintained at neutral pH with no chemical additives. The water resistivity was maintained above 2 megohm-centimeters during the test runs with chloride maintained below 0.05 ppm. Oxygen and hydrogen were maintained in the water to result in a level in the steam typical of quantities generated radiolytically in a BWR system. The facility operating conditions during the general corrosion test runs are summarized in Table II.

B. Localized Corrosion

To increase the corrosion test capacity with heat transfer, the existing CL-4 boiling water corrosion facility was modified for superheat similar to the previous CL-1 modification. The superheat test capability was essentially duplicated and is represented by the schematic diagram shown in Figure 1. The modified CL-4 facility has been utilized for carrying out stress corrosion evaluations of the high nickel alloys by means of the cycling test developed for the Type 304 stainless steel evaluation (3). The operating conditions were modified to utilize a two-week total cycle. Oxygen and hydrogen were maintained in the water at the same level maintained for general corrosion testing, but the chloride level in the recirculating water was raised to about 1.5 ppm added as sodium chloride. The facility operating conditions during the cycling test runs are summarized in Table III.

Some copper-alloy coupons were added as ballast to each run to provide a corrosion product source of copper of about 0.1 ppm, because of the possible significance of copper chloride salts on the type of localized attack noted previously (3).

The cycle run operation of the CL-4 facility was similar to a corresponding run in the CL-1 facility with one major exception. Operation at a low pressure of approximately 100 psig and low superheat resulted in a much higher liquid carryover as determined by heat balance

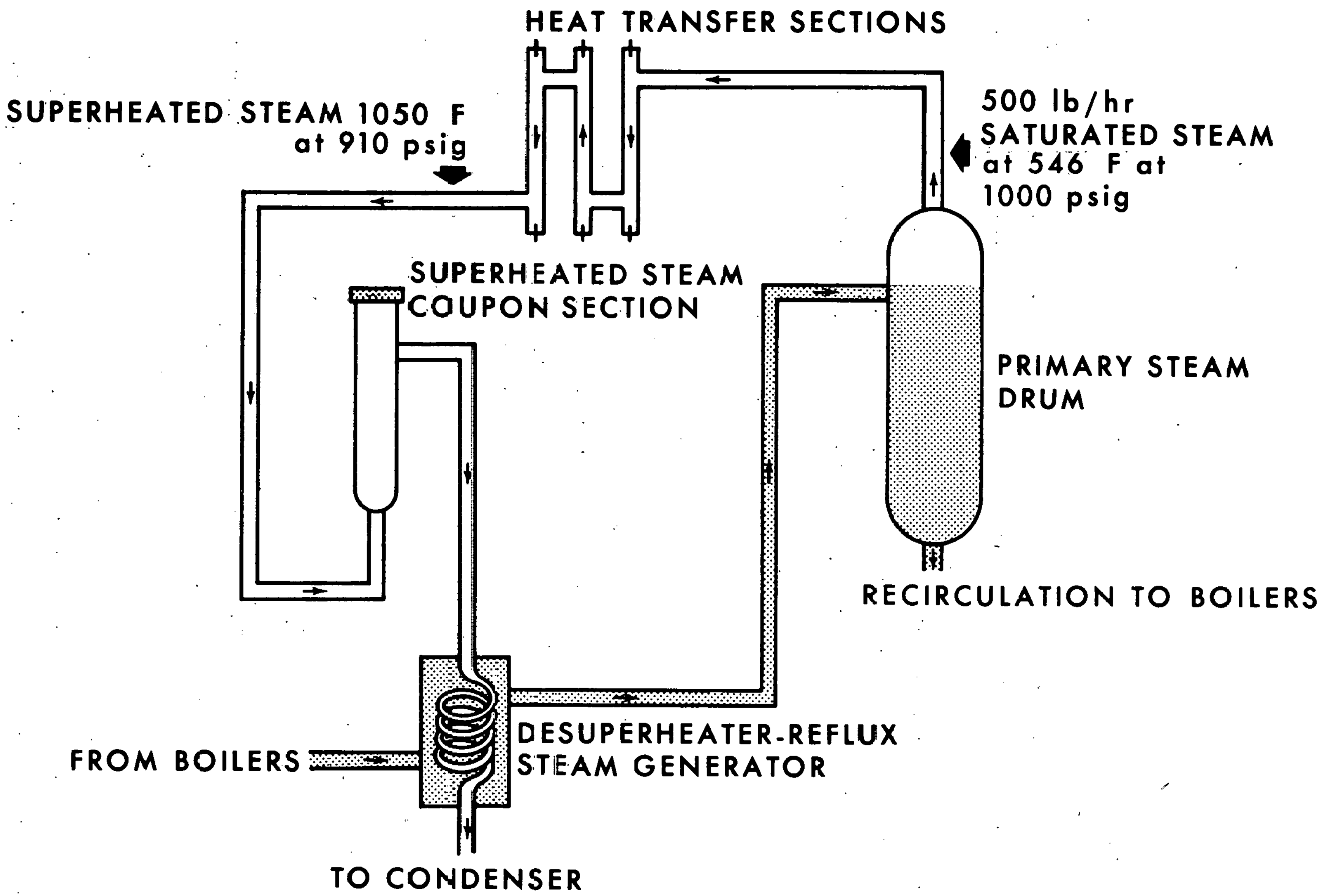

FIGURE 1 SUPERHEAT CORROSION FACILITY

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TABLE II

Operating Conditions General Corrosion Tests

Material Under Test	Inconel	Incoloy	Hastelloy-X
Run No.	52	56	57
Length of Test, hr.	1001	965	988
Steam Flow, lb/hr.	496	439	404
Moisture in Inlet Steam, %		1	1
Steam Temperatures, °F			
Inlet	546	546	546
Outlet of entrance heater	658	660	661
Outlet of middle heater	841	845	841
Outlet of exit heater	1048	1048	1045
Inlet Steam Gas Content			
Oxygen, ppm (range)	6.5-29.6	13.0-42.9	12.5-27.7
(mean)	20.6	18.9	19.7
Hydrogen, ppm (range)	1.7-12.3	1.5-8.0	1.5-3.3
(mean)	3.5	2.4	2.6
Average Heat Flux, Btu/hr-ft^2			
Entrance heater	177,000	167,000	152,000
Middle heater	176,000	168,000	147,000
Exit heater	189,000	171,000	161,000
Applied Stresses, psi			
Entrance sheath	25,000	23,000	25,000
Middle sheath	6,600	9,000	20,000
Exit sheath	2,500	4,500	11,400

Calculated metal temperatures: (all runs)

Entrance sheath	800 - 900 F
Middle sheath	900 - 1100 F
Exit sheath	1100 - 1300 F

TABLE III

Operating Conditions Cycling Tests

Material	Inconel	Inconel	Incoloy	Hastelloy-X
Facility Utilized	CL-1	CL-4	CL-4	CL-4
Run No.	54	26	27	28
Total Elapsed Time, Hours	345	351	367	364
Step One				
Elapsed Time, Hours	92	123	94	117
Steam Temperature, °F				
Inlet of entrance heater	348	365	350	350
Outlet of exit heater	359	388	390	366
Steam Drum Pressure, psig	66	97	90	89
Step Two				
Elapsed Time, Hours	76	64	72	70
Steam Temperature, °F				
Inlet of entrance heater	546	546	546	546
Outlet of exit heater	551	556	559	560
Steam Drum Pressure, psig	967	971	982	982
Step Three				
Elapsed Time, Hours	61	44	65	22
Steam Temperature, °F				
Inlet of entrance heater	546	546	546	546
Outlet of exit heater	1046	1052	1025	1068
Steam Drum Pressure, psig	903	928	920	931
Step Four				
Elapsed Time, Hours	70	73	74	60
Steam Temperature, °F				
Inlet of entrance heater	350	366	349	350
Outlet of exit heater	361	374	386	388
Steam Drum Pressure, psig	68	115	81	82
Step Five				
Elapsed Time, Hours	46	47	62	46
Steam Temperature, °F				
Inlet of entrance heater	546	546	546	546
Outlet of exit heater	550	555	1043	1025
Steam Drum Pressure, psig	968	970	936	942

TABLE III (Continued)

Material	Inconel	Inconel	Incoloy	Hastelloy-X
Step Six				
Elapsed Time, Hours				49
Steam Temperature, °F				
Inlet of entrance heater				349
Outlet of exit heater				360
Steam Drum Pressure, psig				72
Applied Stresses, low superheat, psi				
Entrance sheath	25,000	25,000	25,000	25,000
Middle sheath	25,000	25,000	25,000	25,000
Exit sheath	25,000	25,000	25,000	25,000
Applied Stresses, full superheat, psi				
Entrance sheath	25,000	25,000	24,400	25,000
Middle sheath	6,800	6,800	13,000	20,000
Exit sheath	2,600	2,500	4,500	11,000
Ballast, coupons	Monel	Copper-Nickel Monel	Copper	Copper

~ 20 ppm Oxygen in steam

~ 2.5 ppm Hydrogen in steam

~ 1.5 ppm Chloride in recirculating water as NaCl measurements. Also, the amount of carryover cycled so that the actual point of initiation of superheating varied on the heaters with the net effect of spreading the solids deposit over a larger portion of the 3-heater assembly and allowing moisture to come in contact with previous deposits. In all cases, the steam leaving the exit sheath was superheated. Inconel sheaths were run in both facilities for comparative purposes.

RESULTS

A. General Corrosion

After exposure, examination up to 40× showed no evidence of any localized attack on the alloys. The scale appeared to adhere tightly and the color darkened uniformly with temperature. Ultrasonic examination gave no indications of localized damage.

The descaled weight losses and the calculated metal to system losses are summarized in Table IV. The Type 304 stainless steel values are shown for comparison purposes.

TABLE IV

Superheated Steam

Corrosion with Heat Transfer

Calculated Metal Temperature 1100 F - 1300 F*

Alloy	Time Hours	Descaled Wt. Loss mg/dm^2	Metal-to-System Loss** mg/dm^2
Type 304 stainless steel	1032	284	62
	950	452	120
	2465	354	74
Incoloy	965	165	31
Hastelloy-X	990	151	74
Inconel	1000	97	34

* Stress applied to give 0.1% creep in 1000 hours at 1300 F.

** Corrosion Scale assumed to be 72% metal.

The results of the coupons exposed isothermally to 1050 F superheated steam are listed in Table V.

