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CAUSTIC STRESS CORROSION CRACKING

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INTRODUCTION

Liquid Metal Fast Breeder Reactors (LMFBRs) use sodium as a coolant for transfer of heat from the core to the steam generators. Maintenance and examination of the system require removal of sodium from components of the system. One process for removal reacts the sodium with water vapor and removes the residual sodium hydroxide from the components by rinsing with liquid water. This process exposes components such as pumps, heat exchangers, valves, and fuel-handling machines to contact with aqueous NaOH solutions in various concentrations over a range of temperatures and times. Since stress can be present in these components, as generated by fabrication, structural loads, deformation in service, and possible wedging action by corrosion products, conditions are potentially available for the mechanism of caustic stress corrosion cracking (CSCC). Since LMFBR components are fabricated from Types 304 and 316 stainless steels which have been found to be susceptible to CSCC, it was therefore considered necessary to establish the threshold of CSCC so that the components could be processed under conditions avoiding CSCC.

Early case histories of CSCC related to the removal of sodium from nuclear components are summarized in Table I, along with the conditions of the exposure as reported in the technical literature.[1] In each case, either the temperature, time, or stress level was reported to be high; that is, beyond what is considered good practice to avoid CSCC.

As a result of the above requirement and experience, a program was initiated under the sponsorship of the Energy Research and Development Administration as part of the LMFBR program at the Hanford Engineering Development Laboratory to define the conditions under which CSCC could be expected to occur so that sodium removal processing parameters could be established to avoid such conditions.

PROCEDURES

The materials used in the testing program included heats of Types 304 and 316 stainless steel, Inconel 600 and 718, hardfacing deposits of Stellite 6 and

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156, and three special, wear-resistant, carbide-type materials. The analysis of these materials is tabulated in Table II. Although the ductile alloys were strained, the carbide materials were exposed unstrained because of limited materials availability, difficulty of machining, and absence of ductility.

Specimen development was extensive and complex because obtaining consistently reproducible CSCC was prerequisite to acceptance of a qualified specimen design. Details of this experience will be discussed in a future paper. The final specimen consisted of a standard ASTM 0.25-inch (0.64-cm) diameter, round specimen mounted in a compression sleeve that could be strained to a fixed amount and maintained at constant strain with closure nuts at each end, as shown in Figure 1. Passages were drilled in the outer sleeve for both sodium and rinsing media access to the surface of the reduced section of the specimen. The key to reproducible CSCC testing was the crevice produced by application of sleeves over the reduced section of the specimen. The sleeves were split to make assembly possible, and they were held in position with set screws. All the fixtures except the set screws were fabricated from Type 304 austenitic stainless steel to minimize the effects of galvanic attack. The same stainless fixtures were used for alloys other than stainless steel, accepting the uncertainties of galvanic attack as a conservative prototype of the components.

The specimens were assembled, wetted in liquid sodium for five days at 1050°F (565°C), and cooled to room temperature to introduce the sensitizing effects of the microstructure as would be anticipated by reactor service in high-temperature sodium. Specimens were strained to 0.0047 inch (0.012 cm), which was calculated to be equivalent to 100% of the 0.2% off-yield strength of 304 stainless steel. Although initial specimens were strained using a micrometer over the overall specimen length, precision was improved on subsequent specimens which were strained in an Instron tensile machine using dial gages on the head travel to measure the strain, which was then taken up by the nuts acting against the compression sleeve.

Test conditions exposed specimens to NaOH by hanging from stainless steel wire in the prescribed caustic solution in a nickel pot heated to indicated temperatures under air. Evaporation was minimized by closing the system with neoprene "O" rings. A check analysis showed that the final solution composition was within 4 w/o of the original NaOH nominal composition.

Although several non-destructive methods of detecting CSCC were investigated, metallography was demonstrated as the most reliable. Longitudinal sectioning of the full length of the reduced section, fillet, and the first 0.25 inch (0.64 cm) of the shank of the specimen provided a random sample of the surface of the specimen. Locating cracks of 0.005-inch depth by examining both sides of two specimens yielded a probability of finding cracks of about 10%. This required a larger statistical population and more replication of exposed specimens to the same conditions. Although these random samples are not efficient, other techniques were even less satisfactory. As a compromise with available test facilities and costs, triplicate replication was applied in this study. Compositing all the samples investigated contributes additional confidence to the indication of onset of CSCC. The significant depth of cracking was established by fracture mechanics calculations of the service application of two components. A crack depth of 5 mils (0.127 mm) was estimated to be conservative to the anticipated structural loads of critical subassemblies of a pump and heat exchanger.

