NUREG/CR-0858
BNL-NUREG-51027

STRESS CORROSION CRACKING OF INCONEL 600 TUBING IN DEAERATED HIGH TEMPERATURE WATER

T.S. Bulischeck, Y.S. Park, and D. van Rooyen

Date Published - June 1979

CORROSION SCIENCE GROUP
DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Contract No. EY-76-C-02-0016

NUREG/CR-0858
BNL-NUREG-51027
R-5

STRESS CORROSION CRACKING OF INCONEL 600 TUBING IN DEAERATED HIGH TEMPERATURE WATER

T.S. BULISCHECK, Y.S. PARK, AND D. VAN ROOYEN

Manuscript Completed - April 1979
Date Published - June 1979

CORROSION SCIENCE GROUP
DEPARTMENT OF NUCLEAR ENERGY
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UPTON, NEW YORK 11973

PREPARED FOR THE UNITED STATES NUCLEAR REGULATORY COMMISSION
DIVISION OF REACTOR SAFETY RESEARCH, OFFICE OF NUCLEAR REGULATORY RESEARCH
UNDER CONTRACT NO. EY-76-C-02-0016
NRC FIN NO. A-3208

Available from
National Technical Information Service
Springfield, Virginia 22161

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

ABSTRACT

Inconel 600 is known to undergo stress corrosion cracking (SCC) at grain boundaries when subjected to a high stress and exposed in the laboratory to water without oxygen at elevated temperature. In operating plants, very few service failures have occurred to date from the primary side under normal conditions, but extensive intergranular cracking has also occurred in plants that experienced "denting." All of these cracks were from the primary side. The process of denting produced high strains and stresses in the tubing, as well as slow strain rates during deformation. So far, the literature is silent on effects of slow strain rates or cyclic stresses on SCC of Inconel 600 in deaerated, high temperature aqueous media such as pure or primary water. Because of the importance of avoiding primary-to-secondary leaks through the Inconel 600 pressure boundary, a research program was started at Brookhaven National Lab. in an attempt to improve the qualitative and quantitative understanding of factors influencing SCC in deaerated high temperature aqueous media. These data are also intended for predicting service performance under given sets of conditions. This report includes preliminary results which indicate that intergranular SCC is produced quite readily in some heats of tubing when exposed at (a) constant deflection, (b) when slightly cold worked and subjected to straining at low rates (c) when subjected to slow cyclic stress or (d) when the electrochemical potential of stressed pieces is controlled. It is significant that cracking has now been produced in Inconel 600 under conditions that had not been examined and reported before. First trends of temperature dependence of SCC are discussed. Stress effects will be analyzed when more data are obtained, at which time crack velocity and strain rates will also be discussed more fully. Some tentative correlations are made with microstructural variables, although a simple relationship with such structure or prior processing has not been defined. Heating at 700°C for about 15 hours improved the SCC resistance dramatically. Future tests will include primary and secondary water ingredients and some impurities.

STRESS CORROSION CRACKING OF INCONEL 600 TUBING IN DEAERATED HIGH TEMPERATURE WATER

T.S. Bulischeck, Y.S. Park and D. van Rooyen

A. INTRODUCTION:

As discussed in a 1975 review paper,(1) which included references to the work of Coriou, Grall and others, Inconel 600 can undergo stress corrosion cracking (SCC) at grain boundaries when subjected to a high stress and exposed to water without oxygen at elevated temperature. Since that time, work at Babcock and Wilcox also showed this effect, and reported observations on some aspects of microstructure and heat treatment(2). In operating plants, very few service failures have occurred so far from the primary side under normal conditions. However, extensive intergranular cracking has occurred in plants that experienced "denting." Denting, i.e. deformation of the steam generator tubes and support plates, occurred as a result of impurity-induced corrosion of carbon steel and the concomitant accumulation of large amounts of magnetite in tube-to-support-plate crevices(3). The Inconel 600 cracking was found in distorted small radius U-bends at the top of the tube bundle where ovalization had occurred, as well as at deformation sites at support plate intersections. All cracks were from the primary side. The process of denting produced high strains and stresses in the tubing, as well as slow strain rates during deformation. It is yet not certain which specific factor was responsible for the in-service cracking, i.e. whether the act of straining caused SCC or whether failures would continue even if it is possible to arrest denting, or whether perhaps cyclic (operational) stresses played a part. So far, the literature is silent on effects of slow strain rates or cyclic stresses on SCC of Inconel 600 in deaerated, high temperature aqueous media such as pure or primary water. There is a paucity of quantitative information concerning the subject of SCC of Inconel 600 in deaerated, high temperature aqueous media.

Because of the obvious importance of avoiding primary-to-secondary leaks through the Inconel 600 pressure boundary, a research program was started at Brookhaven National Laboratory in an attempt to improve the qualitative and quantitative understanding of factors influencing SCC in deaerated high temperature aqueous media. The acquisition of such data would be for the purpose of predicting service performance under given sets of conditions.

This report describes the scope of the work, and includes preliminary results which indicate that intergranular SCC is produced quite readily in some heats of tubing when exposed at (a) constant deflection, (b) when straining at low rates (c) when subjected to cyclic stress or (d) when the electrochemical potential of stressed pieces is controlled. Additional separate reports and papers are planned to provide more details on the effects of the individual test conditions when more data are available. The unique aspect of the present work is the fact that cracking has been produced in Inconel under conditions that had not been examined and reported before.

During the first year of the present work (FY 1978), the laboratory apparatus and 13 heats of Inconel were obtained and testing was started in pure water without any additions. The tests were as mentioned in the previous paragraph. Plans for the latter part of FY 1979 include tests at known stress levels, SCC tests under conditions that simulate "denting," and the introduction of primary water ingredients to evaluate their adverse, beneficial or neutral effects. After that phase, secondary water and impurities will be added. Facilities for slow strain rate testing will be expanded. It is expected that first quantitative data would be presented as a usable formula to the NRC by late 1979, involving pure water and "worst case" SCC resistance of production tubing. These data will relate static stresses to failure time and temperature. By early 1980, we expect to have some similar data for primary water, as well as sets of slow strain rate data. The two sets (i.e. static and dynamic strain) would represent the two practical conditions where (a) denting occurred but is arrested and (b) denting is active. The data will be incomplete, since tests at lower stresses, temperatures and with the more resistant alloys take longer than the others to produce the necessary cracking.

B. EXPERIMENTAL PROCEDURE

1. General

Testing was carried out in one and two gallon pressure vessels made from 316 stainless steel. These vessels, containing support stands for the U-bends, were pre-cleaned by exposing them to 365°C deionized water for 24 hour periods until the conductance of the water at the end of the run was less than 5 μs.

Distilled deionized water without additions was used in all tests except the controlled potential experiments. The water had a conductance of ≤ 0.5 μs at start-up. Oxygen removal from the water was achieved by an initial 5 minute evacuation of the filled vessel followed by five pressure-vent cycles with 3.4 MPa (500 psig) of high purity N_2. The vessel was again evacuated and 15% of its water volume steamed off when the temperature reached 110°C. The oxygen concentration of the water was determined using a commercially available colorimetric method. In agreement with previous experience of two of the authors in different laboratories, tested oxygen levels were in the range of 0 to 5 ppb after this procedure.

The Inconel alloy 600 specimens used in this program were cut from plate, ingot and production steam generator tubing obtained from several sources. Many of these had a microstructure thought to be susceptible to stress corrosion cracking based on prior experience and published literature(2). Essentially, the grain boundaries did not show much evidence of chromium carbide networks when etched electrolytically in phosphoric acid. Table 1 details the mechanical properties and chemical composition of these materials. A possible effect of N_2 content of alloys on SCC susceptibility, was considered, and analyses were obtained for some of the materials used, with the results shown in Table 2. Various heat treatments, cold working, and pickling of the ingot and plate materials that were also used as part of the program are shown in Tables 3 & 4. Details of the HNO_3-HF pickling solution described by Coriou et al.(4) which was used where indicated, prior to bending, are shown in Table 5.

Table 1

Mechanical Properties and Chemical Composition of Materials Tested

MATERIAL IDENTIFICATION	ULTIMATE STRENGTH psi	YIELD POINT psi	ELONGATION %	ROCKWELL HARDNESS	CHEMICAL ANALYSIS										
					C	Mn	Al	S	Si	Ni	Cr	Ti	Cu	Fe	Co
Ingot Heat #1					.08	.44		.003	.17	74.1	15.6		.36	9.27	
Tubing Heat #2	104,000	56,000	39.	R_B86	.05	.28	.19	.003	.24	73.94	15.69	.20	.33	9.47	.05
Tubing Heat #3	100,000	48,000	43	$R_B83.5$	.03	.30	.13	.007	.15	74.82	15.48	.16	.29	8.55	.06
Tubing Heat #4	91,285	46,680	48	R_B79-82	.01	.26		.004	.10	76.74	15.10		.21	7.56	
Tubing Heat #5	94,085	54,930	44	$R_B83.5$	.01	.28		.006	.08	75.59	15.76		.31	7.94	
Tubing Heat #6 (unannealed)					.029	.28		.003	.20	75.40	15.78		.01	7.99	.045
Plate Heat #8	96,000	37,750	45	R_B78-81	.05	.25		.004	.07	75.73	14.57		.29	9.04	
Tubing Heat #9	100,000	48,000	44.5	R_B81	.03	.28	.23	.006	.11	75.87	15.14	.25	.23	8.33	.05
Tubing Heat #10	99,000	48,000	45.5	79	.02	.30	.32	.0006	.14	75.95	15.17	.28	.22	8.19	.84
Tubing Heat #11	97,000	51,000	42.5	R_B83	.03	.30	.17	.004	.18	74.64	15.18	.17	.34	9.33	.04
Tubing Heat #12* (cold worked)	122,990	119,060	10	R_C24											
Tubing Heat #13	96,300	44,200	47	R_B84	.03	.19		.001	.29	75.48	15.93		.02	7.52	.051

*Heat #5 with 40% cold work

Table 2

Nitrogen Content and Average Failure Times of Inconel 600

Heat #	Wt % N_2		Av. Failure Time of U-bend in 365°C D.I. H_2O (WEEKS)
	Fixed	Free	
2	.0068	.0042	2.2
4	.003[illegible]	.0052	11.
5	.0034	.0044	12.6
10	.0063	.0047	2.
11	.0089	.0021	4.
3	.0073	.0067	No Cracks After 20 Wks.
13	.0058	.0082	" " " " "

Table 3

Specimens Fabricated from Ingot and Exposed @ 365°C

Material	First treatment	Second treatment	Third treatment	Pickled	No. of spec.	Exposure (weeks)
INCONEL 600 4" x 4" INGOT Heat #1 Held @ 1900°F for 3 hr. then reduced in 5 passes to 3/4" thick $T_{initial}$=1725°F T_{final} =1700°F	1600°F/3hr in air then rolled @ 1800°F to .175" thick	3.5 hr in air @ 1700°F		yes	5	14
	1600°F/20 hr in air then rolled @ 1800°F to .175" thick	3.5 hr in air @ 1700°F		yes	5	14
		15 min in H_2 @ 1775°F		yes	4	14
	1600°F/20 hr in air then rolled @ 1800°F to .30" thick	3.5 hr in air @ 1700°F then cold rolled 40%	15 min in H_2 @ 1710°F	yes no	2 2	6 6
			15 min in H_2 @ 1775°F	yes no	2 2	6 5
	1700°F/1 hr in air then rolled @ 1800°F to .175" thick	15 min in H_2 @ 1775°F		yes	4	14
	rolled @ 1800°F to .175" thick	15 min in H_2 @ 1775°F		yes	4	14
	1800°F/30 min in air then cold rolled 40%	10 min in H_2 @ 1775°F		yes no	2 2	6 6

Table 4

Specimens Fabricated from Plate and Exposed @ 365°C

Material	First treatment	Second treatment	Pickled	No. of specimens	Exposure (weeks)
INCONEL 600 1/2" x 4" plate Heat #8	1775°F/15 min in air then rolled @ 1800°F to .30" thick. Cold rolled 40%	10 min in H_2 @ 1700°F	yes no	2 2	6 6
		10 min in H_2 @ 1735°F	yes no	2 2	6 6
		10 min in H_2 @ 1775°F	yes no	2 2	6 6
		10 min in H_2 @ 1800°F	yes no	2 2	6 6
	1775°F/15 min in air then rolled @ 1800°F to .175" thick.	1 hr in air @ 1680°F	yes no	2 2	6 6
		1 hr in air @ 1725°F	yes no	2 2	6 6
		1 hr in air @ 1775°F	yes no	2 2	6 6

Table 5

HNO_3-HF Pickling Solution

Constituents	Requirements
HNO_3 (sp. gr. = 1.33)	275 parts by volume
HF (40%)	50 parts by volume
H_2O	65 parts by volume
Temperature	122°F to 140°F
Time	15 min.