TABLE V

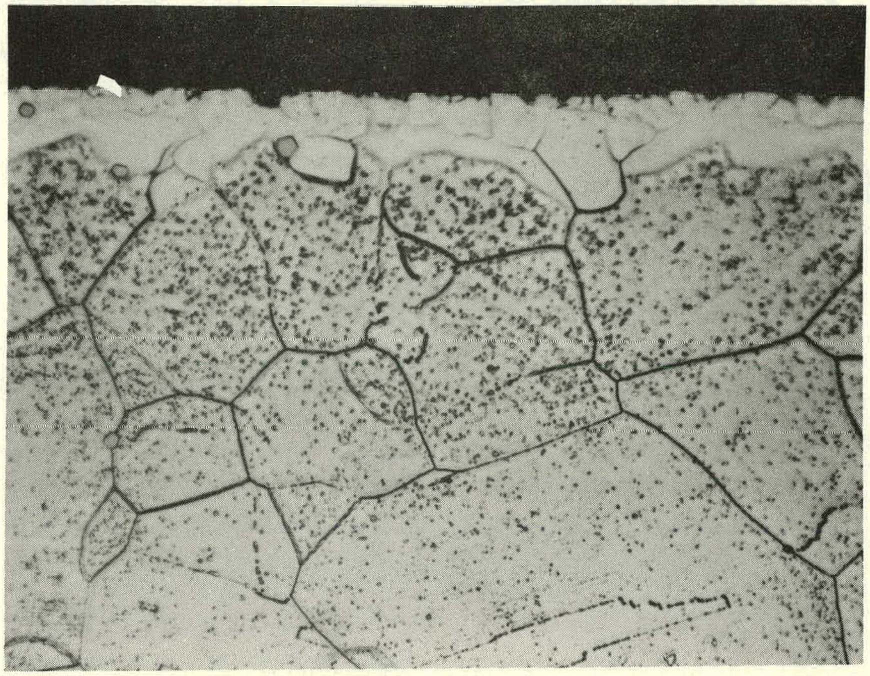
Corrosion in 1050 F Superheated Steam

Alloy	Descaled Wt. Loss mg/dm^2 1000 hrs.	2000 hrs.	5200 hrs.
Inconel	30	33	46
Incoloy	108	115	140
Hastelloy-X	94	85	134
Type 304 stainless steel	227	276 (2465 hrs)	372 (4500 hrs)

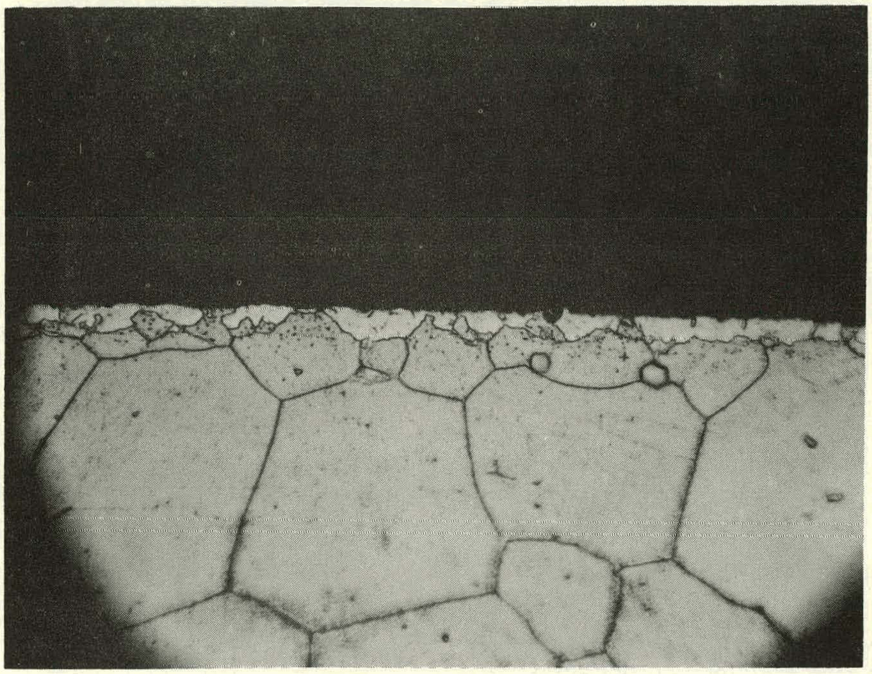
The three high-nickel alloys have excellent corrosion resistance especially in comparison to the previously tested Type 304 stainless steel. Although the Incoloy heat transfer sheaths indicated a higher corrosion than Inconel in 1000 hours, the Incoloy appears to lose only about 1/5 of its corrosion product to the system as compared to 1/3 in the case of Inconel. Since the latter contains over twice the nickel content, Incoloy would offer much less of an activity problem from Cobalt-58 (resulting from an n, p reaction with nickel) and Cobalt-60 (resulting from activation of residual cobalt contained in nickel).

The descaled weight loss data of the coupons exposed isothermally to 1050 F superheated steam for 5200 hours indicate little corrosion occurring after the first 1000-hours exposure.

Metallography showed the development of an alloy layer apparently different from the base composition on the exit heater sheaths examined (1100 - 1300 F metal temperature) for all three alloys exposed for 1000 hours as heat transfer specimens. Sections of the heat transfer sheaths at metal temperatures of 1100 and 1300 F are shown in Figures 2 to 4. Note that in Inconel the compositionally disturbed layer apparently is thinner at the 1300 F temperature than at 1100 F. The low corrosion rate of the Inconel in the 1100 - 1300 F range over a 3.2 dm^2 area would indicate that the thin layer at 1300 F is not caused by a high corrosion rate in that area. The compositional disturbance noted with Incoloy and Hastelloy-X apparently increases in depth with increase in temperature.



a. CALCULATED METAL TEMPERATURE – 1100 F



b. CALCULATED METAL TEMPERATURE – 1300 F

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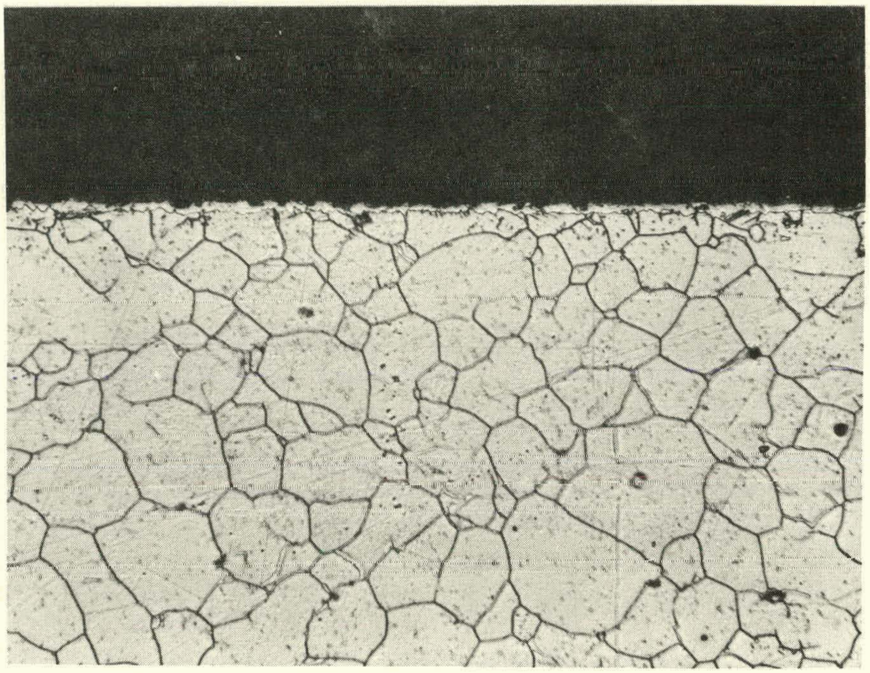
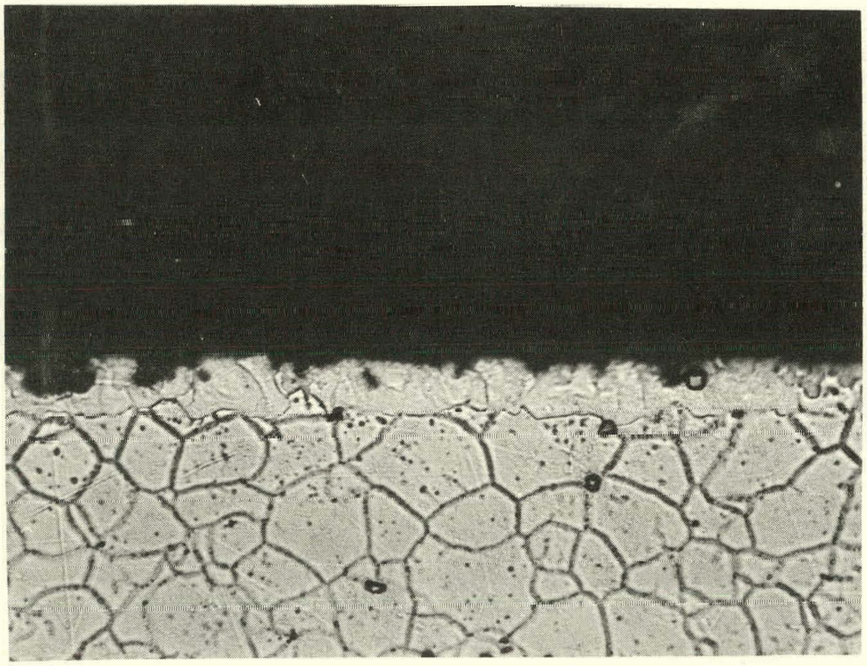
FIGURE 2 INCONEL HEAT TRANSFER SPECIMENS 1000 HOURS, DESCALED 3% NITAL ELECTROLYTIC ETCH 750 X



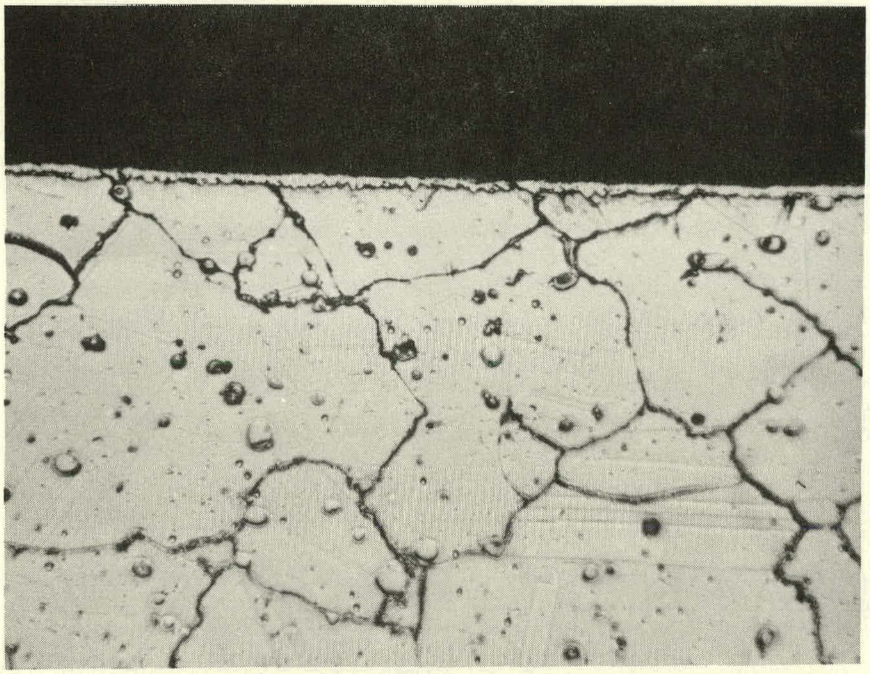
a. CALCULATED METAL TEMPERATURE – 1100 F



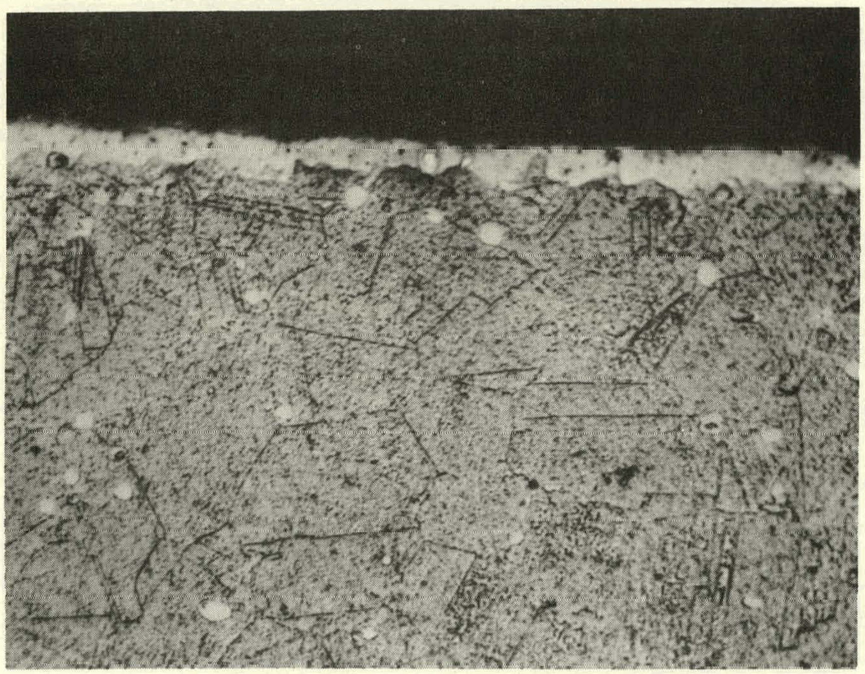
b. CALCULATED METAL TEMPERATURE – 1300 F

1037–12

FIGURE 3 INCOLOY HEAT TRANSFER SPECIMENS 965 HOURS, DESCALED 10% OXALIC ACID – ELECTROLYTIC ETCH 750 X



a. CALCULATED METAL TEMPERATURE – 1100 F



b. CALCULATED METAL TEMPERATURE – 1300 F

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FIGURE 4 HASTELLOY X – HEAT TRANSFER SPECIMENS 988 HOURS, DESCALED – 10% OXALIC ACID – ELECTROLYTIC ETCH 750 X

Electron beam microprobe analyses were performed on several of the descaled samples of the heat transfer specimens to determine the composition gradients of iron, chromium and nickel near the surface and to determine whether any compositional disturbance occurred in the grain boundaries. The traverses across the disturbed layer on the Incoloy samples were made in two locations in a direction normal to the surface and with traverse steps of one micron using a one-micron diameter probe. The microprobe analyses carried out on the Inconel and Hastelloy-X specimens utilized a continuous machine scan traverse taken at a 45 degree angle to the surface in two locations. In all cases the data have been corrected for absorption and secondary fluorescence.