The depth of the crack was measured at 100x using a Filar micrometer. A light (5% electrolytic) oxalic acid etch enhanced the visibility of the very tight CSCC. Although both sides of the entire length of the reduced section, fillet, and shank were observed, only the largest crack was used for the evaluation of the structural integrity of the specimen, which would then be used as a criterion for the requalification of the structural integrity of the component.

RESULTS

Observations of CSCC on caustic-exposed specimens ranged from pitting without cracking to 100% crack penetration of the reduced section of the specimen. The CSCC fracture mode in austenitic stainless steel at the temperatures of these testing conditions was transgranular. This was most frequently observed at the center of the reduced section under the split sleeve. This was the location of maximum stress intentionally because the section was of minimum thickness to reduce the incidence of failure in the shoulder radii. Results of the metallographic examination measuring the depth of cracking with the conditions of temperature, time, and NaOH concentrations are summarized in Table III and Figure 1. Examination of the plot in Figure 2 provides estimates for predicting times for cracking to a specific depth. Fracture mechanics calculations on two critical subassemblies of LMFBR components indicate that a crack depth limit of 0.005 inch is conservative to assure that cracking will not be propagated by structural loading.

The depth of cracking observed metallographically has been described by Eckel in 1962 on stainless steel in $MgCl_2$:[3]

$$\log t = \frac{D}{M} + \log t_o$$

in which t is the total elapsed time, t_o is the time to initiate cracking, D is the crack depth, and M is the slope of the crack propagation rate.

The effect of temperature on crack depth and crack propagation rate is the single most influential parameter. This is shown by the steep slope of the threshold limit in Figure 2, as well as the crack propagation rates in Figures 3 and 4, supported by Table III.

The effect of NaOH composition is illustrated in Figure 4, supported by Table IV, in which the crack propagation rate of 0.000185, 0.000126, and 0.000196 in/day (0.00469, 0.0032, and 0.00498 mm) is not significantly different from 50, 60, and 70 w/o NaOH.

The effects of uniaxial stress show a wide spread of results in Table V, but comparison of the plot of the data in Figure 6 shows a trend to reduce the depth of cracking penetration as the stress is reduced from 100 to 33 percent of the 0.2% offset yield. More significant is that reduction of the stress to one-third of yield still does not eliminate the penetration depth of CSCC, at least under the condition of 20-day exposure to 50 w/o NaOH at 250°F (121°C), as shown in Figure 7.

The effect of alloy composition is illustrated in Figure 8 in which the CSCC depth and the microstructure are shown for heat-treated Inconel 718 and A286, as well as annealed Inconel 600, Type 316 stainless steel, and carbon steel. CSCC appears to be resisted by the higher alloy compositions, as compared to the performance of 304- and 316-type stainless steels under the conditions of testing. Although the carbon steel showed no evidence of CSCC or pitting, considerable solution forms of corrosion were observed. Type 316 strip stock exposed to sodium service for 5000 hours at 1200 (649) and 1350°F (732°C) stress to 100% of the 0.2% offset yield exhibited CSCC, as shown in Figure 9. The interesting observation here is that the mode of fracture changed from transgranular in the austenitic to intergranular type of attack in the ferrite surface of the sodium-exposed specimens.

CONCLUSIONS

- The depth of CSCC in caustic solutions can be predicted for austenitic alloys for a given temperature and time of exposure.
- Temperature is the single most significant parameter affecting the initiation, propagation rate, and crack depth of CSCC.
- Although caustic composition in aqueous solutions does not greatly change the depth of CSCC in the conditions tested, 50 w/o NaOH has been found to be the most aggressive concentration.
- Alloy compositions containing high nickel (heat-treated Inconel 718 and A286 and annealed Inconel 600) resist CSCC more effectively than Types 304 and 316 stainless steels under the conditions tested sufficiently to justify their application to critical components such as bolts and bellows.
- Reduction of the state of stress (from 100 to 33% of the 0.2% offset yield) does not prevent CSCC that will produce 0.005-inch (0.127-mm) deep cracks. Control of the stress state is a promising approach to the control of CSCC.
- Cracking fracture mode of CSCC under the conditions of these tests between 210 and 330°F (99 and 166°C) is transgranular in austenitic microstructures.