2. Constant Deflection Test

Specimens were machined from the ingot or plate material to 8.9cm x 1.3cm x .38cm (3.5" x .5" x .150") strips, ground to a 35 micro inch finish and then some of them were subjected to additional heat treatments in H_2 or pickled before bending. These specimens, Figure 1, were bent into a U-shape using a fixture with a 1.9cm (.75") dia. mandrel. The tube type U-bends were prepared by splitting pieces of tubing on their longitudinal axis then bending with a modified tubing bender. This formed a U-bend with the original inside surface of the tubing in tension and a 1.3cm (0.5") inside radius of bend. Standard type C-ring specimens were also machined from the tubing. The C-rings were expanded to provide specimens for testing in two series, i.e. at stresses of 95% and 110% Y.S. on the inside surface of the tubing.

All specimens were first cleaned in a commercial alkaline phosphate solution, ($\text{Alconox}^{\text{TM}}$) then successively rinsed in dionized water in an ultrasonic bath until no change in the conductance of the rinse water was noted. The specimens were then dipped in methanol and air dried.

Tests with replicate U-bend and C-ring type specimens were started and are continuing in high purity, deaerated water at 290°C, 325°C, 345°C and 365°C. Specimens in each test are being examined every two weeks except for the test at 290°C which is being examined at six week intervals.

3. Constant Extension Rate Test (CERT)

The CERT apparatus shown in Figure 2 is a modified version of one originally designed at the General Electric Corporation. An A.C. motor is used to drive a series of three continuously variable speed reducers, each with a 0 to 400 rpm output at 1875 rpm input. The output of the last reducer is coupled to a 20 to 1 gear reductor which drives a worm screw jack. The worm screw translates the motion to a linear pull rate of .0254cm per revolution. The extension rate range of this apparatus is 10^{-4} to 10^{-9} cm sec^{-1}.

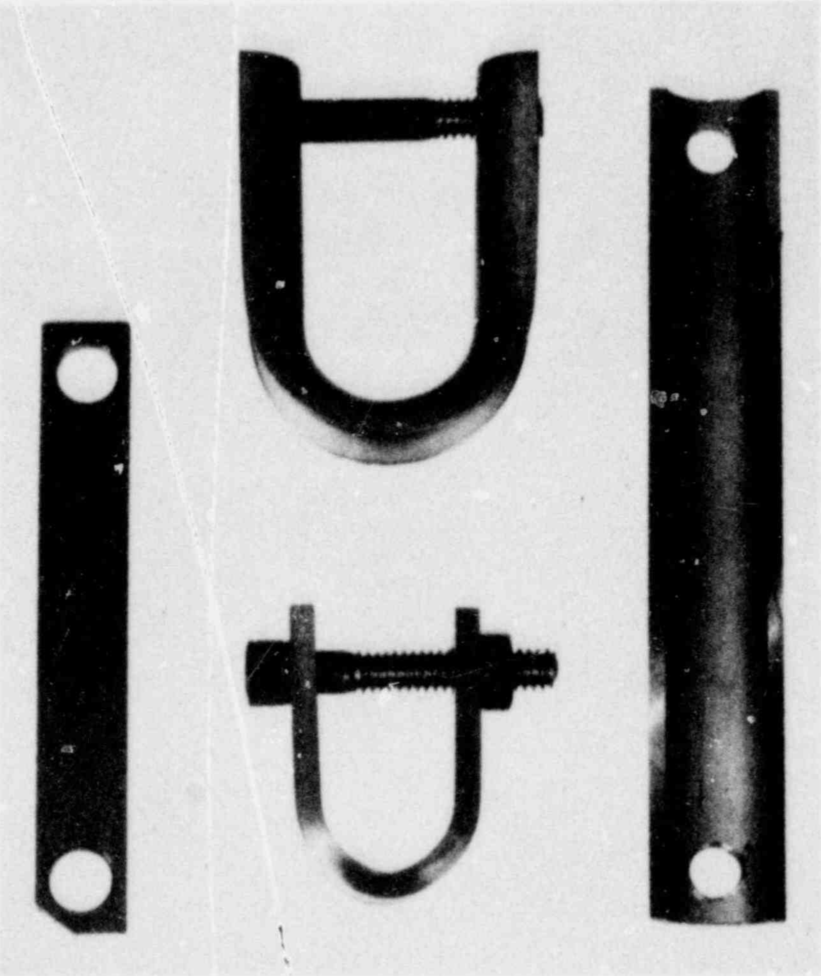


Figure 1. Tube and plate U-bend specimens.

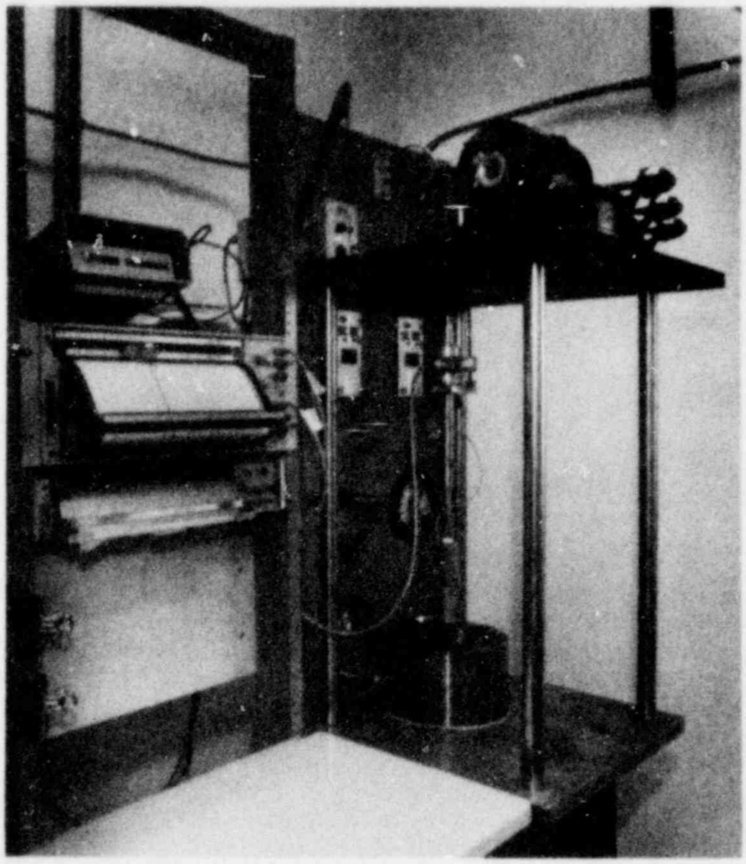


Figure 2. Constant extension rate test.

POOR ORIGINAL

The load cell that is connected between the worm screw and the pull rod has a 1 volt output at its maximum capacity of 907kg (2000 lbs.). The Inconel 600 pull rod, which is connected to the specimen by a clevis, enters the autoclave through a teflon sealed Conax fitting. This fitting is mounted on a high pressure cone type nipple which is threaded into the autoclave head. This nipple was originally cooled by an external water jacket, but it was discontinued because local temperature fluctuations due to a reflux of water around the pull rod resulted in load oscillations. Air cooling does not have this effect, and has been adopted as standard procedure. A linear variable differential transformer (L.V.D.T.) with a range of 5cm and an output of 4v/cm is used to monitor the specimen extension.

Tensile specimens were fabricated from tubing that was split in half and then rolled very carefully to obtain flat pieces with a minimum reduction. Measurements showed that the rolling resulted in a one to two mil reduction from the original wall thickness, i.e. test pieces were about 3% cold worked. The specimens were machined in accordance with ASTM A370 and had a .635cm x 2.54cm (.25" x 1") gauge section. The faces corresponding to the inside and outside wall of the tubing were not machined or polished. In order to examine the effect of the small amount of cold work, specimen designs have been selected for future tests where the flattening and rolling will be eliminated.

4. Constant Stress Test

The apparatus shown in Figure 3 is designed to provide a constant stress on a series of C-ring specimens and indicate a definite time to failure. The stress is applied to the series of 5 C-rings by an Inconel 600 spring which fits between the two plates on the underside of the autoclave head. Specimen failure will relieve the tension on the spring and cause the plate closest to the head to make contact with an electrode which cannot be seen in this photograph. Several difficulties were at first experienced with this system, but they have been overcome and the test is now operating at 365°C with the specimens stressed to 130% Y.S. Additional experiments are being started at lower stress levels. This procedure eliminates the need for opening the autoclave for interim inspections before a failure occurs.

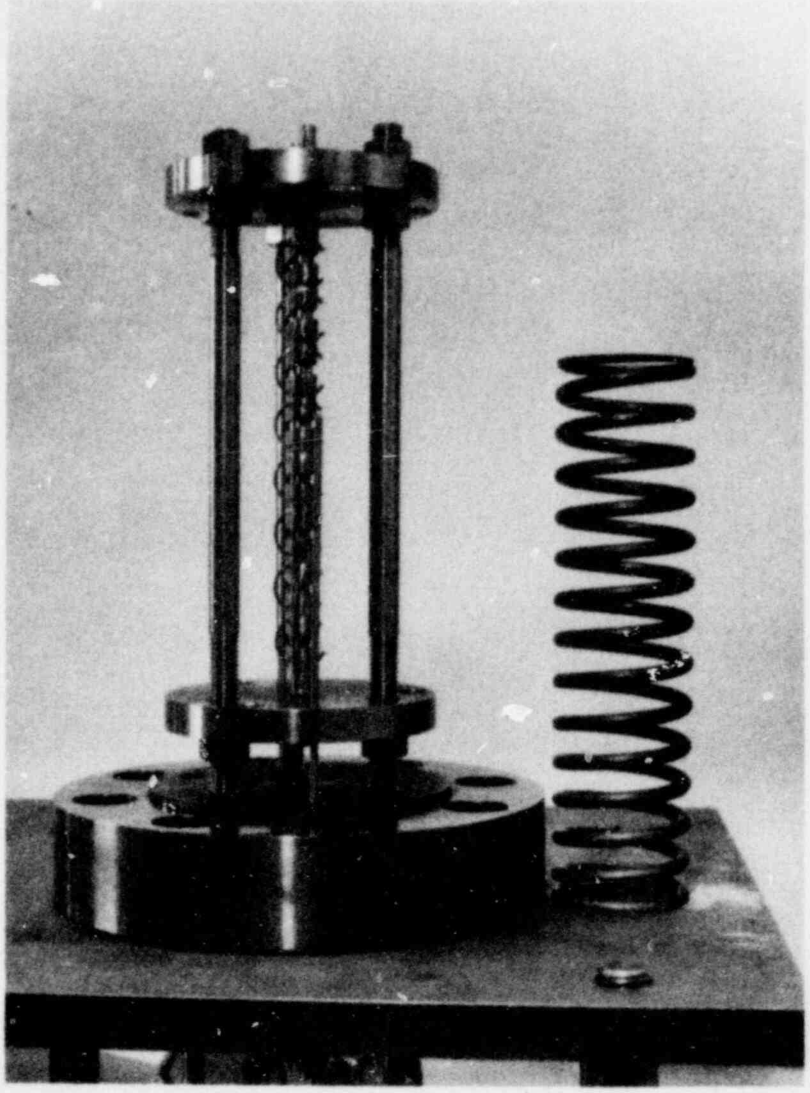


Figure 3. Constant stress test fixture.

5. Electrochemical Potential Control

Effects of controlled potential are being investigated at 365°C with a series of tube U-bend specimens from a heat of Inconel 600 that has been found to crack in about 10 weeks when tested as U-bends in pure water at 365°C. Figure 4 shows the head of the Inconel 600 autoclave and Inconel 600 fixture supporting the specimens. The specimens are separated and supported by ZrO_2 insulating spacers and electrically connected with resistors made from 20 mil diameter Inconel wire. The electrical connections to the ends of the series and two Pt reference electrodes were passed thru the autoclave head with 4-wire, water-cooled, Conax connector providing the high pressure seal. This method is an adaptation to SCC testing of the pitting corrosion procedure invented by Seys(5), who used the iR drop principle to create a potential gradient along a test piece in an aggressive electrolyte. In our work, the 20 mil Inconel wires are used to provide the potential drop from one specimen to the other. Conditions were chosen to provide a maximum shift of only about 100mV between the U-bends at the extremes.

The test solution was typical PWR primary side H_2O containing 10^{-4} M LiOH and 650 ppm B as boric acid. After deoxygenation, argon with 5% H_2 was admitted to the head space of the vessel under 2.1MPa (300 psi) pressure at 110°C. The temperature was then raised to 365°C and maintained for 24 hours before applying current. The potentials were held at their starting levels for 4 days, at 365°C, at which point the controls were switched off, the vessel cooled and the 6 specimens removed for inspection. When cracking occurred, the failed specimen was removed and replaced with a fresh one.

6. Cyclic Load Test

Cyclic load tests have been started and a program is planned to examine the effects of stress level, frequency, wave form, and slow strain with a superimposed cyclic load in high temperature aqueous media. First tests are in pure deaerated water at 365°C, but future test media will include simulated primary and secondary water, as well as impurities.