The microprobe analyses of the Incoloy specimen exposed at a metal temperature of 1100 F for 1000 hours to superheat steam indicated that bulk diffusion to depths greater than one micron from the surface has not occurred. The 1300 F Incoloy specimen exhibited a bulk diffusion reaction which extended to an average depth of 9 microns. A plot of the traverses is shown in Figure 5. A decrease in chromium content of 6-percent occurred with an attendant increase in nickel and iron content.

The microprobe analyses of the 1100 F Inconel specimen exposed for 1000 hours indicated the bulk diffusion extended 25 microns from the surface. A micrograph of the probe traverse indicated a change of the etched surface at a depth of 13 microns (as seen in Figure 2a). A plot of the traverses is shown in Figure 6. A decrease in both iron and chromium is seen with a corresponding increase in nickel. The 1300 F Inconel specimens indicated a compositional disturbance of only 8-microns depth but slightly steeper than noted with the 1100 F specimen as compared in Figure 6.

The compositional disturbance was found to exist at least 32 microns from the surface of the 1300 F Hastelloy-X specimen exposed for 1000 hours. The exact surface was difficult to identify because of the type of mount used, however, the traverses plotted in Figure 7 represent a good approximation. A trace was run for the molybdenum content across the layer. The molybdenum was found to vary in segregated areas by 0.5 percent with no noticeable change relative to distance from the surface. No microprobe analysis was carried out with the 1100 F Hastelloy-X specimen.

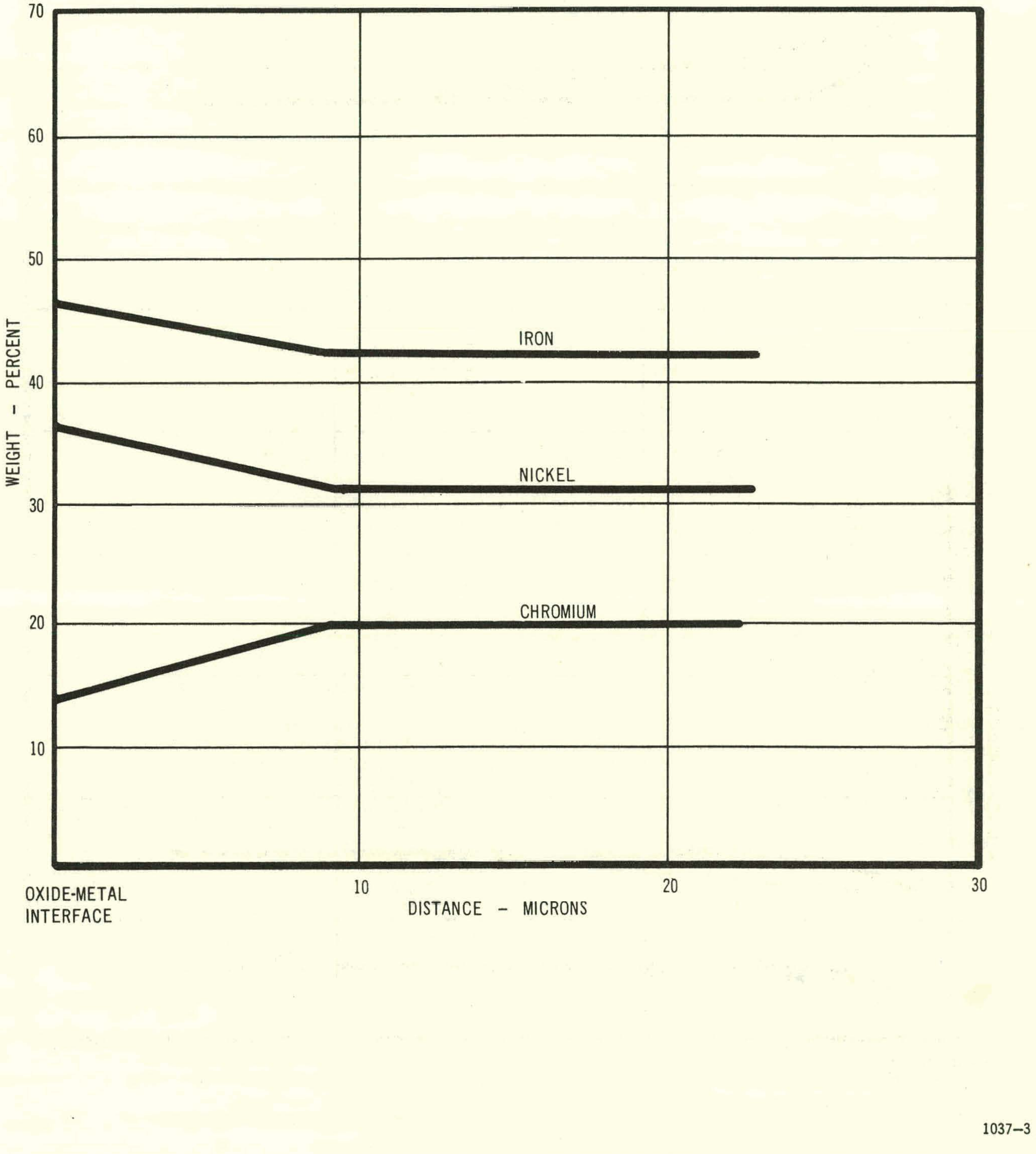

FIGURE 5 INCOLOY - CONCENTRATION GRADIENT ACROSS DESCALED HEAT TRANSFER SPECIMEN 1300 F – 965 HOURS.

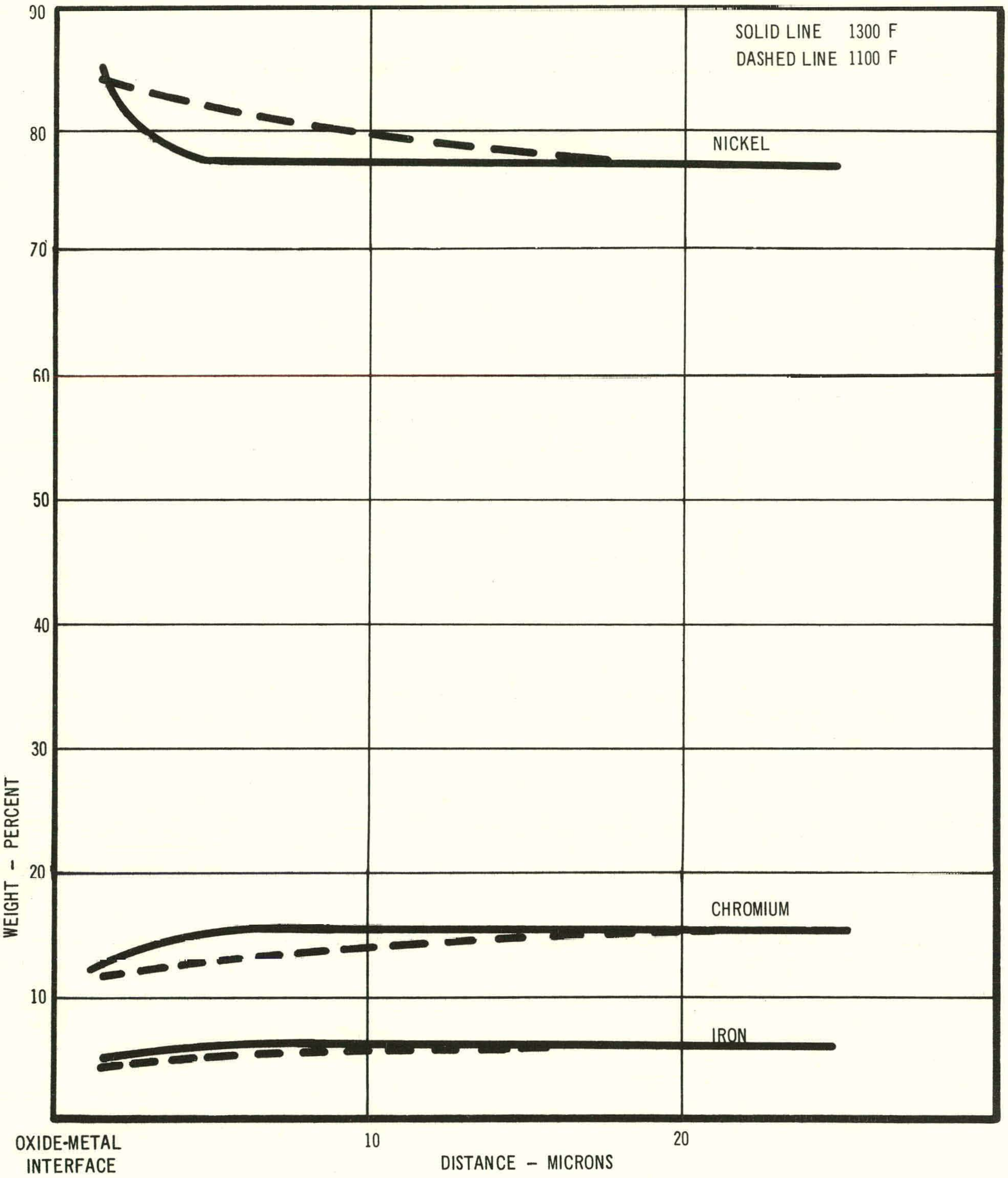

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FIGURE 6 INCONEL – CONCENTRATION GRADIENT ACROSS DESCALED HEAT TRANSFER SPECIMEN 1000 HOURS.