LIST OF TABLES

LIST OF FIGURES

REFERENCES

1. AEC TID 26513, Decontamination of Plant Components for Sodium and Radioactivity: Summary Report, Specialist Meeting, Dounreay Experimental Reactor Establishment, Caithness, Scotland; April 2-12, 1973.
2. LMEC 73-11, Stress Corrosion in the Pump Bearing Test Facility, 1974.
3. J. F. Kokel, Corrosion, 18, 270t (1962).

TABLE I

CASE HISTORIES OF CAUSTIC STRESS CORROSION CRACKING ASSOCIATED WITH SODIUM

EXAMPLE	EXPOSURE CONDITIONS	OBSERVATIONS	REFERENCES
SEAWOLF Superheater (GE)	High-temperature, superheated steam	Severe cracking	1
PHENIX reactor charging machine bolts (French)	Steam cleaned 4 times, not disassembled, exposed 2 months in water, overstressed in last sodium exposure	3 bolts ruptured, 20 bolts cracked under head or in first thread	1
Reactor pump bolts (French)	Steam cleaned, not disassembled	Ruptured	1
Piping of pump bearing test facility (Liquid Metal Engineering Center)	200 to 700°F, 2 to 10 days, Type 304SS, 2x6x0.28-inch pipe, unrelieved welds	Transgranular cracking with branching in weld head-affected zone	2
Bolts equivalent to FFTF In-Vessel Handling Machine (Atomics International and Hanford Engineering Development Laboratory)	325 to 400°F in 50 w/o NaOH, 304 Type SS, 0.5-inch dia bolts	Gross cracking 50% of diameter	HEDL and AI

TABLE II

ANALYSIS OF TEST MATERIALS

														1000 psi		%		
Alloy	Heat Number	C	Cr	Ni	Mn	Fe	Mo	Ti	Nb + Ta	Si	S	P	Cu	YTS	UTS	El	R/A	R_b
304	54846	.07	18.67	8.50	1.48	-	-	-	.10	.67	.027	.027	.20	54	89	51	76	89
316H	G5238	.026	17.72	13.56	1.54	-	2.27	-	-	.53	.023	.020	.06	82	101	36	73	19
316H	G5990	.044	17.32	12.29	1.75	-	2.80	-	-	.52	.021	.022	.10	70	92	42	73	21
Inconel 600	31409	.02	15.20	76.26	.31	7.68	-	-	-	.21	.007	-	.29	46	92	49	-	-
Inconel 600	29596	.04	14.72	75.66	.27	8.74	-	-	-	.17	.007	-	.37	42	97	44	-	-
Inconel 718	*	-	18.50	52.50	-	19.00	3.05	-	5.13	-	-	-	-	181	203	16	-	393
A286	*	.08	13.50-16.0	-	2.00 max		1.0-1.5	1.9-2.35		1.00 max	.003 max	.004 max	-	-	-	-	-	-
Hastalloy 6	*	1.10	28.0	3.0 max	-	3.0 max	-	-	Co Bal	1.00	-	-	-	4-W	-	-	-	-
Stellite 156	*	1.60	28.0	3.0 max	-	-	-	-	Co Bal	1.10	-	-	-	1-W	-	-	-	-
CN-1b-2-9 (LC-1H)	-	-	20.0	80.0	Cr_x	C_y	15% NiCr	-	-	-	-	-	-	Cr	-	-	-	-
LC-1C-2-2 (LC-1C)	-	-	20.0	80.0	Cr_x	C_y	12% NiCr	-	-	-	-	-	-	-	-	-	-	-
CN-1A-24 (LC-1H)	-	-	20.0	80.0	Cr_x	C_y	15% larger particle sizes NiCr					-	-	-	-	-	-	-