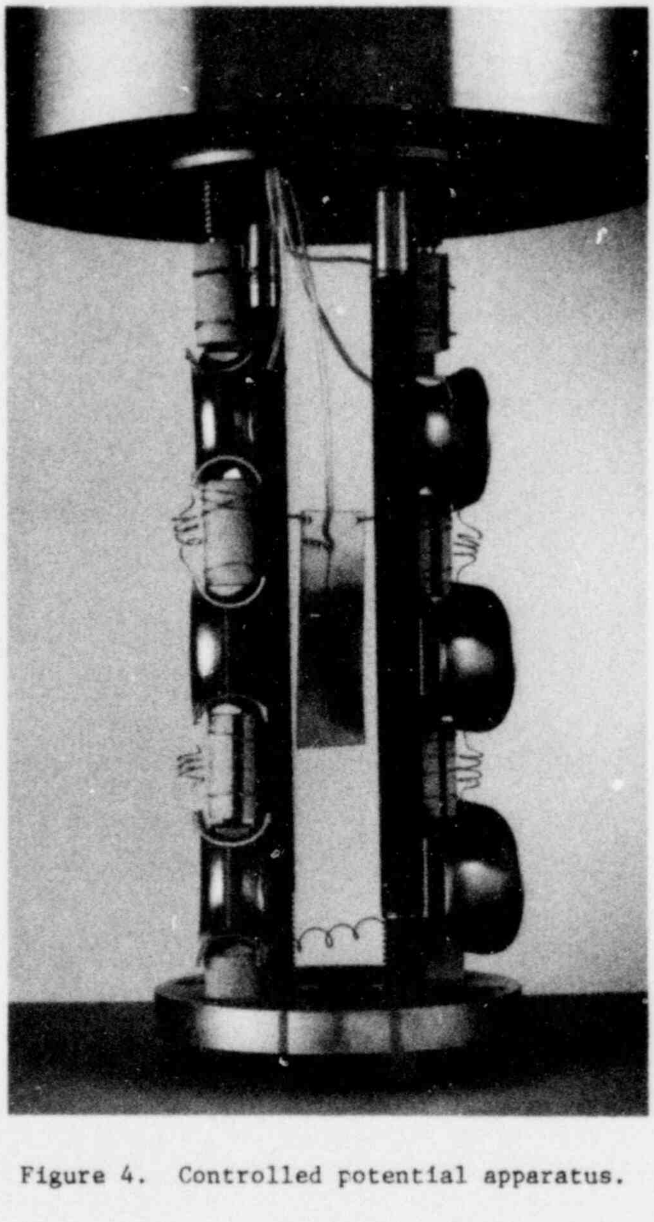


Figure 4. Controlled potential apparatus.

An MTS closed-loop, electronically controlled, hydraulic system, with an overhead actuator is used to apply a programmed load cycle to a tensile test piece in addition to a constant load; in simpler terms, the cycles are tension-tension type, with a pre-selected spread. A one gallon stainless steel pressure vessel is bolted to the base of the MTS with asbestos sheets between the two to provide thermal insulation. The specimen mounting, pull rod and shaft seal are identical to that mentioned earlier for the slow strain tests.

During the test, the load cycle and the strain occurring in the specimen are continuously recorded.

C. RESULTS

The results obtained with each of the test methods used to accelerate the intergranular SCC of Inconel 600 in high temperature deaerated water are discussed separately below, after a few details of the materials are reviewed.

1. Materials and Properties

One of our first objectives is to establish quantitative relationships between temperature, stress, and failure times of several heats of Inconel 600, including production tubing. This susceptibility of Inconel 600 intergranular SCC is generally associated with a microstructure that is free from intergranular chromium carbide precipitates.(1) A number of samples of ingot, plate and production tubing were obtained for this study. Their physical properties and chemical analyses are summarized in Table 1. All of the compositions fall within the specifications for Alloy 600. Carbon contents ranged from 0.01% to 0.08%. N_2 analyses are given separately in Table 2. The tubing samples were from regular mill production; heats #6 and #12 were in the cold worked condition, and the remainder were typical of nuclear grade production methods. It should be noted that the very recent 20 hour 700°C heat treatment that is now preferred by several manufacturers was not included in the tubing as purchased, although we did heat treat a few specimens in this manner in the laboratory. The commercial tubing, therefore, is typical of Inconel 600 production methods for material already in service in operating plants, but the "700°C specimens" are not necessarily representative of current production. It is also possible that the alloys with very low carbon content would not have been considered for steam generator service in more recent designs. The various heat treatments that were used in the laboratory for the 2 lots of cold worked tubing, the cold worked plate and ingot are given in Tables 3, 4 and 7. Pickling was also included as a variable. Details of pickling are given in Table 5.

2. Constant Deflection Tests

Also see Table 6. With U-bends, the most accelerated SCC of Inconel 600 occurred at 365°C. The more susceptible heats of production tubing were found to crack in the apex region of U-bends in the first exposure period of 2 weeks.

Table 6

Specimens Failed in D.I. H_2O

Heat No.	C, Co & Free N Concentrations w/o	Specimen Type	Heat Treatment	Test Temp. (°C)	Time to Failure (WEEKS)
2	.05 C	Tube U-bend	As Received	365	2 to 4
	.05 Co	" " "	"	365	2 to 4
	.0042 N_2	" " "	" "	365	0 to 2
		" " "	" " + Pickled	365	2 to 4
		" " "	" " + Pickled	365	0 to 2
		" " "	15 min in H_2 @ 1775°F	365	6 to 8
		" " "	" " " " " "+Pickle	365	0 to 2
		" " "	As Received	345	10 to 12
		" " "	" " + Pickled	345	12 to 14
4	.01C	Tube U-bend	As Received	365	10 to 12
	.0052 N_2	" " "	" "	365	10 to 12
		" " "	" " + Pickled	345	12 to 14
		" " "	" " + Pickled	345	6 to 8
5	.01C	Tube U-bend	As Received	365	8 to 10
	.0044 N_2	" " "	" "	365	10 to 12
		" " "	" "	365	16 to 18
		" " "	" "	365	16 to 18
		" " "	" " + Pickled	365	8 to 10
		" " "	As Received	345	12 to 14
		" " "	" " + Pickled	345	10 to 12
		" " "	" " + Pickled	345	14 to 16
6	.029 C	Tube U-bend	As Received (cold worked)	365	0 to 2
	.045 Co	" " "	" " "	365	0 to 2
		C-Rings*	" " "	365	0 to 2
		C-Rings**	" " "	365	0 to 2
		C-Rings*	" " "	345	0 to 2
		C-Rings**	" " "	345	0 to 2
		C-Rings*	" " "	290	0 to 9
		C-Rings**	" " "	290	0 to 9
10	.02 C	Tube U-bend	As Received + Pickled	365	2 to 4
	.84 Co	" " "	" " " "	365	0 to 2
	.0047 N_2	" " "	" " " "	345	6 to 8
		" " "	" " " "	345	2 to 4
11	.03 C	Tube U-bend	As Received	365	12 to 14
	.04 Co	" " "	" " + Pickled	365	2 to 4
	.0021 N_2	" " "	" " + Pickled	365	4 to 6
		" " "	" " " "	345	12 to 14
12	.01 C	Tube U-bend	As Received (cold worked)	365	0 to 2
	.0044 N_2	" " "	" " " "	365	0 to 2
		" " "	" " " "	365	0 to 2
		C-Rings	" " " "	365	0 to 2
		C-Rings	" " " "	365	0 to 2
		C-Ring	" " " "	345	4 to 6
		C-Rings	" " " "	345	4 to 6

*Stressed to 95% Y.S.
**Stressed to 110% Y.S.

Table 7

Treatment of Cold Worked Tubing Before Forming into U-bend Specimens

Specimen from Heat #6 were given the following treatments then exposed to $365^{\circ}C$ deaerated H_2O for 24 weeks without any evidence of I.G.S.C.C.

15 min in H_2 @ $1710^{\circ}F$
15 min in H_2 @ $1710^{\circ}F$ + pickle
15 min in H_2 @ $1775^{\circ}F$
15 min in H_2 @ $175^{\circ}F$ + pickle

Specimens from Heat #12 were given the following treatment then exposed to $365^{\circ}C$ deaerated H_2O for 22 weeks without any evidence of I.G.S.C.C.

10 min in H_2 @ $1600^{\circ}F$
" " " " " " " + pickle
10 min in H_2 @ $1625^{\circ}F$
" " " " " " " + pickle
10 min in H_2 @ $1650^{\circ}F$
" " " " " " " + pickle
15 min in H_2 @ $1710^{\circ}F$
" " " " " " " + pickle
15 min in H_2 @ $1740^{\circ}F$
" " " " " " " + pickle
15 min in H_2 @ $1775^{\circ}F$
" " " " " " " + pickle
15 min in H_2 @ $1800^{\circ}F$
" " " " " " " + pickle

Companion specimens also cracked in the second period i.e. in 2-4 weeks. In the same test, there are other heats that have shown longer times to failure, including some that have survived without any observable cracking in 6 months. Replicate specimens agree reasonably well, but there are some exceptions, typical of the "usual scatter" that is often encountered in corrosion experiments of this nature.

For tests that have been done to date, data are only available at 365°C and 345°C. In the "as-received" condition, mill annealed tubing heats #2, #4, #5, and #11 have shown cracking, and after laboratory pickling, heat #10 is added to this group. Because of the scatter mentioned above, and the fact that the data for 325°C and 290°C are still to become available, it is not possible to establish any reliable quantitative trends at this time from the cracking times at the two higher temperatures. Any quantitative relationships in the discussion that follows must remain tentative until the temperature range is extended to the lower values.

Table 6 lists the failure times and conditions of the cracked U-bends. In the "as-received" condition, heat #2 was the most susceptible with failure times (T_F) in the range 0-4 weeks at 365°C. The other 3 heats, as received, took 3 weeks or more before SCC was first seen.

The pickled specimens have shown a somewhat erratic correlation with the as-received replicates, depending on the heat involved. (It should be noted that pickling was done before bending and bolting the specimens). Thus, heat #2 appeared indifferent to pickling; heats #10 and #11 crack much more readily at both 365°C and 345°C after pickling; heats #4 and #5 crack mostly when unpickled at 365°C and mostly when pickled at 345°C. This strange variation with heat of the alloys has to be verified and explored further. One difference that may or may not be related is carbon level (#2=.05%, #4 and #5=.01%, #10=.02% and #11=.03%). Heat #10 also has a noticeably higher Co content than the rest, but again its significance is not established.

The general temperature trends are shown in Figs. 5,6 and 7. A T_F increase by a factor of up to 5 accompanies the 20°C drop from 365°C to 345°C. Tentatively, in the middle of the range covered by the sets of curves, the

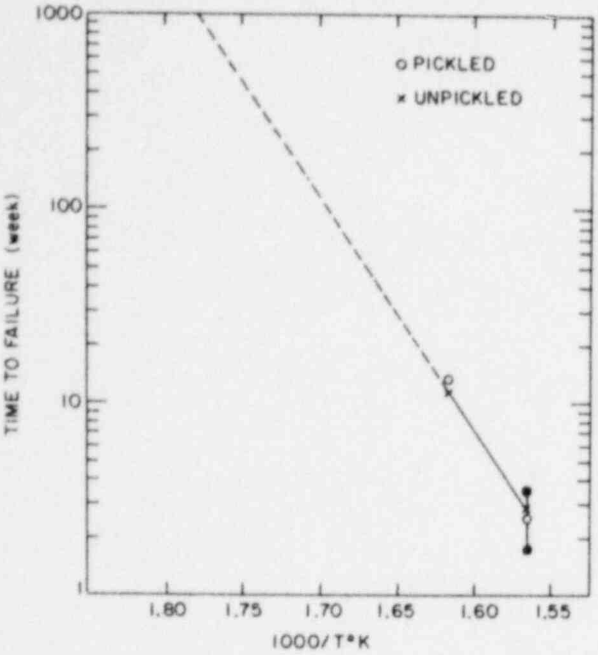


Figure 5. Failure time vs. temperature for SCC of heat #2 U-bend specimens in pure deaerated water.

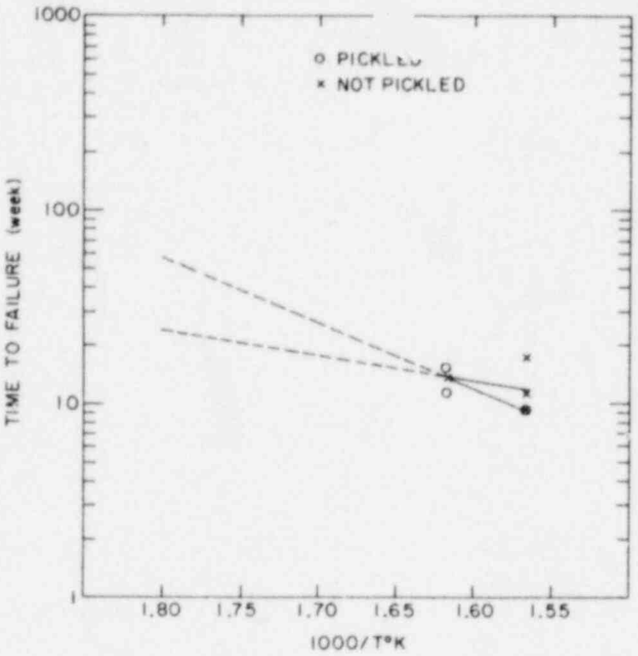


Figure 6. Failure time vs. temperature for SCC of low carbon (.01c) heat #5 U-bend specimens in pure deaerated water.