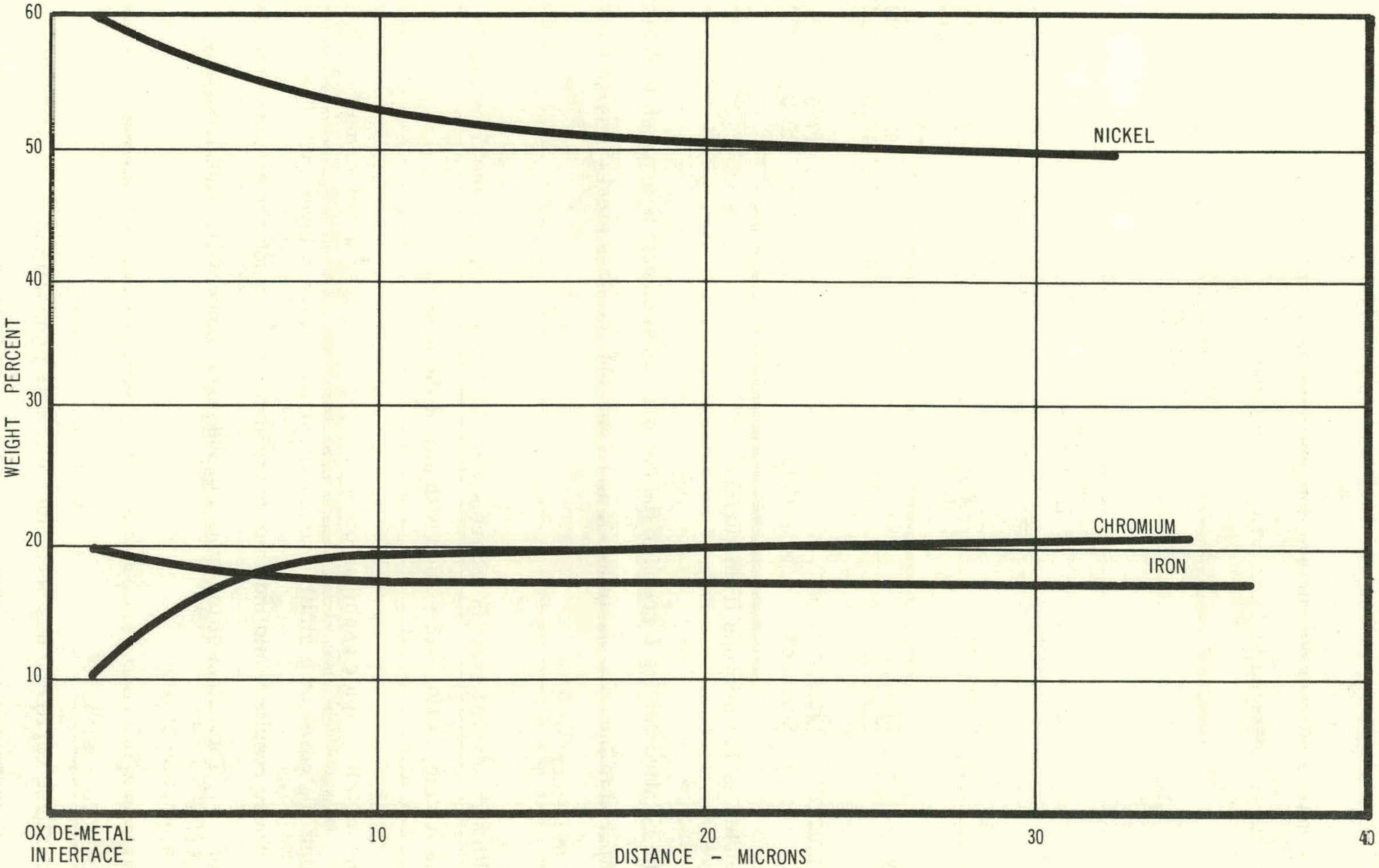


FIGURE 7 HASTELLOY X - CONCENTRATION GRADIENT ACROSS
DESCALED HEAT TRANSFER SPECIMEN 1300 F. 988 HOURS.

1037-2

The estimated average surface compositions as compared with the average matrix compositions are summarized in Table VI to the nearest 0.5%.

TABLE VI

Metal	Composition Location	Metal Temperature of Exposure °F	Depth Compositional Disturbance microns	Percentage Iron	Percentage Chromium	Percentage Nickel
Inconel	Matrix			6.0	15.5	77.5
	Surface*	1100	25	4.5	11.5	84.5
		1300	8	5.0	12.5	85.0
Incoloy	Matrix			42.0	20.0	31.0
	Surface	1300	9	46.0	14.0	36.0
Hastelloy-X	Matrix			17.5	21.0	50.0
	Surface*	1300	32	20.0	10.0	60.0

* Reported as 1.4 microns from surface

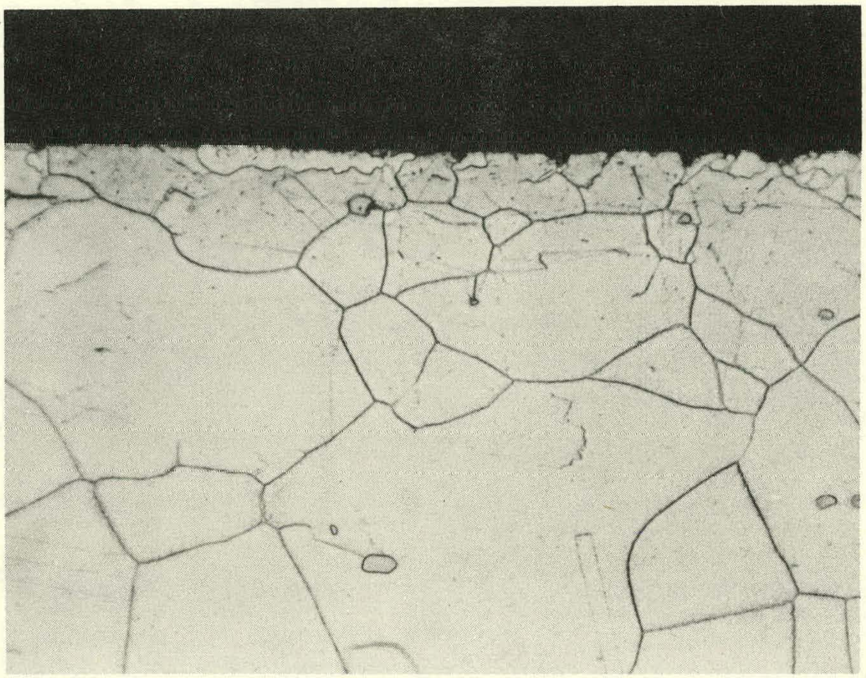
The relative driving forces for the compositional change is apparently different for Inconel as compared to Incoloy, Hastelloy-X and Type 304 stainless steel (5) as reflected by the direction of movement of iron.

Although several grain boundaries were included in each of the traverses no significant changes in composition were noted with any of the materials.

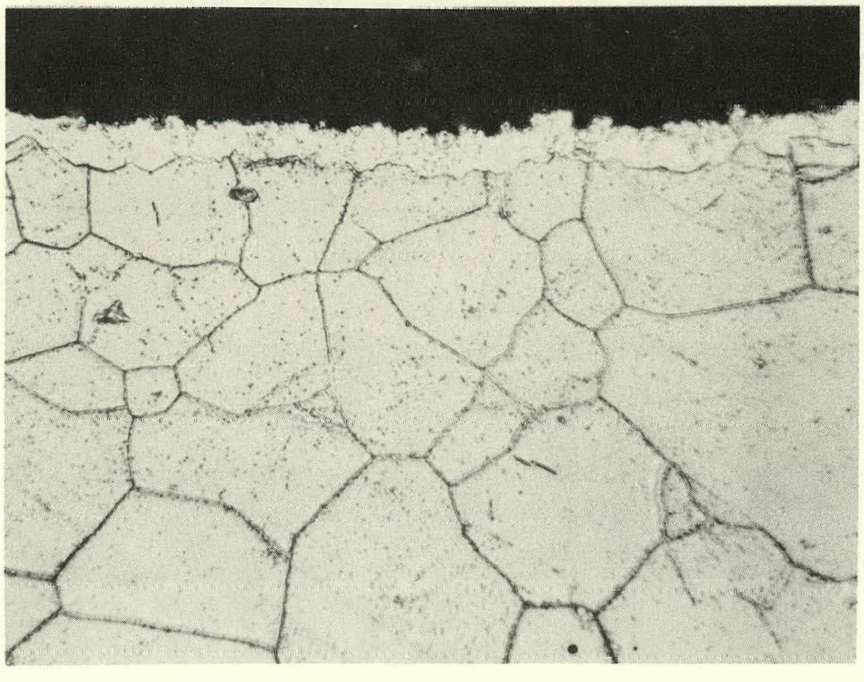
The metallographic examination of the specimens tested isothermally at 1050 F, Figures 8 through 10, revealed a similar compositionally disturbed layer that appears to grow with time. These results would indicate that heat transfer is not a prerequisite to the compositional disturbance. The extent of the growth of the disturbance will be an important parameter to follow as a function of time.

B. Localized Corrosion

Localized corrosion has been studied to date primarily in conjunction with the cycle runs. Visual, ultrasonic and metallographic examination of the Inconel and Incoloy sheaths disclosed no evidence of localized attack above one mil. Similar examination of the Hastelloy-X sheaths



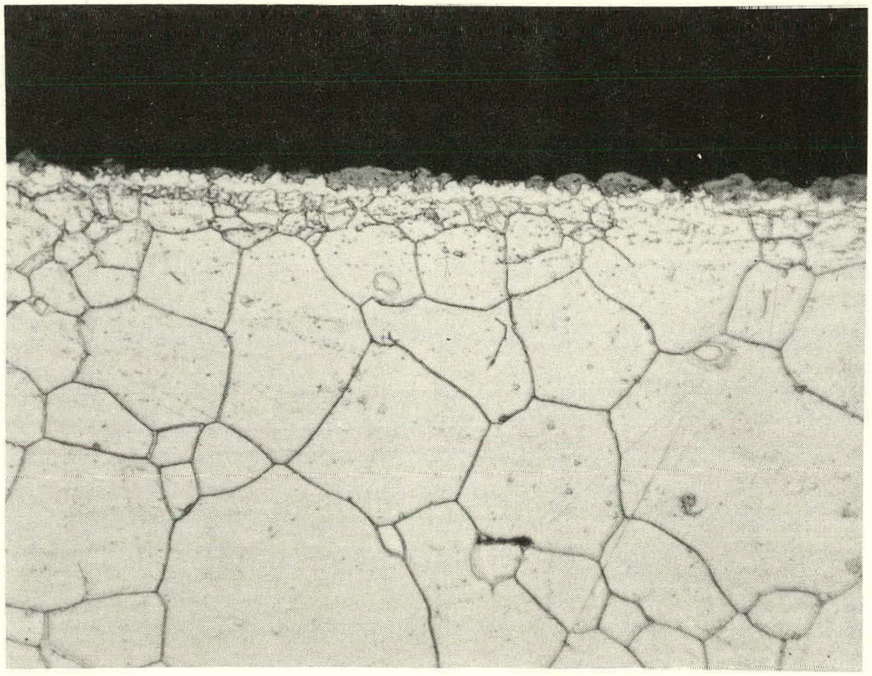
a. 1000 HRS.



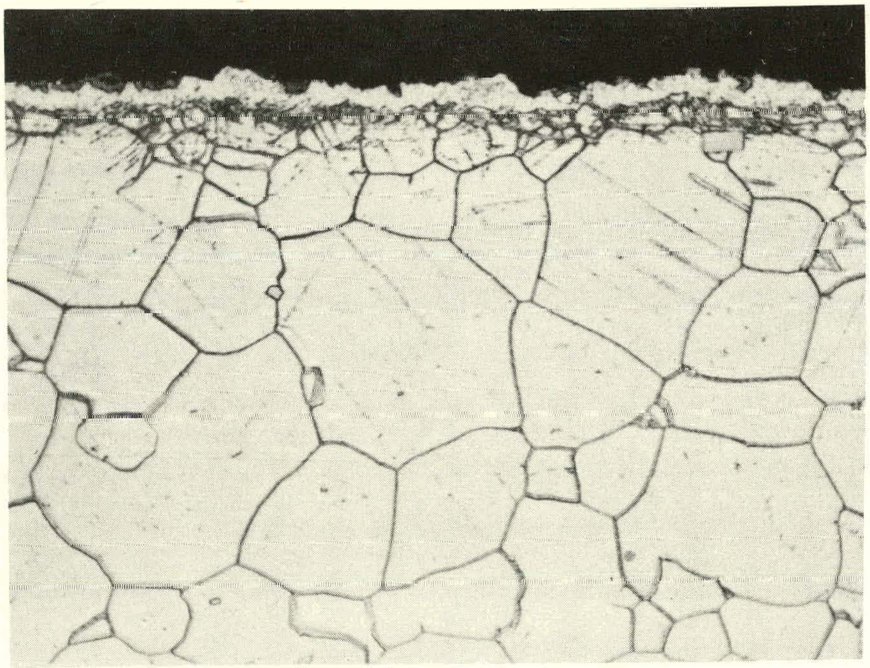
b. 2000 HRS.