* = nominal analysis

TABLE III

SUMMARY OF RESULTS OF METALLOGRAPHICALLY MEASURED CRACK PENETRATION DEPTH AS AFFECTED BY CONDITIONS OF TEMPERATURE, TIME, AND NaOH COMPOSITION

	DEPTH OF CRACK (0.001 INCH)/EXPOSURE TIME (DAYS)					
CONCENTRATION NaOH (w/o)	10	40	50	60	70	80
Temperature						
377°F (192°C)					200/25 10/ 7 2.7/ 3	
330°F (166°C)				12.9/24 9.5/ 8 3.4/ 3		
300°F (149°C)						5/29 3.8/20 1.8/5
296°F (147°C)				15.1/24 1.1/ 8		
280°F (138°C)					5.8/32 2.0/ 7 1.3/ 3	
250°F (121°C)			4.7/25 3.0/12 2.4/ 6 0.9/ 3	2.7/21 1.3/ 8 0.4/ 3		
210°F (99°C)	2.5/25 2.4/15 1.5/ 4	3.0/24 1.9/15 0.7/ 4	1.1/22 0.7/10 0.5/ 7 0/ 7 0/ 6	0.3/25 0.3/ 7	1.2/31 0.3/ 8 0.3/ 4	

TABLE IV

CRACK PROPAGATION RATES

Temperature, °C (°F)	Crack Propagation Rate (in/yr) NaOH (w/o) 50	60	70
192 (377)	--	--	0.246
166 (330)	--	0.189	--
138 (280)	--	--	0.638
121 (250)	0.066	0.045	0.070
96 (210)	0.0175	0.0042	0.0136

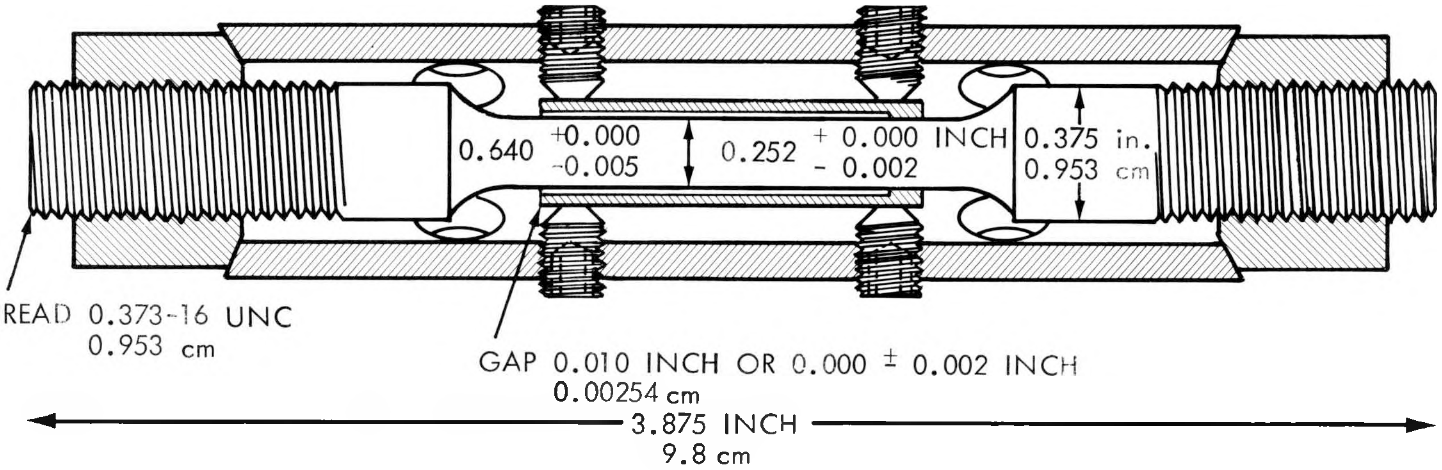
TABLE V

EFFECT OF STRESS ON CSCS

STRESS LEVEL (%)	EXPOSURE CONCENTRATION NaOH	TEMPERATURE, °C (°F)	TIME (DAYS)	CSCC MAXIMUM DEPTH METALOG (INCH)
100	50	138 (280)	14	0.005
100	50	138 (280)	14	0.006
67	50	138 (280)	14	0.005
67	50	138 (280)	14	0.005
33	50	138 (280)	14	0.004
33	50	138 (280)	14	0.005