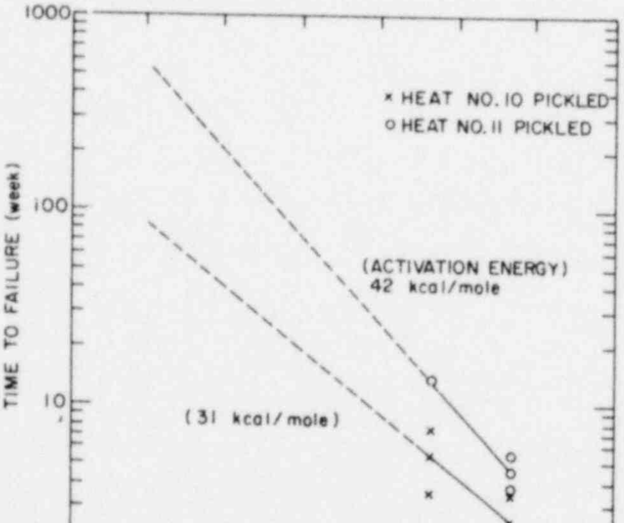


Figure 7. Failure time vs. temperature for SCC of U-bend specimens in pure deaerated water.

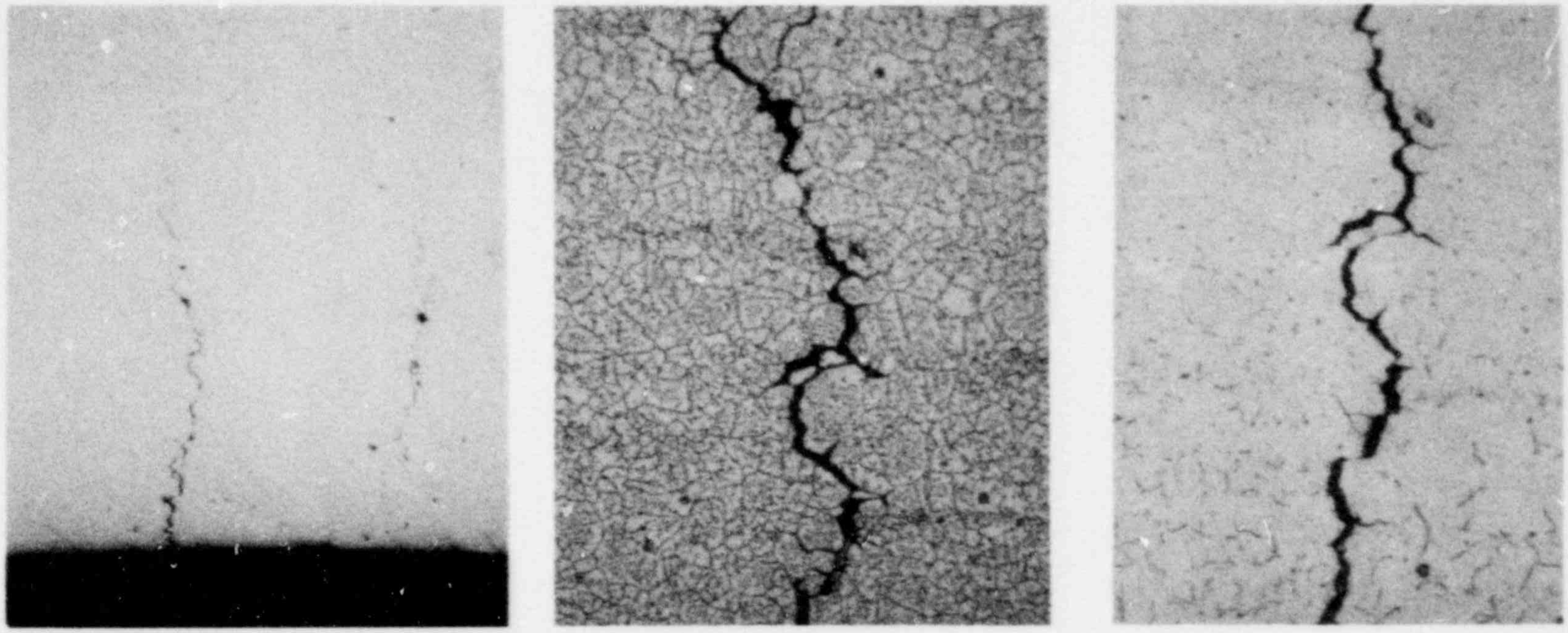
activation energy is 30 to 40 Kcal/mole; it will be better calculated when more points are obtained, so that we can ascertain the existence of a straight line semi-log plot and, if so, improve the value to be used for its slope. With the scatter and narrow temperature difference so far, it is not too surprising that the results cannot be more quantitative. Another aspect that will be clarified by more data points is the present trend for lower carbon samples to show a smaller temperature dependence, i.e. a lower activation energy.

Cold worked heats #6 and #12 were quite susceptible to SCC, even at test temperatures lower than 365°C, and at lower amounts of strain i.e. at 95% and 110% of the yield stress. In fact, one unsplit tube section, 40% cold worked, cracked in half without any applied stress other than the residual stress. However, since tubing is not placed in service in this state, it is not certain how relevant these results are to service life. They do, however, warn against rough handling of tubes during installation; where local damage may be cause for concern. Also, the effect of cold work should be taken into account in rolling tubes into the tube sheet, where one plant had some SCC difficulties several years ago.

Crack directions in regular production-annealed tubing are generally longitudinal, i.e. along the axis of a U-bend, showing that a considerable hoop stress is introduced during bending. Occasionally, the cracks would deviate from this path and run for a short distance at nearly right angles before resuming the axial path. Also, a few short cracks were found in the transverse direction, at the edge of an occasional U-bend. Microscopic examination of cracked and uncracked specimens has been made:

1. Cracks were always intergranular.

2. The microstructures of the cracked specimens (Figs. 8-12) typically showed poorly defined grain boundaries after an electrolytic phosphoric acid etch, suggesting that there were very few intergranular chromium carbide particles present. At the same time, however, it was observed that the microstructures of some of the more resistant heats had similar features (Figs. 13,14 & 15). Therefore, it appears that an accurate prediction of U-bend performance