1037–11

FIGURE 8 INCONEL – ISOTHERMAL EXPOSURE – 1050 F
WITH SCALE 3% NITAL ELECTROLYTIC ETCH 750 X



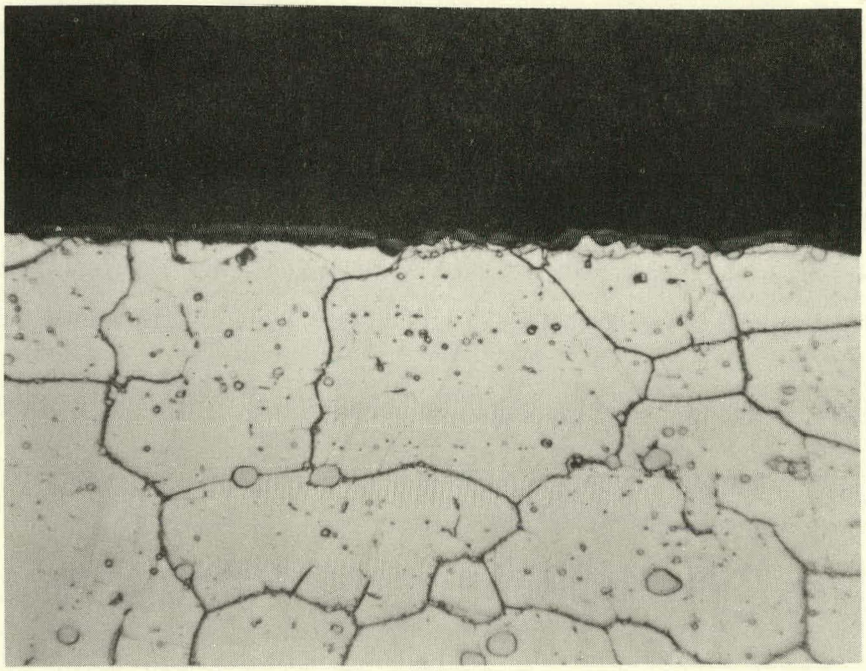
a. 1000 HRS.



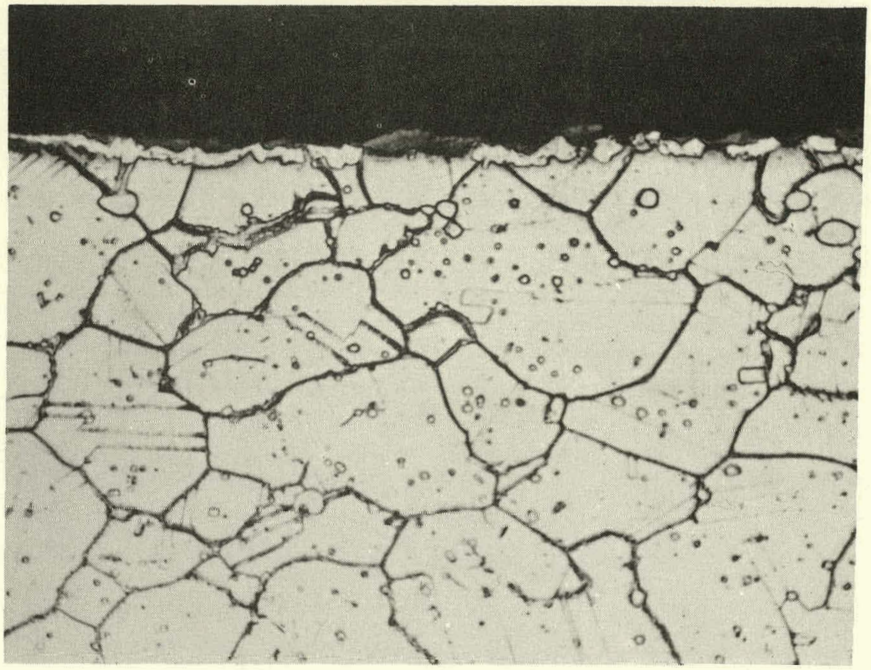
b. 2000 HRS.

1037–15

FIGURE 9 INCOLOY – ISOTHERMAL EXPOSURE – 1050 F
WITH SCALE. 10% OXALIC ACID – ELECTROLYTIC ETCH
750 X



a. 1000 HRS.



b. 2000 HRS.

1037–13

FIGURE 10 HASTELLOY X – ISOTHERMAL EXPOSURE – 1050 F
WITH SCALE. 10% OXALIC ACID – ELECTROLYTIC ETCH
750 X

showed no evidence of localized attack. The greatest attack noted was several random pits found on the Inconel. These were approximately 1 mil deep and metallographic examination showed no intergranular attack proceeding from them.

Small areas of damage, possibly caused by deposited salts, Figures 11 and 12, were found on both the Inconel and Incoloy but the damage appears to be of little significance.

Metallography of the Hastelloy-X showed damage even more negligible than that reported above.

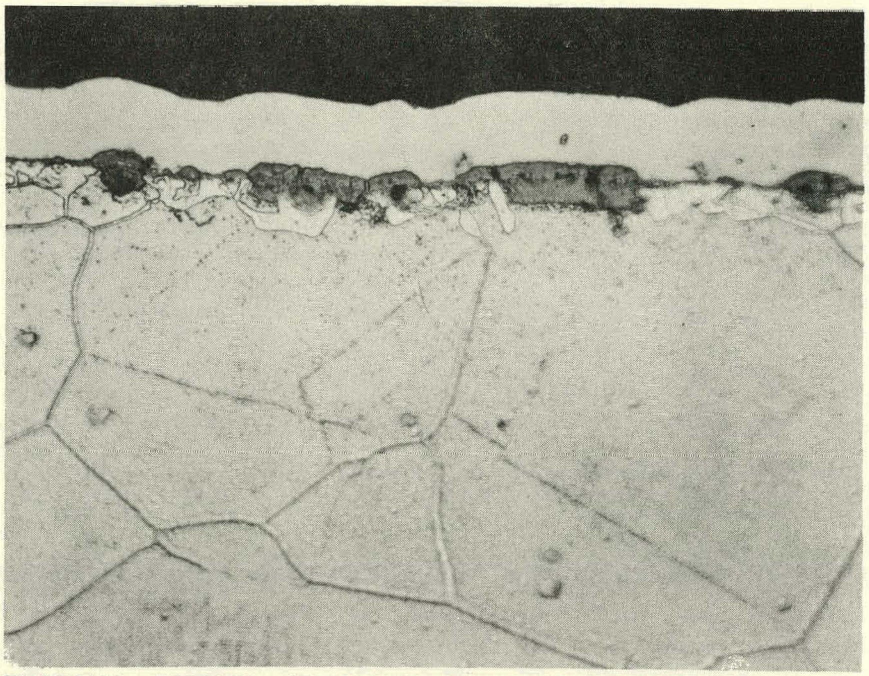


FIGURE 11 INCONEL, 351 HOURS EXPOSURE TO CYCLE RUN, 3% NITAL ELECTROLYTIC ETCH. 1250 F HIGHEST METAL TEMPERATURE (TOP LAYER NICKEL PLATING) (750 X)

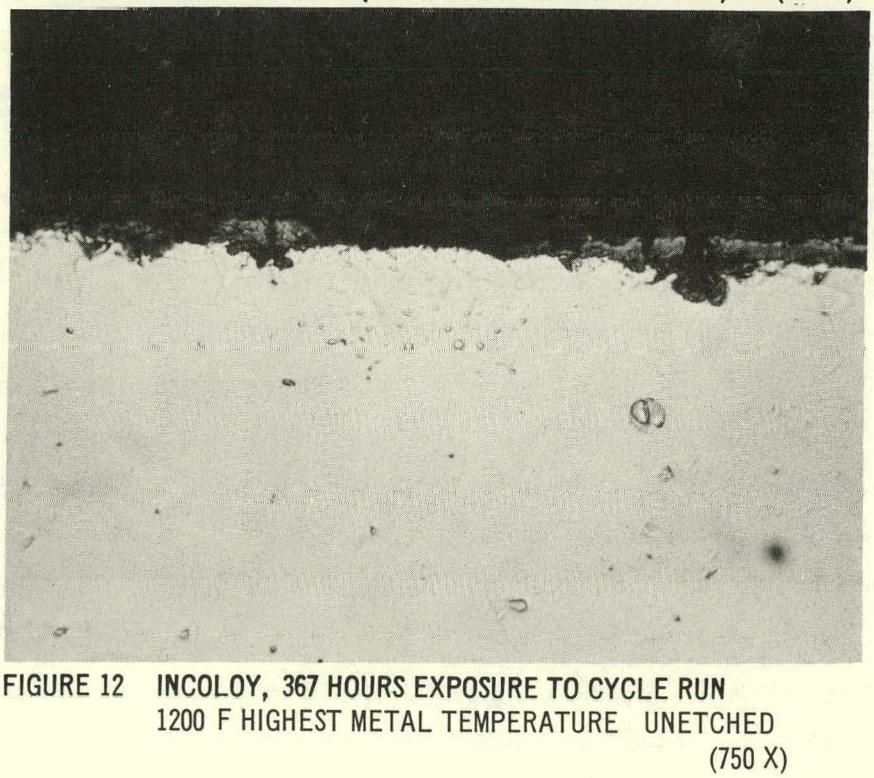


FIGURE 12 INCOLOY, 367 HOURS EXPOSURE TO CYCLE RUN 1200 F HIGHEST METAL TEMPERATURE UNETCHED (750 X)

1037–5

DISCUSSION

The cycle runs have been set up to simulate a condition that can and has existed in the VBWR. It includes many variables all acting simultaneously and is a constructive test for screening out materials that offer little prospect to resist localized attack in steam supplied from boiling water reactor type systems.

The type of cracking that has occurred to date has been primarily of a transgranular nature on the 300-series stainless steels. The SADE fuel element failures, on the other hand, have been predominantly an intergranular attack. It must be concluded, therefore, that the typical cycle run utilized to date does not duplicate the major cause or effect experienced in the reactor system failures.

The high-nickel alloys tested and reported herein have performed well both from the standpoint of general corrosion resistance and resistance to localized attack within the limitations of the cycle runs. Some additional testing was performed on these materials to try and establish other possible corrosion limitations. A summary of these tests has been included in the Appendix.

It was indicated on unstressed specimens of Type 304 stainless steel, Incoloy, Inconel and Hastelloy-X that atmospheric boiling water solutions of cupric chloride ($CuCl_2$) chemically attacked the sensitized Type 304 stainless steel and sensitized Incoloy intergranularly. Inconel and Hastelloy-X were attacked to a lesser degree. In the as-received condition, the Type 304 stainless steel, Incoloy and Inconel were pitted while the Hastelloy-X was not attacked by a similar $CuCl_2$ solution. Further testing in $CuCl_2$ solutions with both stressed and unstressed Type 304 stainless steel containing various degrees of cold work have revealed transgranular cracks associated with pits in the stressed unsensitized samples and intergranular attack in the sensitized materials regardless of stress. These results, plus additional investigations of equipment failures reported elsewhere (7), indicate that sensitized Type 304 stainless steel is attacked intergranularly by $CuCl_2$, with the type of attack not altered by stress. Transgranular cracking of unsensitized Type 304 stainless steel in $CuCl_2$ solutions will occur in the presence of residual and/or applied stresses but not in the absence of stress.

Tests carried out with a mixture of the chloride salts of chromium, copper, iron and nickel coated on the materials of interest and exposed under stress to superheated steam at approximately 1100 F resulted in no conclusive evidence of localized molten salt attack below stress levels adequate to cause eventual stress rupture failures. The chloride salts indicated an increase in general corrosion rates with Hastelloy-X being the least affected.

In the absence of chloride salts, no stress accelerated localized damage was found in comparing stressed and unstressed specimens to 1050 F superheated steam as long as stress levels were below the calculated stress-rupture failure limits.

Based on the increased understanding of the reactions involved, plans are being formulated to modify the cycle runs to more nearly simulate the conditions that result in reactor type failures. Those materials having successfully withstood the present cycle tests will be exposed to the modified condition to obtain a more thorough evaluation of their resistance to localized attack in superheat reactor type environments.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of the Corrosion Engineering Group under the direction of M. Siegler for the operation of the CL-1 and CL-4 superheat facilities; M. D. Fitzsimmons, who designed the new and modified facilities required for the program; A. E. Pickett and D. F. MacMillan, who performed most of the metallography; C. N. Spalaris, who provided expert counseling throughout the program; G. P. Wozadlo who performed the copper chloride attack studies; and F. A. Comprelli, who prepared all stress samples for exposure. The electron beam microprobe analyses on the Incoloy specimens were performed by the Materials Analysis Company of Palo Alto, California; the Inconel and Hastelloy-X analyses by the Advanced Metals Research Corp. of Somerville, Massachusetts.

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APPENDIX

Experience with both the SADE and the CL-1 loop has shown that "carry-over" products are deposited on the superheater surfaces. SADE was operated in such a fashion that during start-up and "hold" operations the deposit was wetted and the soluble part of the deposited material could act as a solution. This could lead to a purely chemical attack, a chloride stress corrosion, an oxygen stress corrosion or some combination of the three. When superheated steam was produced by the fuel, the "carry-over" deposits were dry and could attack as molten salts depending on cladding temperature and type of compound in the deposit.

I. Molten Salt Attack

Some out-of-pile scoping tests were designed to screen materials for susceptibility to the molten salt type of attack. If an alloy system was not subject to the relatively low temperature (300 - 550 F) chloride or chemical attack, it might be vulnerable to the molten salts.

An auxiliary coupon section (ACS-1), utilizing a low-flow bleed off from the CL-1 superheat facility steam supply, was installed and placed in operation in February, 1962. The initial intent of the equipment was to permit essentially static controlled-environment testing of materials in 1050 F superheated steam in the presence of relatively high concentrations of chloride.

The choice of the salts and their deposit density was based on the preliminary data then available. The X-ray fluorescence and diffraction data of deposits appearing on the entrance superheater sheath of CL-1 indicated that the deposit was composed of approximately 38% Cu, 32% Ni, 25% Cr, and 6% Fe as chlorides. An X-ray diffraction pattern of one of the SADE deposits indicated the presence of $CuCl_2$. A chemical analysis of a SADE deposit indicated a concentration of 35 μgms/in^2 of chloride in the sampled area. It was decided to use the metal chlorides in the proportions mentioned above at a surface density of 70 μgms/in^2. Admittedly, with the deposit appearing as it does when a reactor or loop is cycled, there are many other co-deposited compounds acting as a diluent and possible reaction media for the chloride salts.

There are many more variables that could be postulated, including the important one that whereas a relatively large amount of chloride material could be present in the material, the other 99% of diluent could be keeping it from contacting the metal surface.

The tube samples were exposed under stress using a modified version of the capsule configuration developed at Battelle (8) and without stress as 3-inch sections of tubing. The salts were applied by evaporation of a fixed volume of a water-alcohol mixture of the salts on the test surface.

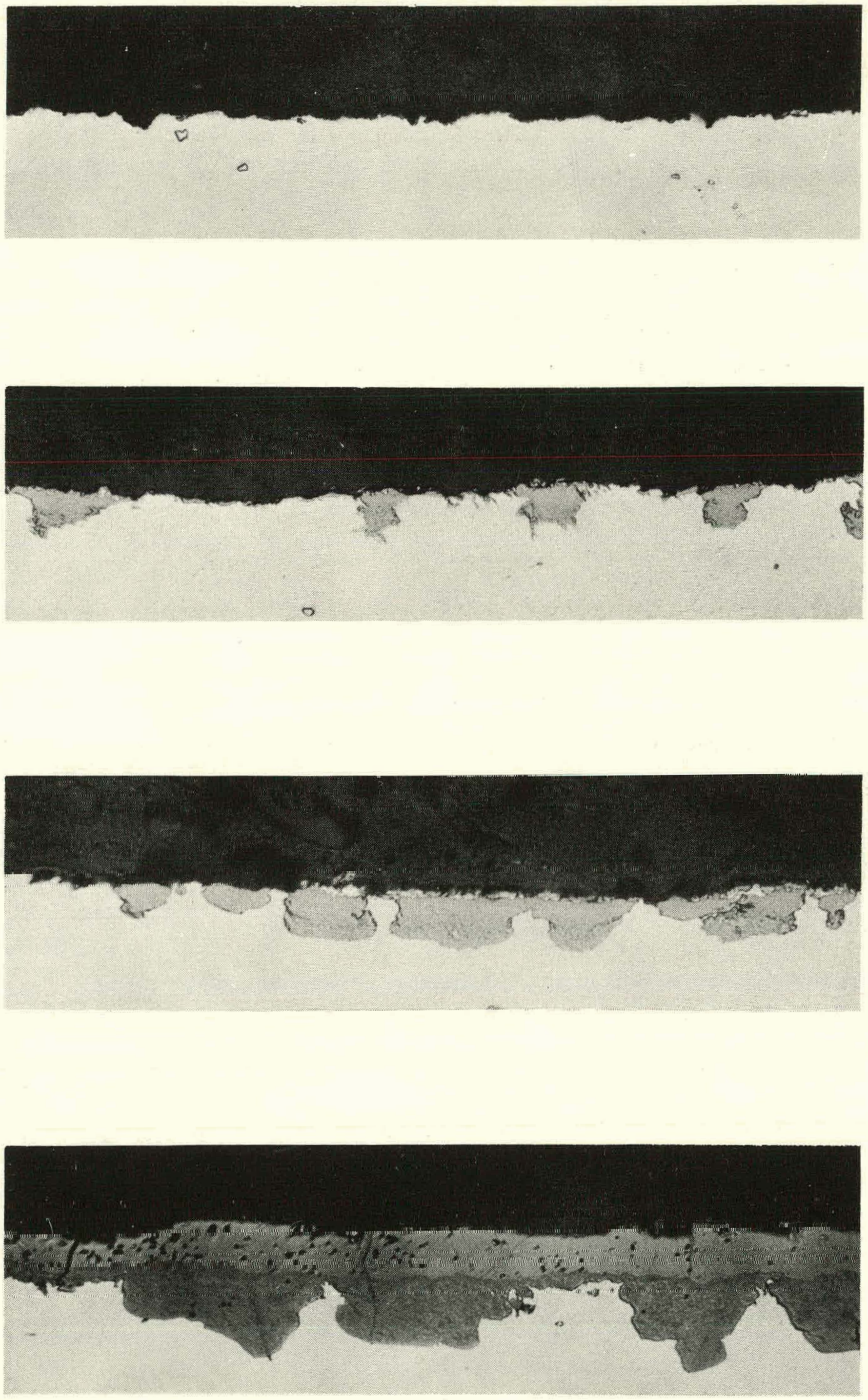
Figures A-1a to A-1d show the type of scale formed on the nonstressed tubes exposed to the salts for 1119 hours at approximately 1100 F. On the basis of depth of penetration, their corrosion resistance to salt attack would be listed in the order Hastelloy-X, Inconel, Incoloy and Type 304 stainless steel.

The stressed runs to date have utilized tubing materials available and as a result, the Type 304 stainless steel reference and the Inconel were tested at stress levels above that required for stress-rupture failure, as extrapolated from the literature, in 1000-1500 hours without the salts. The Incoloy and Hastelloy-X stress samples were below the stress rupture values for the time of exposure.

The attack on the stressed specimens of Incoloy, Hastelloy-X and Type 304 stainless steel appeared generally similar to the attack experienced in a comparable time on the unstressed specimens, except for one Type 304 stainless steel that failed in 1500 hours. In the latter case, severe micro cracking was noted which possibly allowed the salts to locally attack the micro cracks and accelerate the failure. The stressed Inconel specimens all collapsed against the outer shell.

II. Copper Chloride Attack Studies

The results of a preliminary study of the relative attack of copper, nickel, chromium and iron chloride solutions on Type 304 stainless steel was reported previously (3). The $CuCl_2$ was shown to be the most violent of the chlorides in its attack. A program was started to determine the relative susceptibility of Type 304 stainless steel, Inconel, Incoloy, and Hastelloy-X to such $CuCl_2$ attack.



a. HASTELLOY X

b. INCONEL

c. INCOLOY

d. TYPE 304

1037–16

FIGURE A–1 EXPOSURE TO MIXED CHLORIDE SALTS
1119 HOURS, ~ 1100 F IN SUPERHEATED
STEAM (500 X)

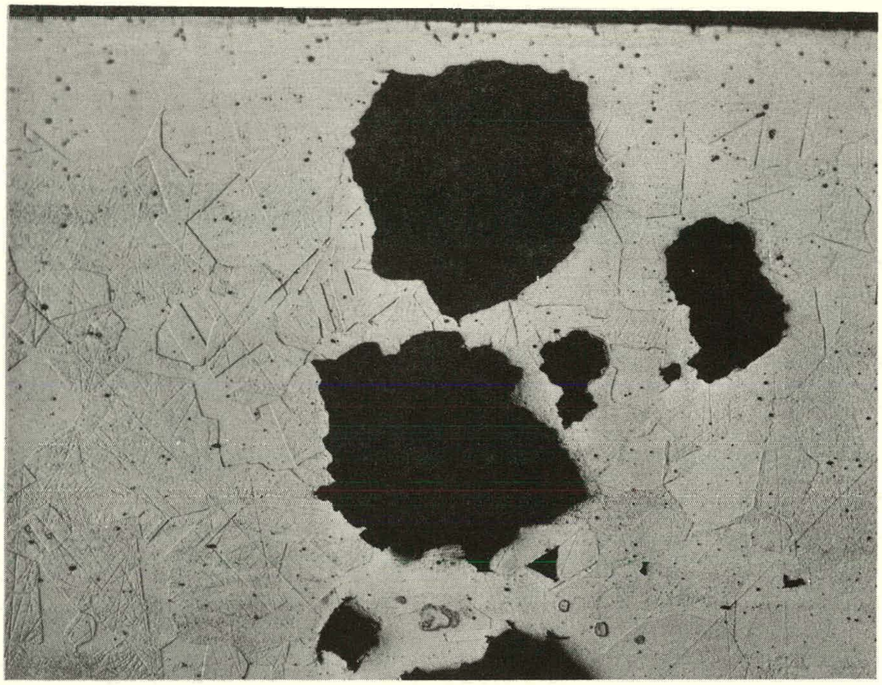
In the as-received condition, the materials were tested in atmospheric boiling $CuCl_2$ at concentrations of 400 and 20, 000 ppm Cl^- for 24 hours and 1 hour respectively. In the 400 ppm Cl^- test, the Type 304 stainless steel, Inconel, and Incoloy specimens were pitted while the Hastelloy-X was not attacked as shown in Figures A-2a to A-2d. The results were the same in the 20, 000 ppm Cl^- solution. It was found that the Inconel had some degree of sensitization in the as-received condition.

Type 304 stainless steel, Incoloy, and Hastelloy-X were heated at 1300 F for 4 hours, and the Inconel for 24 hours. The alloys were then tested as described for the as-received condition. In the 400 ppm Cl^- solution, the Type 304 stainless steel and Incoloy were intergranularly attacked and the Inconel was pitted as shown in Figure A-3a to A-3c. The Hastelloy-X had no metallographically visible attack when a random section was examined. The results were the same in the 20,000 ppm Cl^- solution with the exception of Hastelloy-X which was intergranularly attacked as shown in Figure A-4.