UNETCHED

68X

5% Nital

ELECTROLYTIC ETCH

350X

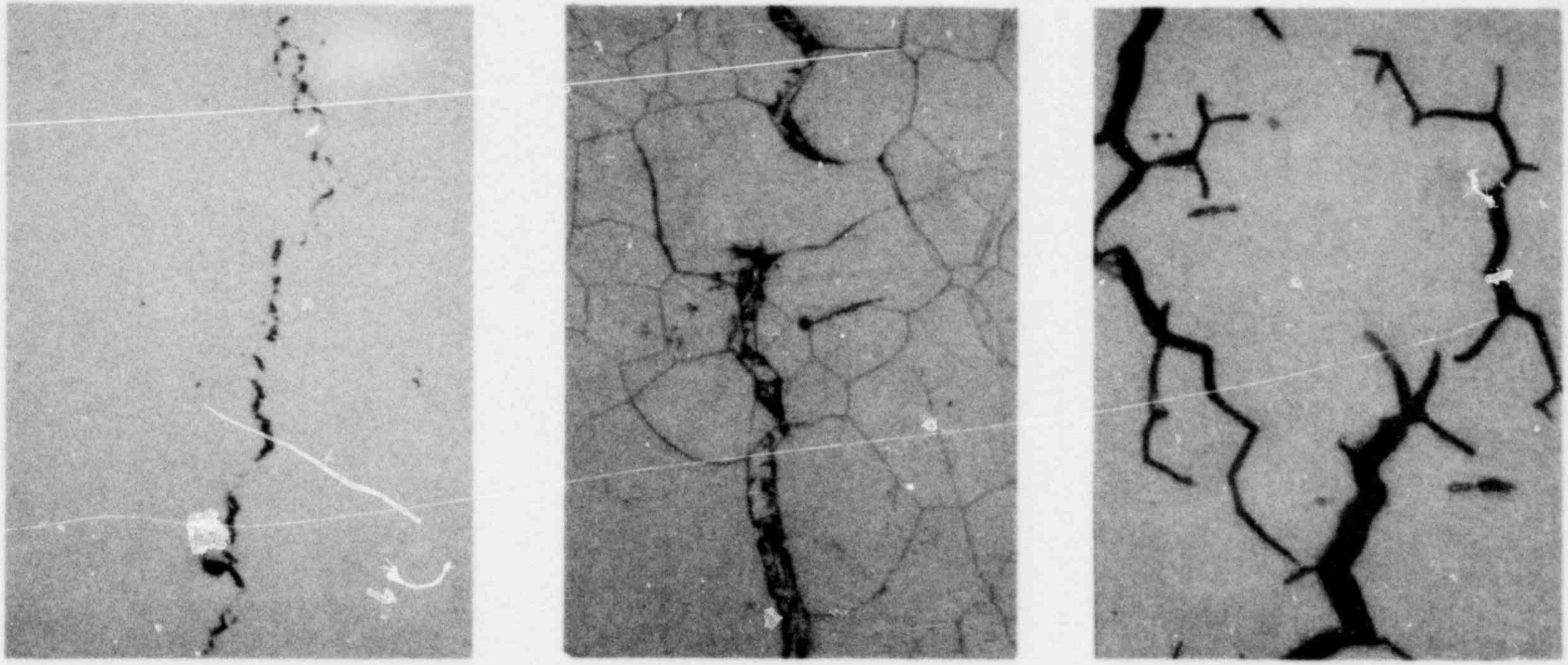
8:1 Phosphoric acid/H_2O

ELECTROLYTIC ETCH

350X

Figure 8

SPECIMEN No. 0-6 HEAT No. 2
D.I. H_2O WITH $[O_2]$ <5 ppb
4 WEEKS @ 365°C



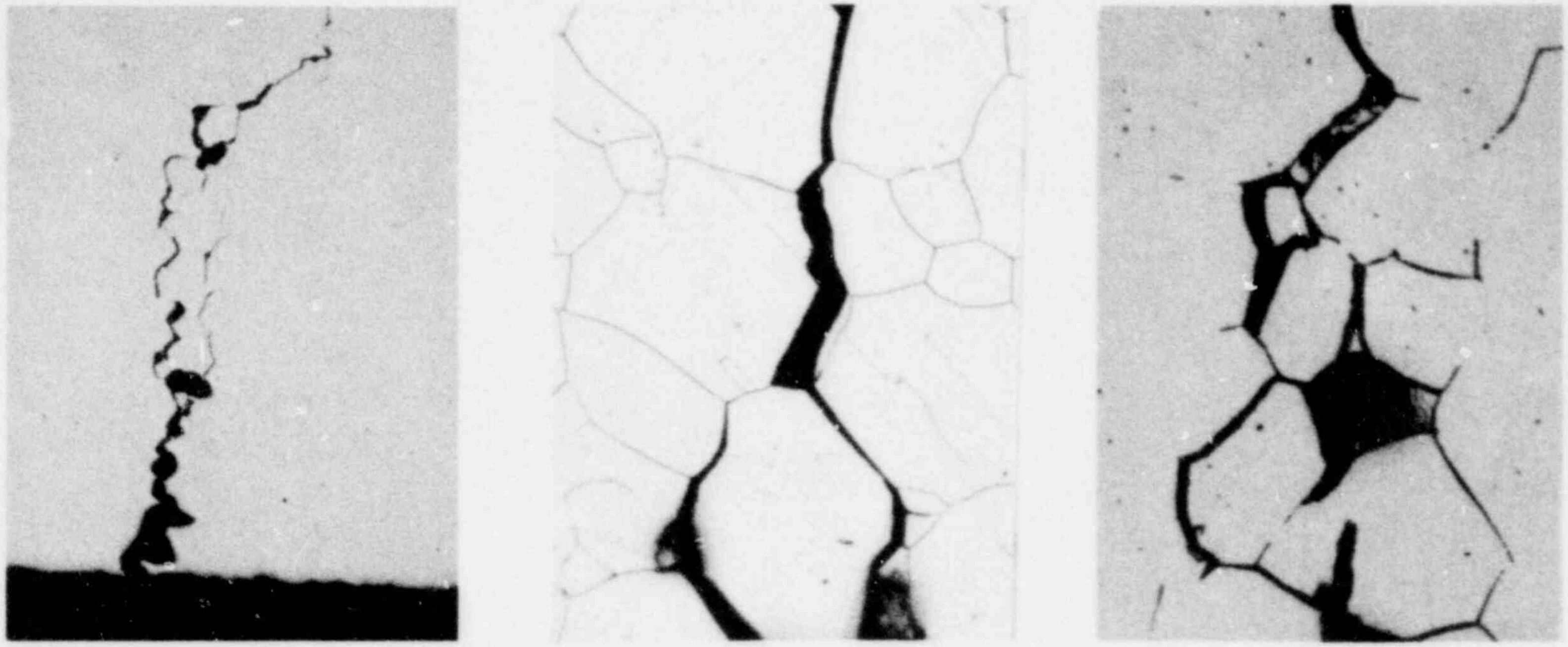
UNETCHED
68X

5% Nital
ELECTROLYTIC ETCH
350X

8:1 Phosphoric acid/H_2O
ELECTROLYTIC ETCH

Figure 9

SPECIMEN No. 1-4 HEAT No. 4
D.I. H_2O WITH $[O_2]$ <5 ppb
8 WEEKS @ 345°C



UNETCHED

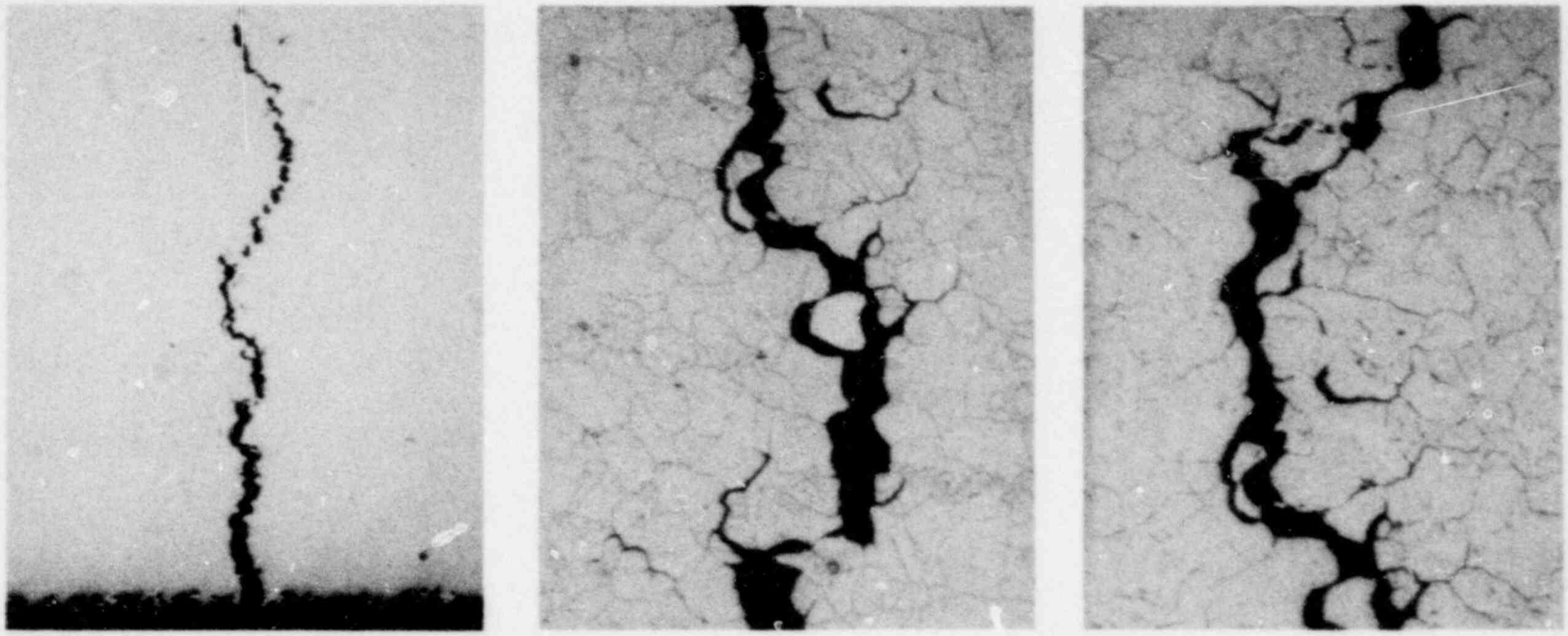
68X

5% Nital
ELECTROLYTIC ETCH
350X

8:1 Phosphoric acid/H_2O
ELECTROLYTIC ETCH
350X

Figure 10

SPECIMEN No. 2 HEAT No. 5
D.I. H_2O WITH [O_2] <5 ppb
8 WEEKS @ 360°C + 2 WEEKS @ 365°C



UNETCHED

68X

5% Nital

ELECTROLYTIC ETCH

350X

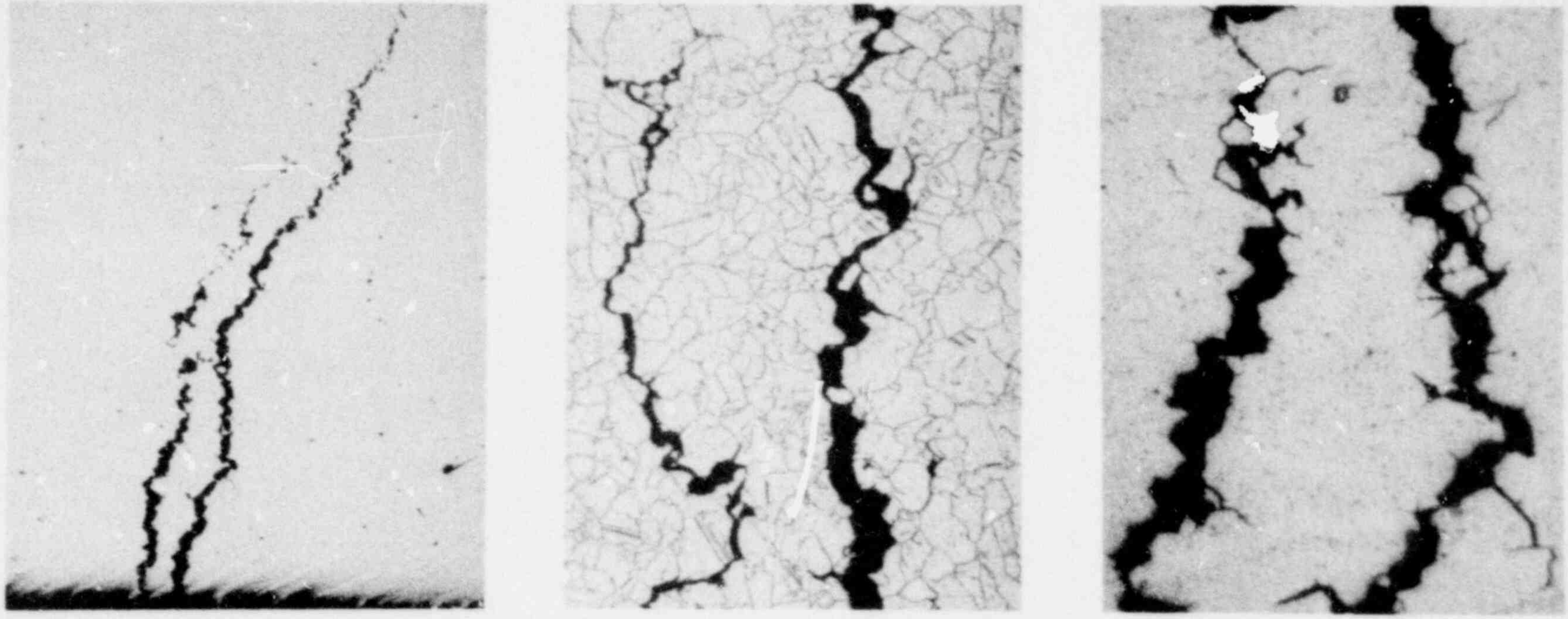
8:1 Phosphoric acid/H_2O

ELECTROLYTIC ETCH

350X

Figure 11

SPECIMEN No. 1-2 HEAT No. 10
D.I. H_2O WITH $[O_2]$ <5 ppb
2 WEEKS @ 365°C



UNETCHED

68X

5% Nital

ELECTROLYTIC ETCH

350X

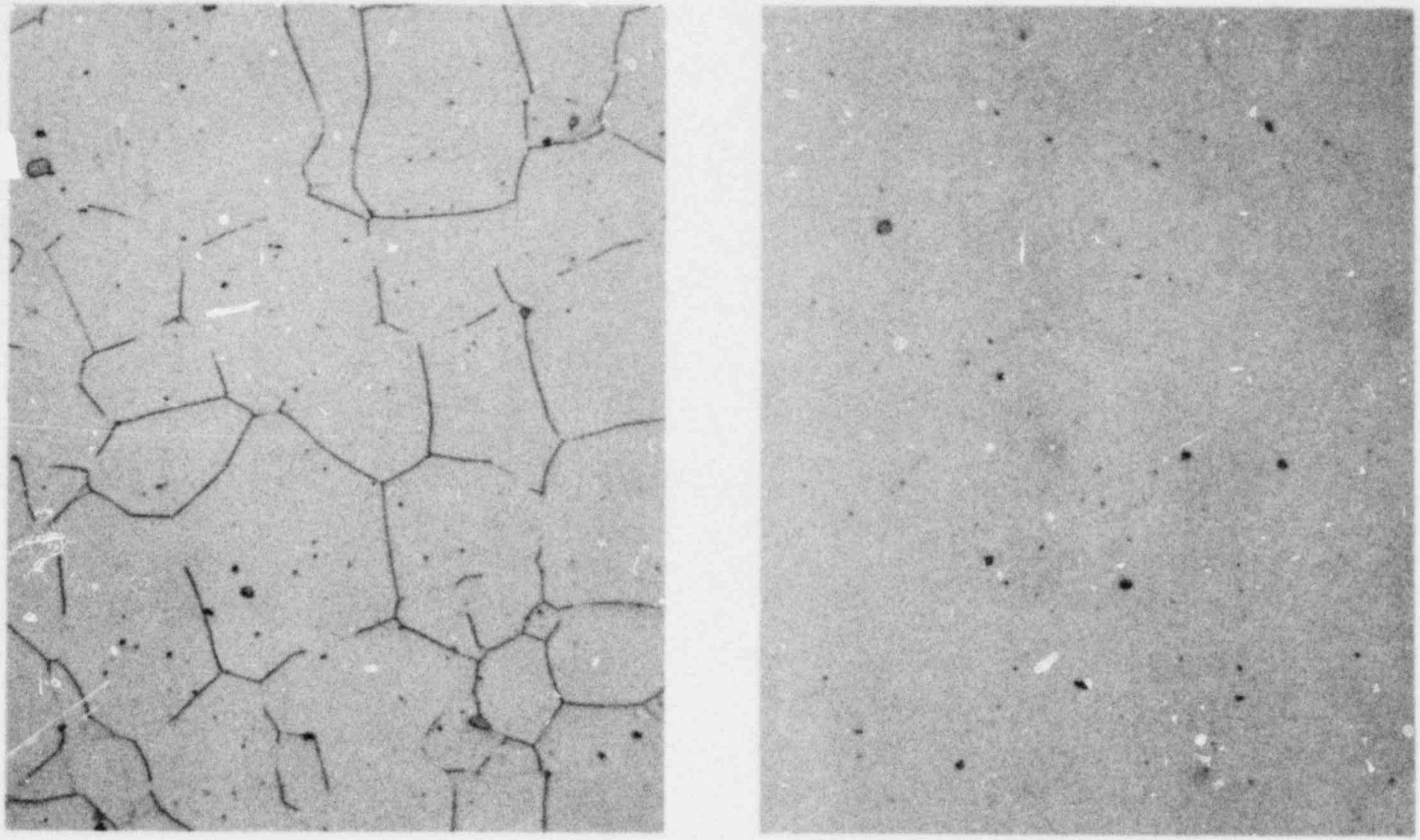
8:1 Phosphoric acid/H_2O

ELECTROLYTIC ETCH

350X

Figure 12

SPECIMEN No. 1-1 HEAT No. 11
D.I. H_2O WITH $[O_2]$ <5 ppb
4 WEEKS @ 365°C

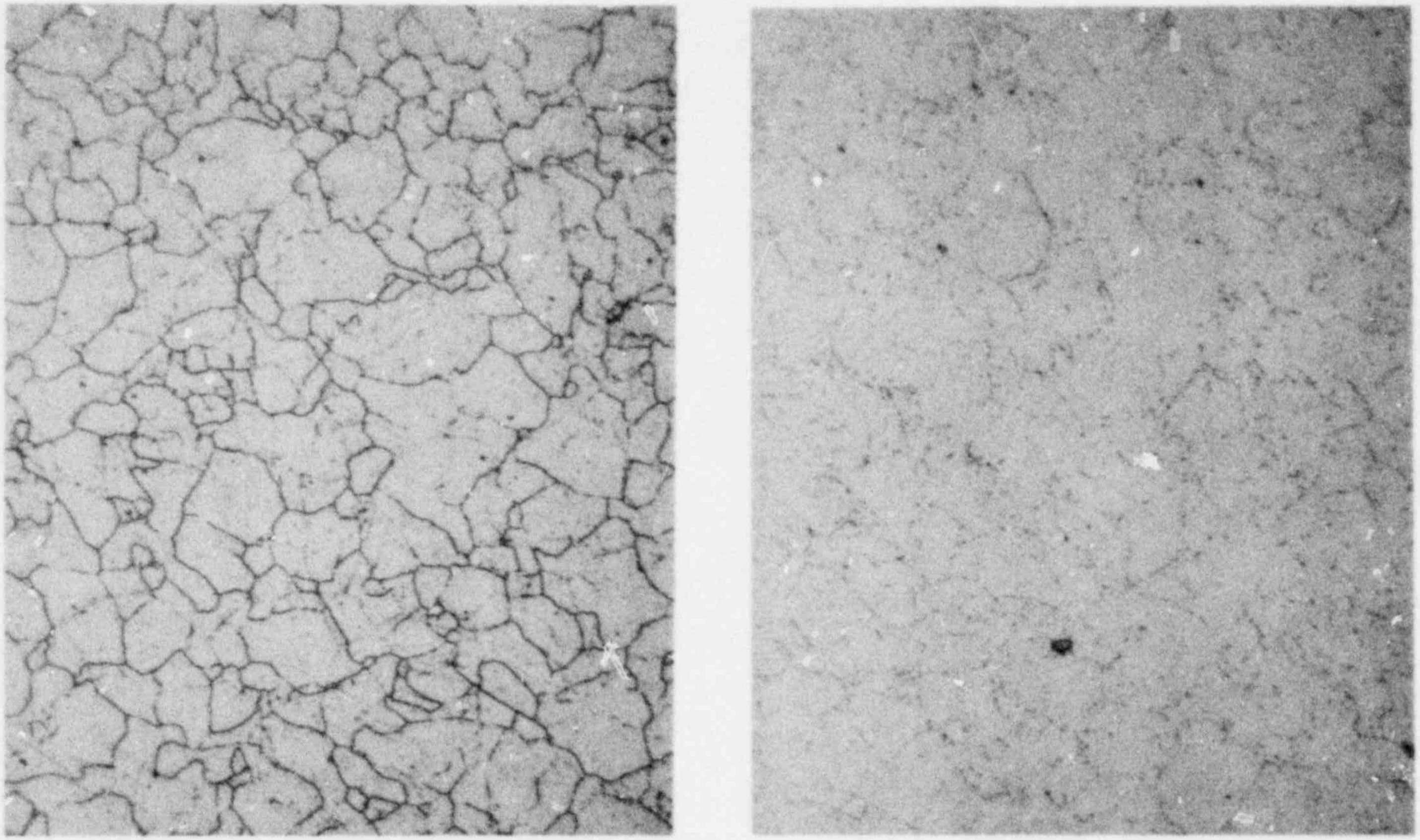


5% Nital
ELECTROLYTIC ETCH
350X

8:1 Phosphoric acid/H_2O
ELECTROLYTIC ETCH
350X

Figure 13

STRUCTURE OF HEAT NO. 3
U-BEND UNCRACKED AFTER
18 WEEKS EXPOSURE @ 365°C

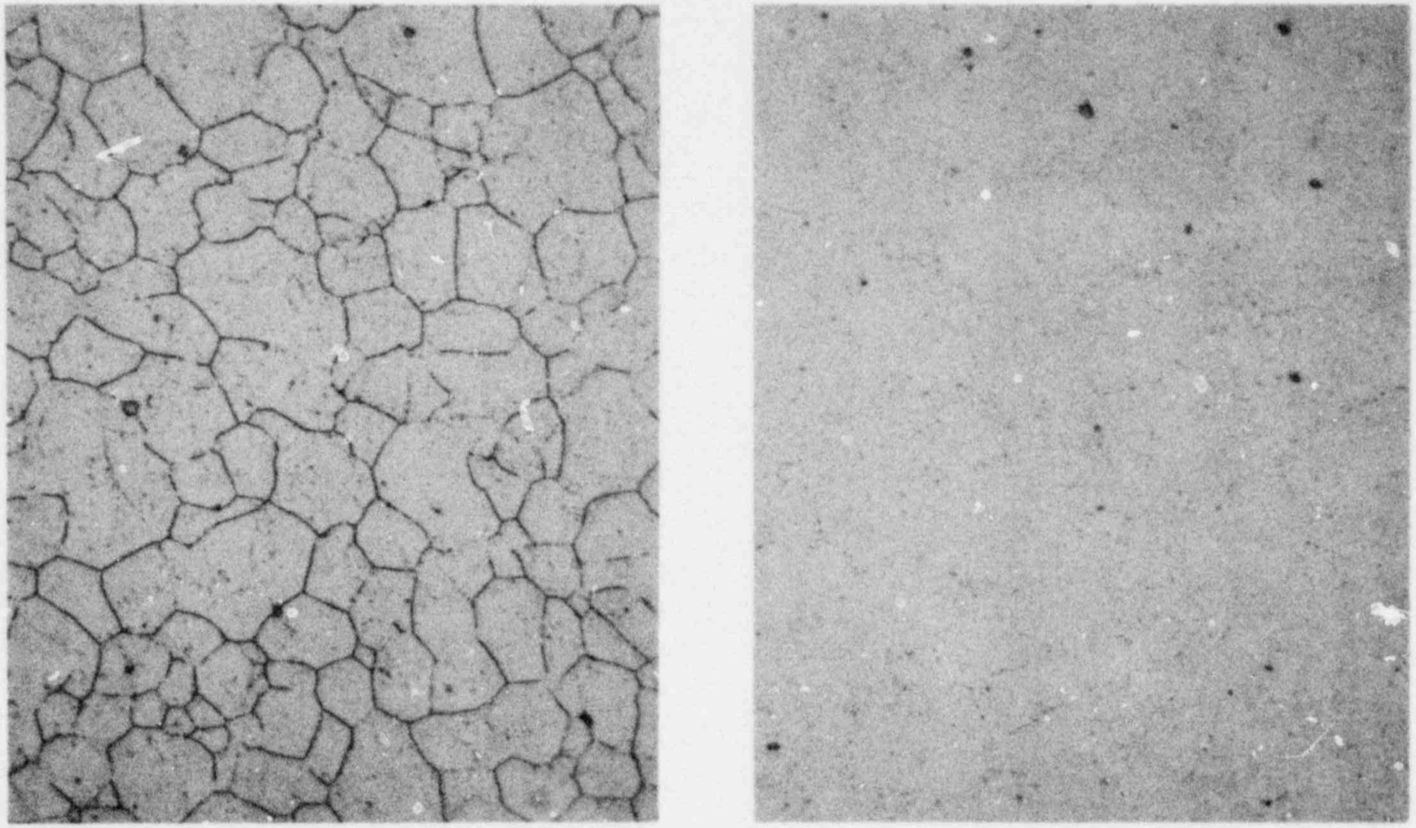


5% Nital
ELECTROLYTIC ETCH
350X

8:1 Phosphoric acid/H_2O
ELECTROLYTIC ETCH
350X

Figure 14

STRUCTURE OF HEAT NO. 9
U-BENDS UNCRACKED AFTER
24 WEEKS EXPOSURE @ 365°C



5% Nital
ELECTROLYTIC ETCH
350X

8:1 Phosphoric acid/H_2O
ELECTROLYTIC ETCH
350X

Figure 15

STRUCTURE OF HEAT NO. 13
U-BENDS UNCRACKED AFTER
18 WEEKS EXPOSURE @ 365°C

in deaerated pure water at elevated temperatures cannot yet be based on microstructure analysis alone.

Heat treatments in an H_2 atmosphere were applied in the laboratory to several specimens before bending and testing. Starting materials included mill-annealed tubing, as well as cold worked tubing and plate. Although the response to temperatures that ranged from 1600°F (871°C) to 1800°F (982°C), (see Tables 3,4, & 7) produced a variety of structures, some of which we felt at the time should be highly susceptible, no SCC has yet been found at 365°C in about 6 months of exposure time. These tests continue.

It is difficult to establish what the differences are between laboratory heat treatments and mill practice, since tube manufacturers follow proprietary procedures. However, it seems quite certain that there is a strong connection between SCC of Inconel 600 in pure high temperature water (and in primary water), and processing history. Small changes that occur within the same mill, and from mill to mill, may well account for the heat-to-heat variations that are evident.

It is expected that the next few months of testing will allow more quantitative conclusions to be drawn and that relationships will be established for use in determining reasonable "worst case" times at which cracks may be expected in regular production tubes with given amounts of distortion. To help with the correlation of U-bend data with tubes, a strain analyzer has been ordered to enable determinations of the amount of strain in the test pieces. In conjunction with tests at lower stress levels, this approach is expected to simplify the translation of laboratory results into more practical terms.

3. Constant Extension Rate Test (CERT)

The slow strain rate tests have proven to be very useful as an accelerated test method. Materials which take many weeks to crack in U-bend tests have cracked in several days and often at a lower strain in the CERT exposures. The series of tests conducted so far (see Table 8) have shown production tubing to be susceptible to intergranular SCC at temperatures of 365°C and lower, and strain rates spanning a range of at least 10^{-6} to 10^{-8} sec^{-1}.

The effect of temperature is being explored with heat #4 which cracked as U-bends in 10-12 weeks. Figure 16 shows a series of stress-strain curves for this material at various temperatures while maintaining the strain rate at approximately 3×10^{-7} sec^{-1}. It can be seen that cracking is produced readily at 365°C and that the ductility increases progressively as the temperature is lowered to 345°C and 320°C. The strain levels corresponding to the point of inflection in load were 7, 16 and 32% respectively. Also, an examination of the fracture surfaces by SEM (Table 8 and Figs. 17, 18 & 19) showed 60%, 39% and 1.5% of intergranular crack propagation at the 3 temperatures, respectively. Obviously, the SCC propagation rate became lower as the temperature decreased; 290°C was not included in this series since SCC was so slight already at 320°C.

In order to start an evaluation of strain rate, the test at 320°C Fig. 20 in pure deaerated water was repeated at $\dot{\varepsilon} = 3.9 \times 10^{-8}$ sec^{-1}. Now only 8% strain had occurred before the load started to drop, and 57% of the fracture was intergranular. In other words, the order of magnitude change in $\dot{\varepsilon}$ now caused SCC at 325°C to the same degree as $\dot{\varepsilon} = 3 \times 10^{-7}$ sec^{-1} at 365°C. At this stage, the test at 290°C was introduced at the lower $\dot{\varepsilon}$. This test ran for several weeks, and started to show a load drop only at about 28% strain, but it could not be completed owing to a power failure during bad weather that occurred at this critical point. Evidence of crack initiation was seen in many places when viewed under the microscope, but all of them were widened by blunting. Some necking down had also started. It seems that SCC propagation rates were slower than the extension of the test piece.

Table 8

C.E.R.T. Results

Material Identification	Test Temp. (°C)	Heat Treatment of "as received" Material	Strain Rate (Sec^{-1})	% Strain at Max. Stress	% of Fracture Face Area Showing I.G.S.C.C.	Time to Failure in C.E.R.T. (Days)	Time to Failure as U-bends (Weeks)
Heat #2	365	None	2.8×10^{-7}	10	71	7	<2 to 4
" #2	365	20 hrs in Ar @ 700°C	3.0×10^{-7}	32	2	12	>14
" #4	365	None	2.6×10^{-7}	7	60	6	10 to 12
" #4	345	None	3.0×10^{-7}	16	39	8	>16
" #4	325	None	2.9×10^{-7}	32	1.5	16	>10
" #4	325	None	3.9×10^{-8}	8	57	32	>10
" #5	365	None	2.0×10^{-6}	34	<1.	2	8 to 18
" #5	365	None	6.4×10^{-8}	*	10 mil deep crack	-	8 to 18

*Specimen pulled to 6.5% strain then the test accidently shut down.