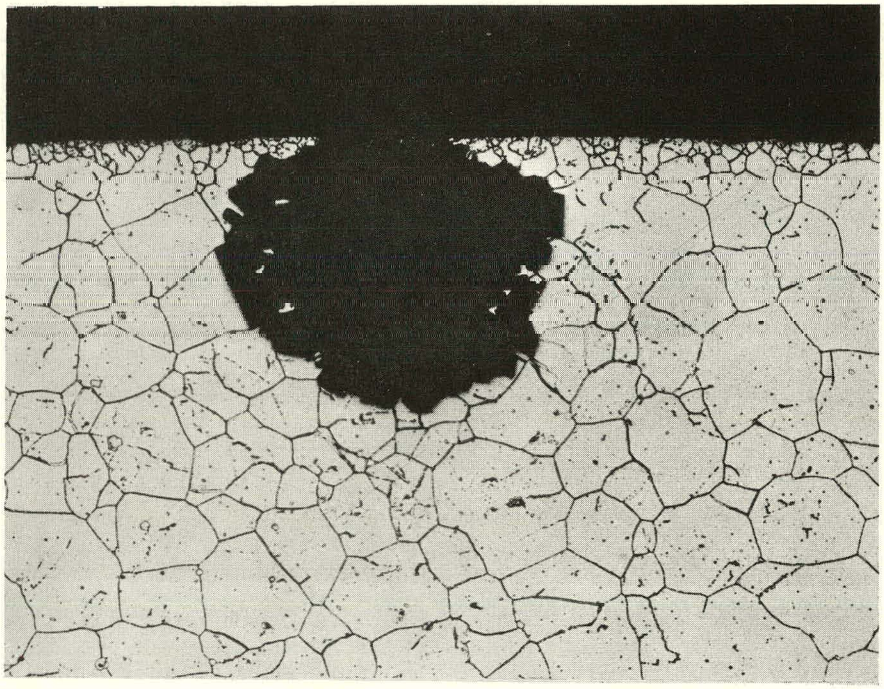
Type 304 stainless steel in the 1/4 hard and 3/4 hard condition was tested in atmospheric boiling $CuCl_2$ with 20, 000 ppm Cl^- for 1 hour. The 1/4 hard material had transgranular cracks as shown in Figure A-5a and the 3/4 hard material, found to have been received in the sensitized condition, was intergranularly attacked as seen in Figure A-5b. U-bends of annealed, 1/4 hard and 3/4 hard Type 304 stainless steel were tested in atmospheric boiling $CuCl_2$ containing 20, 000 ppm Cl^- for 1 hour. All the materials had transgranular cracks associated with pits and the severity of cracking increased with the amount of total stress (residual plus applied).

III. <u>Effect of Stress on Corrosion Without Salts</u>

The alloys being studied were exposed under stress along with the nonstressed general corrosion specimens in the 1050 F superheated steam coupon section. Duplicates of the capsule configurations made up for the molten salt tests in I above were utilized for the stressed specimens. Again the Type 304 stainless steel and Inconel tubing available for test resulted in stresses above those calculated as being necessary for stress-rupture failure in 1000 to 1500 hours.



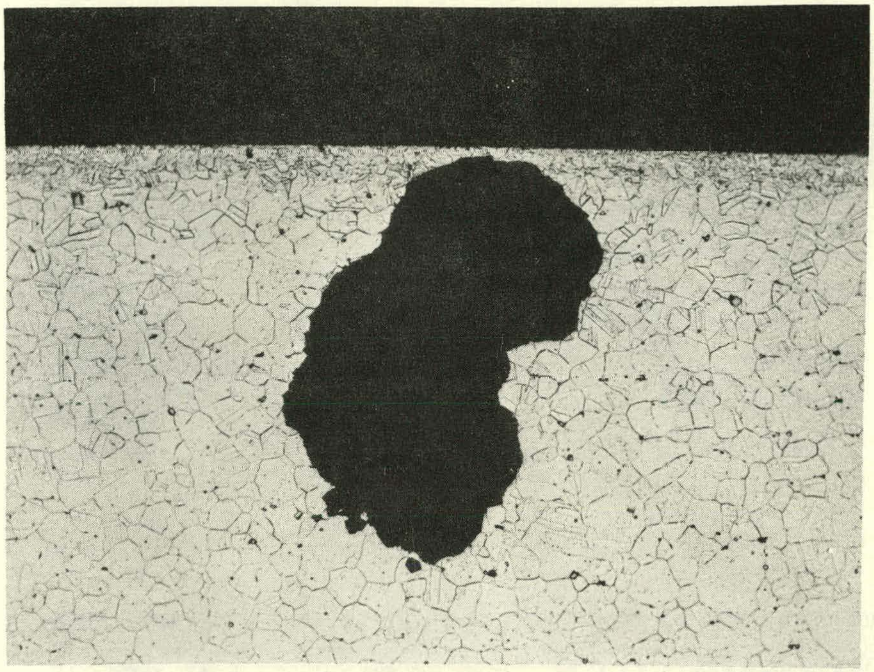
a. TYPE 304 SS



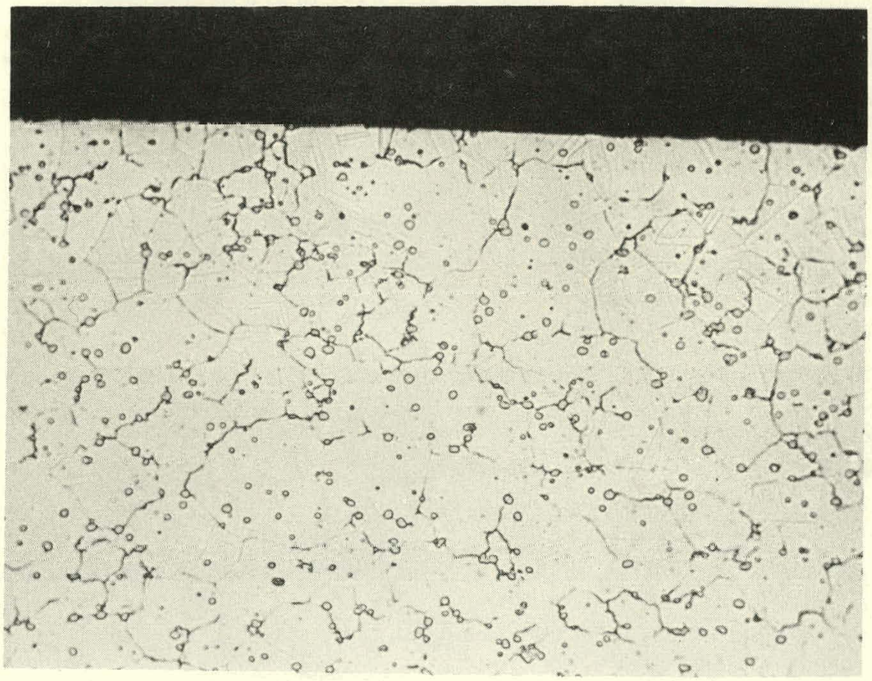
b. INCONEL

1037-4

FIGURE A-2 AS RECEIVED MATERIAL EXPOSED TO CUPRIC CHLORIDE SOLUTION, 210-220 F, 400 PPM CHLORIDE, 24 HOURS
10% OXALIC - ELECTROLYTIC ETCH (250 X)



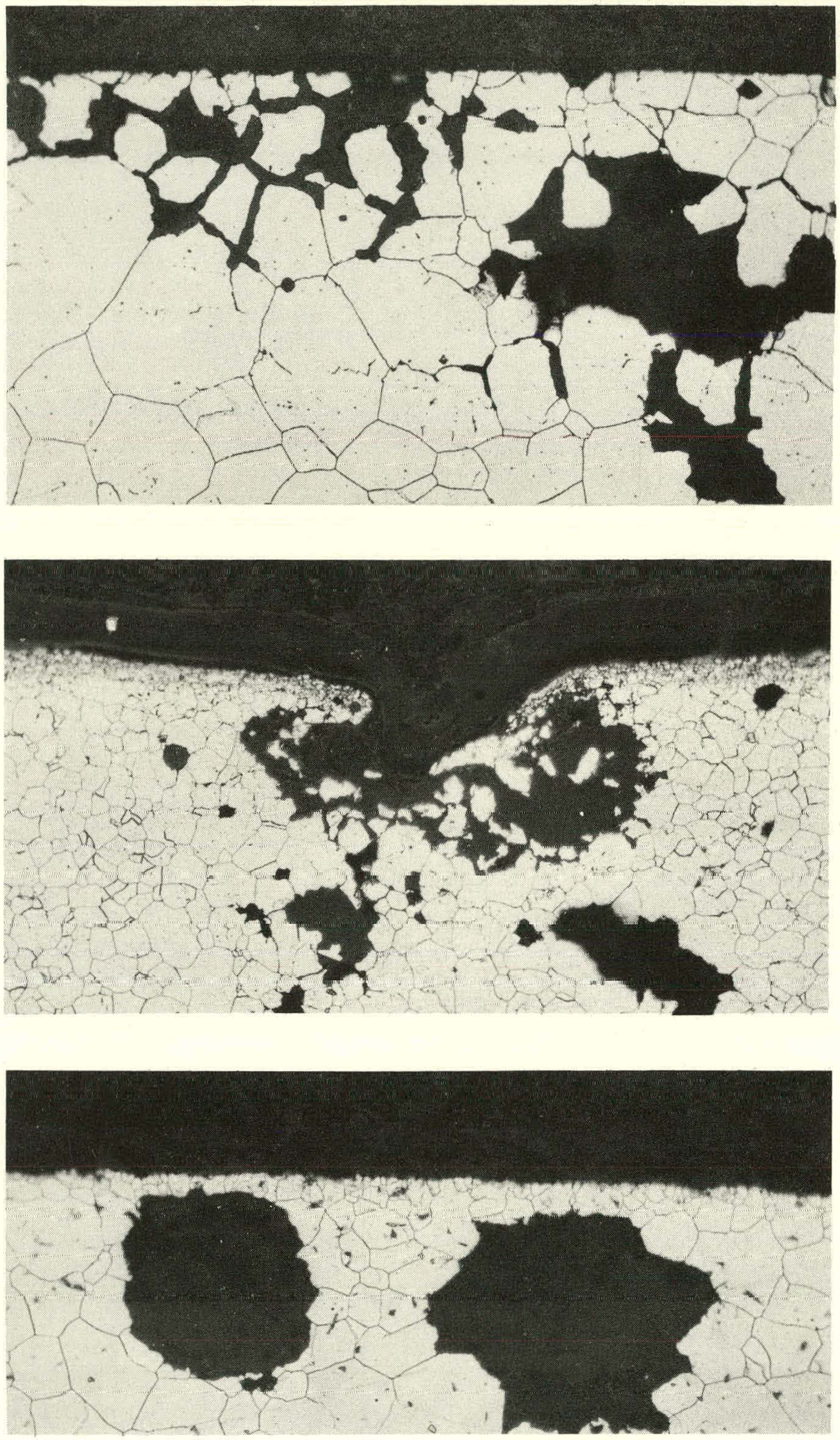
c. INCOLOY



d. HASTELLOY X

1037–4

FIGURE A – 2 AS RECEIVED MATERIAL EXPOSED TO CUPRIC CHLORIDE SOLUTION, 210–220 F, 400 PPM CHLORIDE, 24 HOURS
10% OXALIC – ELECTROLYTIC ETCH (250 X)



a. TYPE 304 SS
HEATED 4 HOURS
AT 1300 F

b. INCOLOY
HEATED 4 HOURS
AT 1300 F

c. INCONEL
HEATED 24 HOURS
AT 1300 F

1037-7

FIGURE A-3 HEAT TREATED MATERIAL EXPOSED TO CUPRIC CHLORIDE SOLUTION, 210-220 F, 400 PPM CHLORIDE, 24 HOURS
10% OXALIC - ELECTROLYTIC ETCH (250 X)