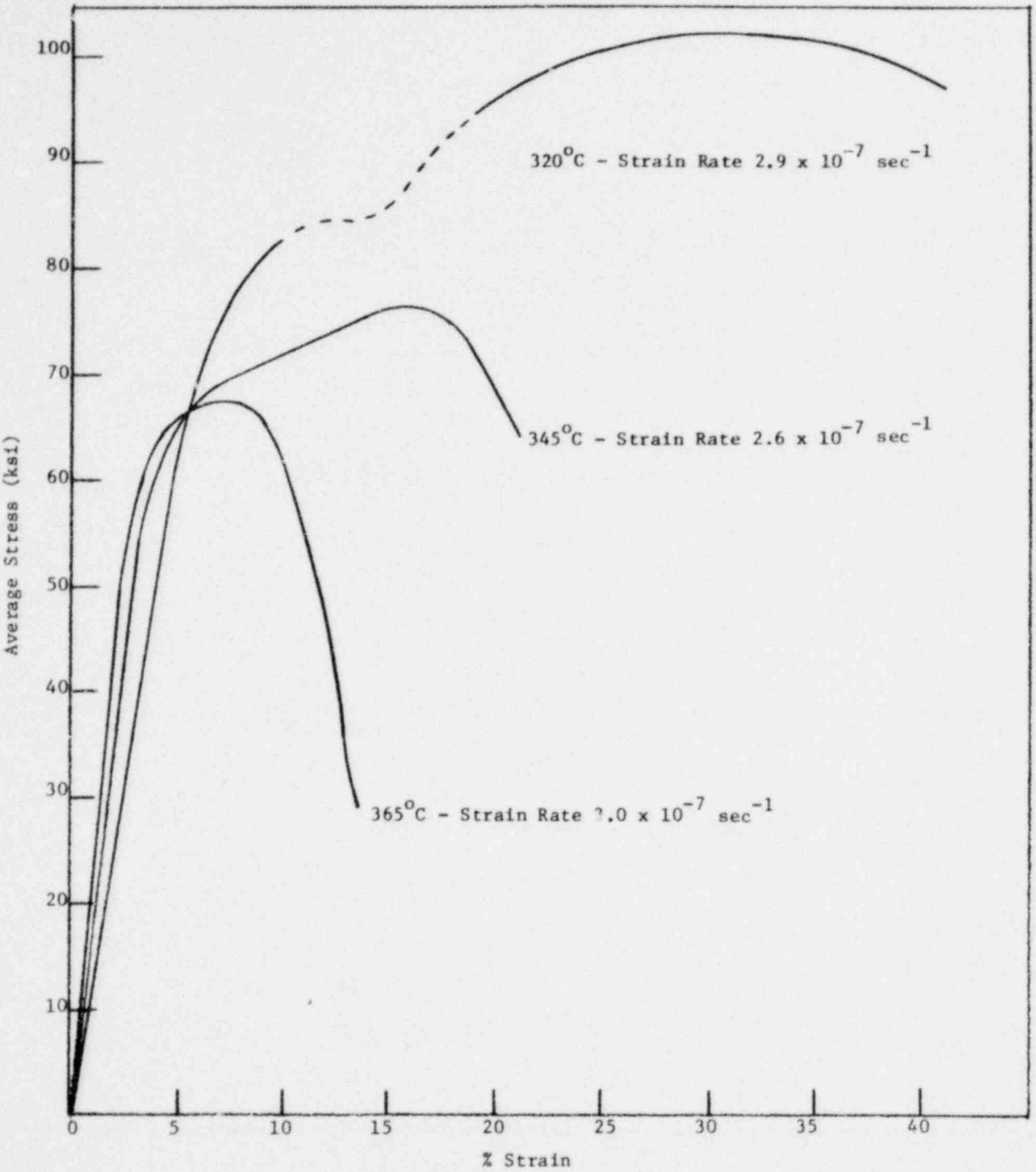
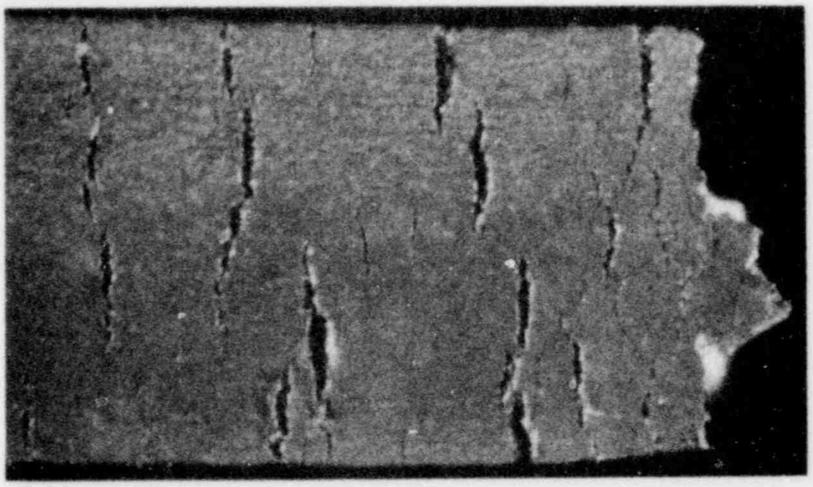
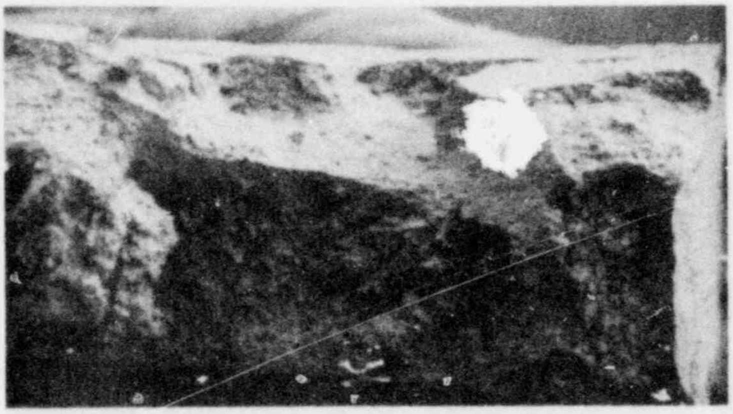


Figure 16. Stress-strain curve for heat #4 in D.I. H_2O.



10X Photo of Fractured Gauge Section

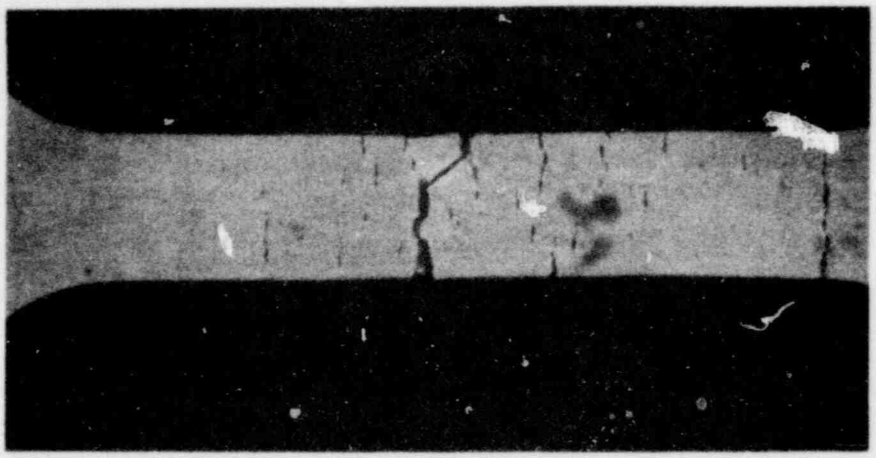


20X S.E.M. of Fracture Face

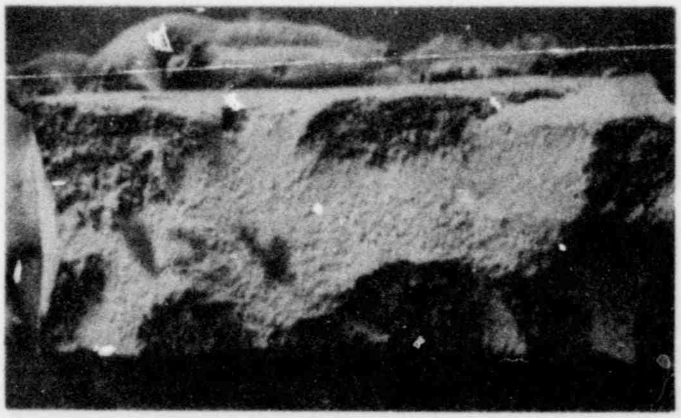
200X S.E.M. of Intergranular Area

Figure 17. Heat #4 fractured in constant extension rate test @ 365°C in D.I. H_2O with a strain rate of 3.0×10^{-7}.

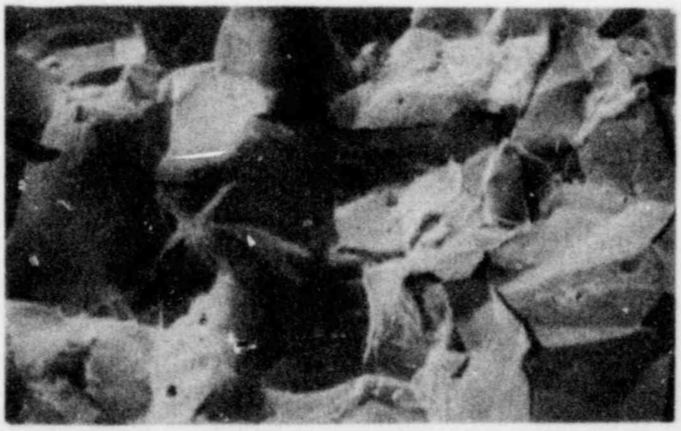
POOR ORIGINAL



3X Photo of Fractured Gauge Section

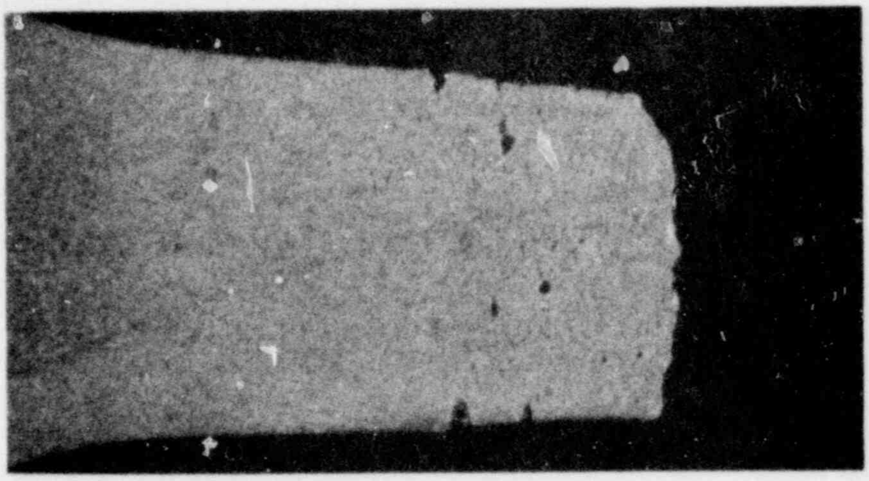


15X S.E.M. of Fracture Face

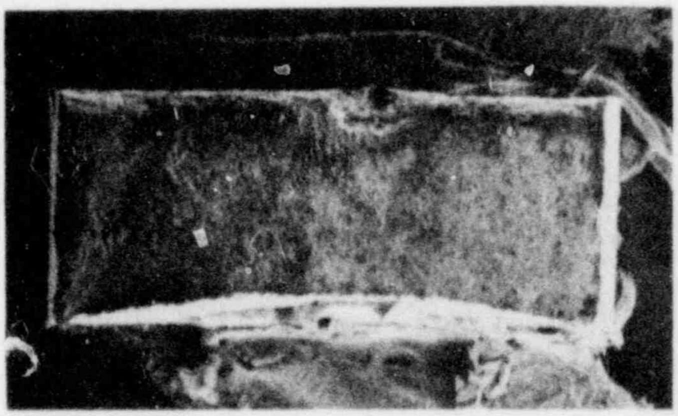


500X S.E.M. of Intergranular Area

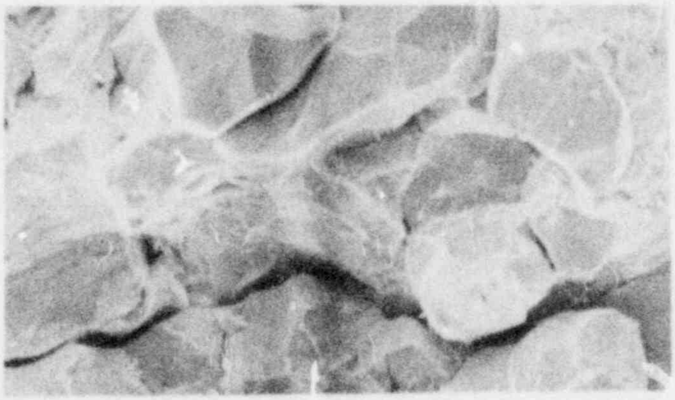
Figure 18. Heat #4 fractured in constant extension rate test @ 345°C in D.I. H_2O with a strain rate of 2.6×10^{-7} sec^{-1}.



8.5X Photo of Fractured Gauge Section



15X S.E.M. of Fracture Face



500X S.E.M. of Intergranular Area

Figure 19. Heat #4 fractured in constant extension rate test @ 325°C in D.I. H_2O with a strain rate of 2.9×10^{-7} sec^{-1}.

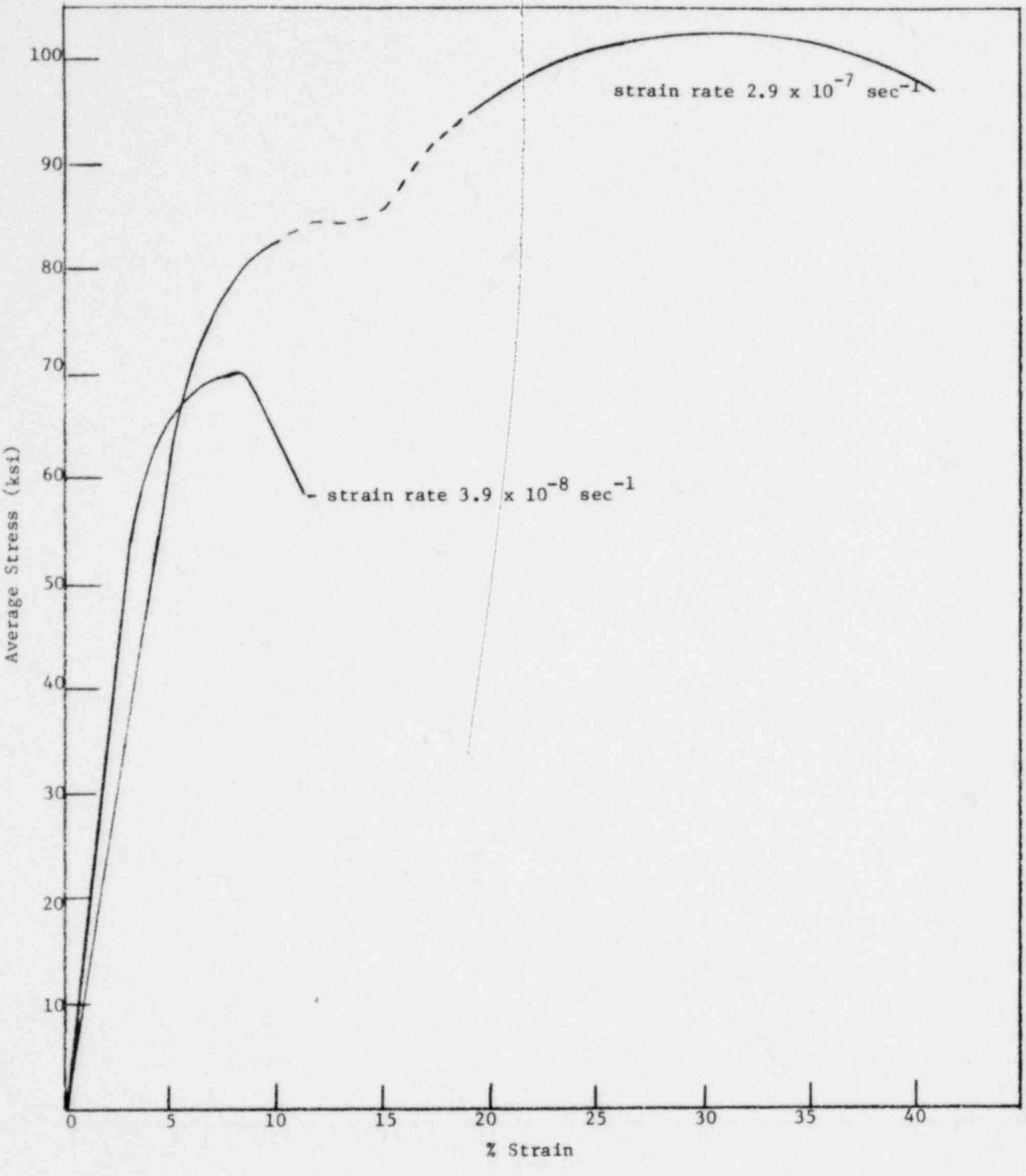


Figure 20. Stress-strain curve for heat #4 in D.I. H_2O at 320°C.

The above results raise the question why we did not find cracking in the laboratory at operating temperature i.e. 290°C, whereas many leaks have occurred in the field during denting. Points now under consideration to explain the difference are as follows:

Question	Approach to Clarify
1. Possible difference between pure and primary water	Carry out test under primary conditions
2. Lower strain rate	Test at 5×10^{-9} or 1×10^{-8} sec^{-1}
3. Aging effect on alloy	a. Age in vacuum at 290°C b. Age in water at 290°C c. Strain age in vacuum at 290°C Follow a. b. and c. with CERT
4. Difference in susceptibility of alloys	Use most susceptible material available
5. Different stress pattern in service	Reproduce denting conditions and tube deformation in laboratory, using susceptible tubing.

The above tests will not only explain differences between laboratory and service observations, but they will help in establishing the basis for the required quantitative estimate of tube life in worst case conditions in a plant that is actively denting. This series of tests contrasts with the earlier section of this report in which constant deflection is discussed, and which corresponds to a situation where denting has proceeded to some degree but is arrested. The two cases, therefore, are strain rate and total strain dependent, respectively.

Figure 21 shows a comparison of the stress-strain curves for heat #2 in the as received, mill annealed condition, and another that was subjected to a heat treatment of 20 hours in Ar at 700°C. This latter treatment is equivalent to the latest commercial method used to induce chromium carbide precipitation

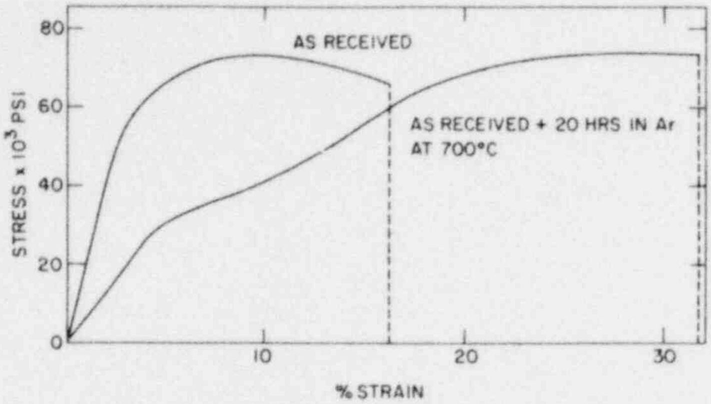


Figure 21. Stress-strain curve for heat #2. The tensile specimens were pulled to failure in D.I. H_2O @ 365°C with a strain rate of 3×10^{-7} sec^{-1}.

Table 9

Results of Cyclic Load Tests on Heat #5 in D.I. H_2O at 365°C

Test	Frequency	Results
#1	10^{-1} Hz	1) failed after 123041 cycles 2) IGC* 3) 17.2% elongation
#2	10^{-2} Hz	1) failed after 11570 cycles 2) IGC 3) 18.7% elongation
#3	10^{-3} Hz	1) failed after 1295 cycles 2) IGC 3) 18.4% elongation

*Intergranular Cracking

followed by chromium rediffusion into the denuded zones, and which is believed to provide resistance to SCC in deaerated high temperature water. The mill annealed material had approximately 50% intergranular failure, whereas the material after 700°C treatment showed a ductile fracture with only extremely shallow intergranular penetration. This is a very encouraging result, because the laboratory heat treatment was but a single step in what obviously was otherwise "adverse" processing in terms of SCC resistance. In production, we believe that the prior processing is arranged to optimize the effects of the final 700°C heat treatment, and may well produce even greater resistance to this kind of SCC.

More tests are now planned with samples of commercial (700°C treated) tubing, and these will include a range of strain rates to obtain comprehensive data, including primary coolant conditions.

4. Controlled Potential Test

In the controlled potential tests, open circuit potentials of the specimens varied from -3mV to 6mV with respect to the hydrogen electrodes. When the current was applied to the series for cathodic polarization, the potential of the first specimen increased by a few millivolts, while the potential of the 6th specimen became more negative at a value less than -100mV relative to the rest potential. Accurate iR-drop corrections are now being made to obtain the precise shifts of potential. Qualitatively, so far, moderate shifts of the potential in the cathodic direction appear to accelerate the SCC cracking. When the iR corrections are completed, the quantitative data will be tabulated and reported.

5. Cyclic Load Test

Plate tensile specimens fabricated from heat #5 in the same way as the CERT specimens were exposed to cyclic stresses in deoxygenated water at 365°C. The applied stress was in the form of a sinusoidal wave with the maximum tension of 130% and the minimum tension of 110% of the yield strength in 365°C water in one series and 110% and 90% in another. Table 9 gives the results for the higher stress levels. All the specimens cracked intergranularly at frequencies of 10^{-1}, 10^{-2}, and 10^{-3} Hz with very little variation in failure times and elongation. As is seen, the total number of cycles varied by a factor of 10 between each test while the time to failure remained relatively constant at 13 to 15 days. This time to failure is 5 to 6 times faster than that of the same material when tested as U-bends. Cyclic frequency, therefore, does not appear to be as critical as the presence of the cyclic stress. The work is proceeding to examine wave form, load range and other parameters.

D. SCHEDULED INVESTIGATIONS:

The denting action of corroded support plates on PWR steam generator tubes provides a very complex stress pattern and also very slow denting rates. To separate the contributions to SCC of each of these effects, two types of capsule tests will be started. Fig. 22 shows a double wall tube with a thinned gauge section machined on the inner tube. These tubes will be placed in primary water at 290°C or 325°C and the annulus between the tubes pressurized over the vapor pressure of the solution to create 30 to 60 mils of denting. These tests will provide information on the effect of stress pattern and the second capsule design will explore the effects of slow denting. Fig. 23 shows a single tube capsule containing a carbon steel slug. This capsule will contain a NiCl or $CuCl_2$ solution to corrode the steel and provide slow deformation rates with stress patterns similar to those involved in denting. These capsules will also be placed in primary water and the pressure of both types will be continuously monitored to provide precise times to failure.

Tests presently being conducted in pure deaerated water, i.e. slow strain, constant deflection, and cyclic load will be carried out in primary, and secondary water to determine if these chemistries cause any beneficial or detrimental effect. Refreshed autoclave systems will be used for this work to insure proper chemistry control.

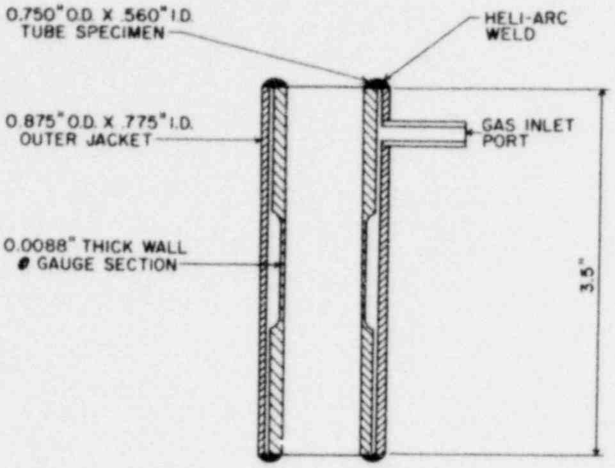


Figure 22. Gas pressurized capsule.

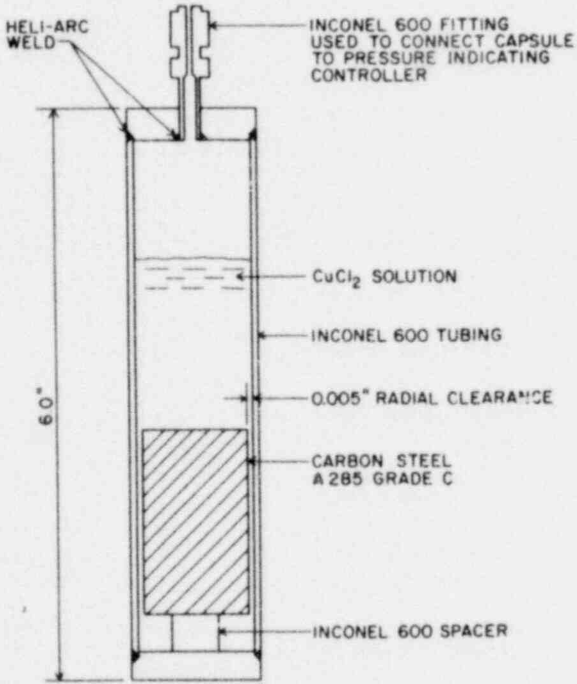


Figure 23. Capsule design used to provide slow deformation rates.

ACKNOWLEDGMENTS

The authors wish to thank Mr. T.C. Roberts and Mr. J. Svandrlik for their invaluable assistance in constructing and operating the test facilities and preparing and examining specimens. We also are indebted to Dr. B. Vyas and Dr. H. Isaacs for valuable discussions. The authors also wish to express their thanks for support of this research work by the Reactor Safety Research Branch of the Nuclear Regulatory Commission. Helpful suggestions were made in planning this work by Dr. J. Muscara and C. Serpan.

REFERENCES

1. D. van Rooyen, "Review of Stress Corrosion Cracking of Inconel 600," Corrosion 31, 327 (1975).

2. H.A. Damian, R.H. Emanuelson, L.W. Sarver, G.F. Theus and L. Katz, "Effect of Microstructure on Stress Corrosion Cracking of Alloy 600 in High Purity Water," Corrosion 33, 26 (1977).

3. D. van Rooyen and J.R. Weeks, "Denting of Inconel Steam Generator Tubes in Pressurized Water Reactors," BNL-NUREG-50778 (1978).

4. H. Coriou. L. Grall, C. Mahiew, and M. Pelos, "Sensitivity to Stress Corrosion and Intergranular Attack of High Nickel Austenitic Alloys," Corrosion 22, 280 (1966).

5. A.A. Seys and A.A. Van Haute, "Pitting Potential Measurements by Means of the Static Potential Band Method," Corrosion 29, 329 (1973).

DISTRIBUTION LIST

R5:

NRC:

Division of Reactor Safety Research:

L.S. Tong
L.C. Shao
C.Z. Serpan
J. Muscara

Office of Nuclear Reactor Regulation:

L.S. Rubenstein

Division of Systems Safety:

J.P. Knight
S.S. Pawlicki
R. Gamble
H.F. Conrad
B. Turovlin

Division of Operating Reactors:
D.G. Eisenhut
V. Noonan
W.S. Hazelton
B.D. Liaw
F.M. Almeter (5)

BNL:

H.J.C. Kouts
W.Y. Kato
D.H. Gurinsky
H.S. Isaacs
Corrosion Science Group (25)