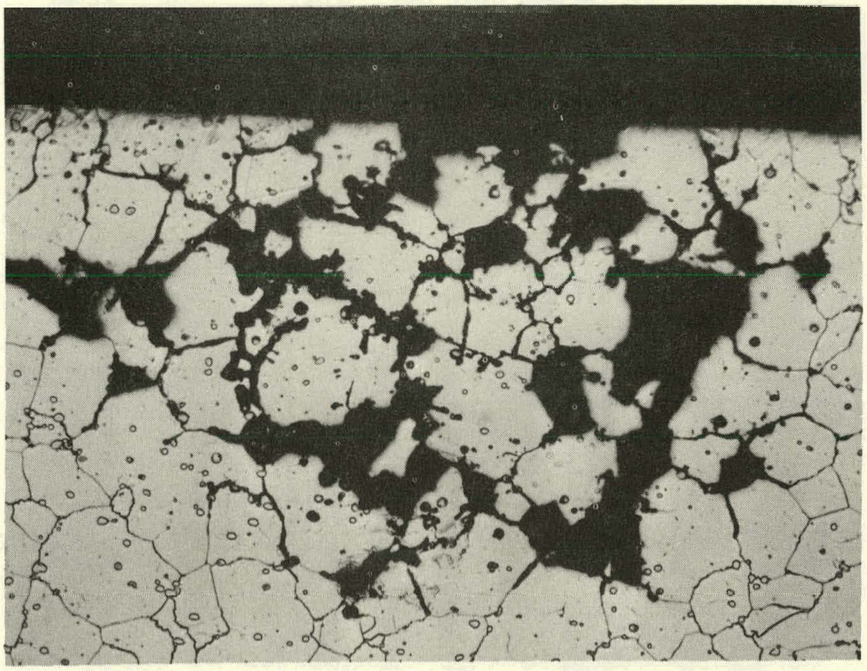
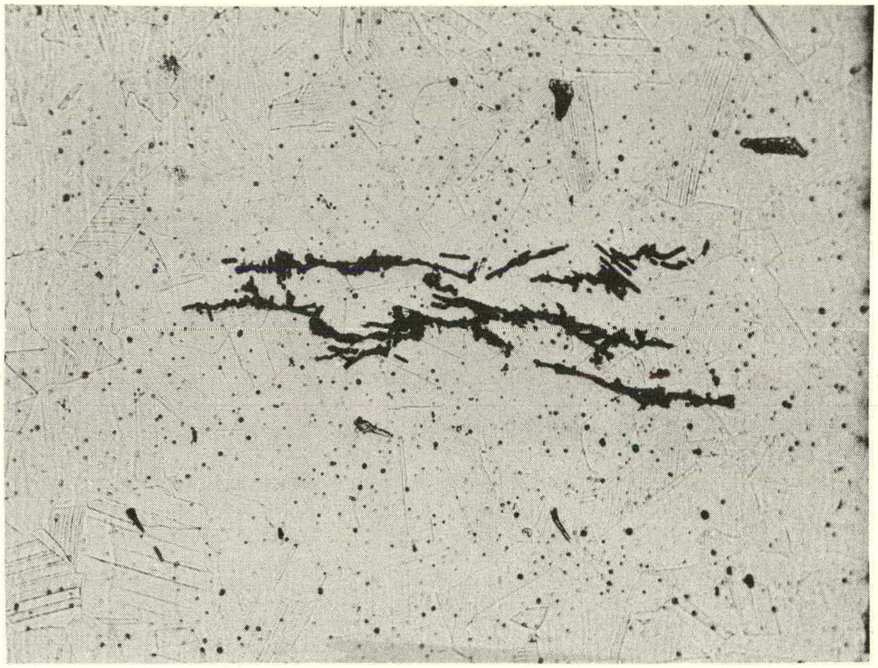


FIGURE A-4 HASTELLOY X, HEATED 4 HOURS AT 1300 F, EXPOSED TO CUPRIC CHLORIDE SOLUTION 210-220 F, 20,000 PPM CHLORIDE, 1 HOUR 10% OXALIC - ELECTROLYTIC ETCH (250 X)

1037-8



a. 1/4 HARD
250 X

b. 3/4 HARD
500 X

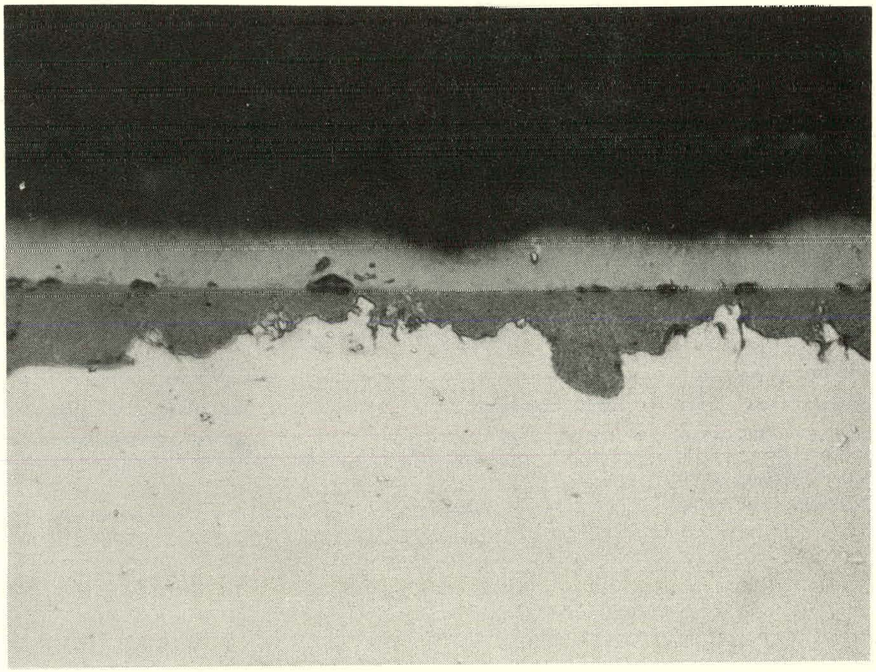
FIGURE A-5 TYPE 304 SS COLD WORKED EXPOSED TO CUPRIC CHLORIDE SOLUTION, 210-220 F, 20,000 PPM CHLORIDE, 1 HOUR OXALIC - ELECTROLYTIC ETCH

1037-9

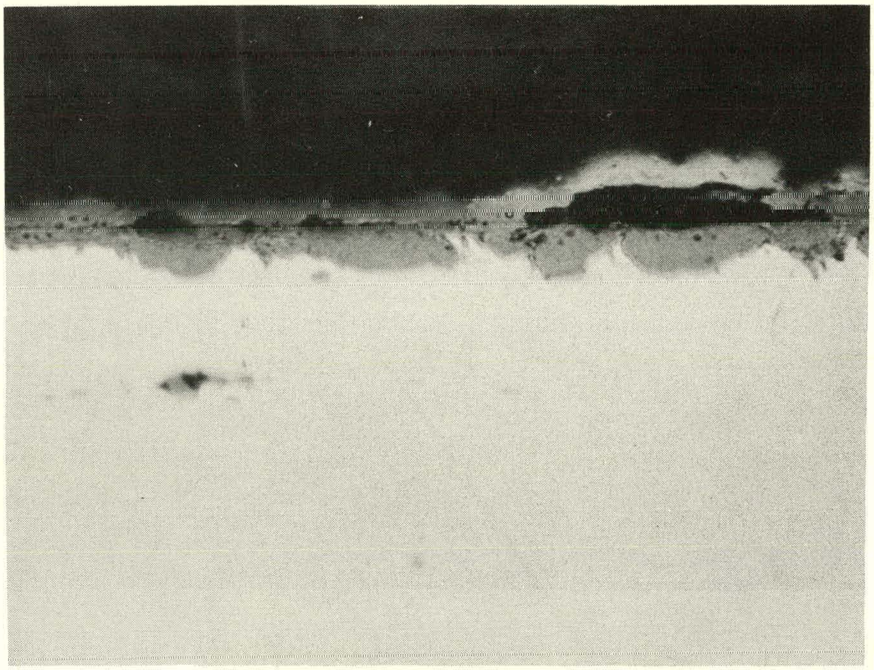
The Type 304 stainless steel appeared to suffer no stress accelerated localized damage. In a 4300-hour exposure, approximately a 1-mil scale penetration was experienced which was comparable to the 4500-hour nonstressed results, see Figures A-6a and A-6b.

No significant difference in corrosion was noted between the stressed and unstressed specimens of Incoloy and Hastelloy-X.

The Inconel specimens show the definite effect of the high stress imparted. Although little corrosion is seen in Figure A-7a in an unstressed specimen exposed for 2000 hours, at least 2 mils penetration was noted on the stressed specimen exposed for a similar time, Figure A-7b. A 3000-hour exposure under the same high stress indicates nearly the same cross-sectional damage on both the corroding and non-corroding sides, as shown in Figure A-7c. No definite conclusion can be made regarding the possible acceleration of corrosion attack on Inconel caused by stress at stress levels below that which would produce cross-sectional damage independent of environment.



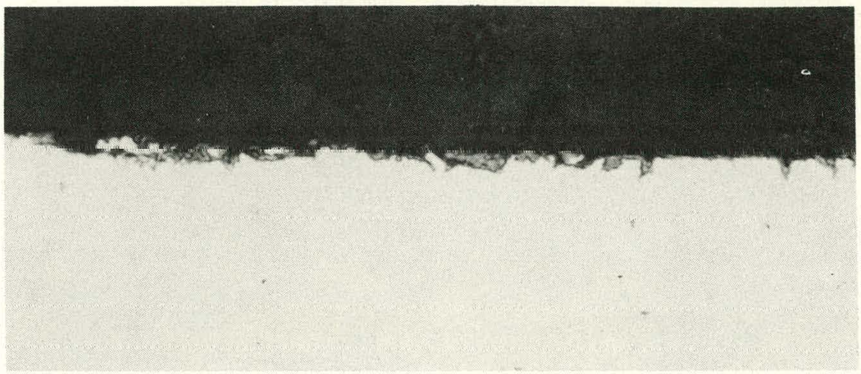
a. 4000 HOURS, STRESSED 23,300 PSI (750 X)



b. 4500 HOURS, UNSTRESSED (500 X)

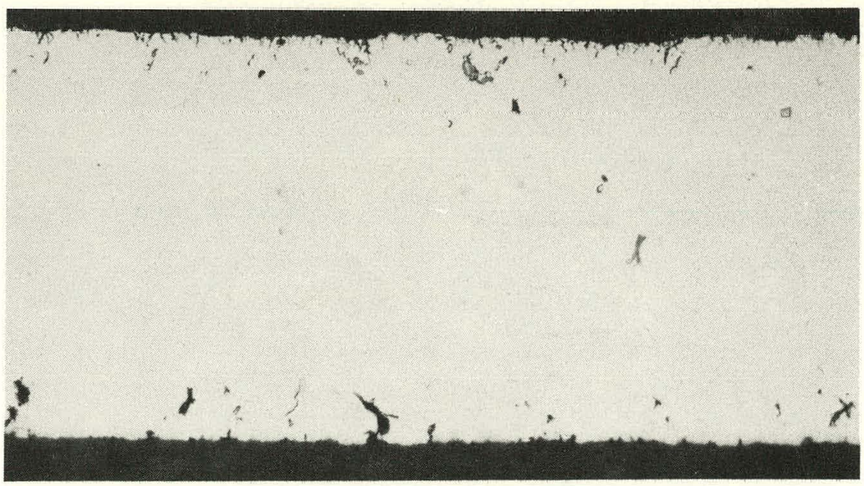
1037–18

FIGURE A–6 TYPE 304 SS EXPOSED TO 1050 F SUPERHEATED STEAM



a. UNSTRESSED,
2,000 HOURS
750 X

b. STRESSED, 23,300 PSI
2000 HOURS 750 X



c. STRESSED, 23,300 PSI
3,000 HOURS 250 X
UPPER SIDE EXPOSED
TO SUPERHEATED
STEAM. LOWER SIDE
EXPOSED TO HELIUM.

FIGURE A-7 INCONEL EXPOSED TO 1050 F SUPERHEATED STEAM

1037-6