SODIUM REMOVAL STRESS CORROSION CRACKING SPECIMENS

(TENSILE BAR FOLLOWS ASTM E8-69)



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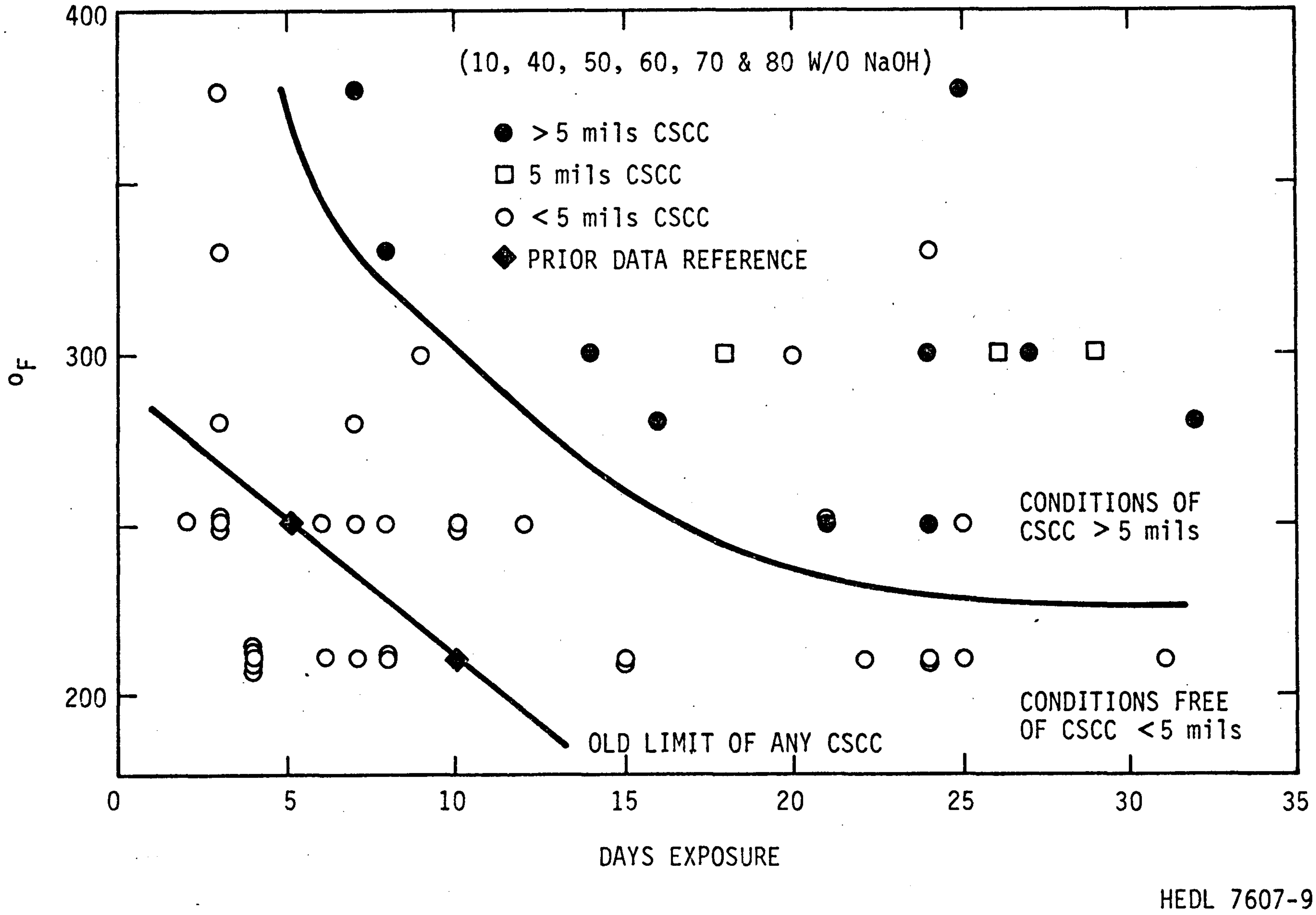


Figure 2. Effect of Temperature, Time and NaOH Concentration on Depth of Crack Penitration

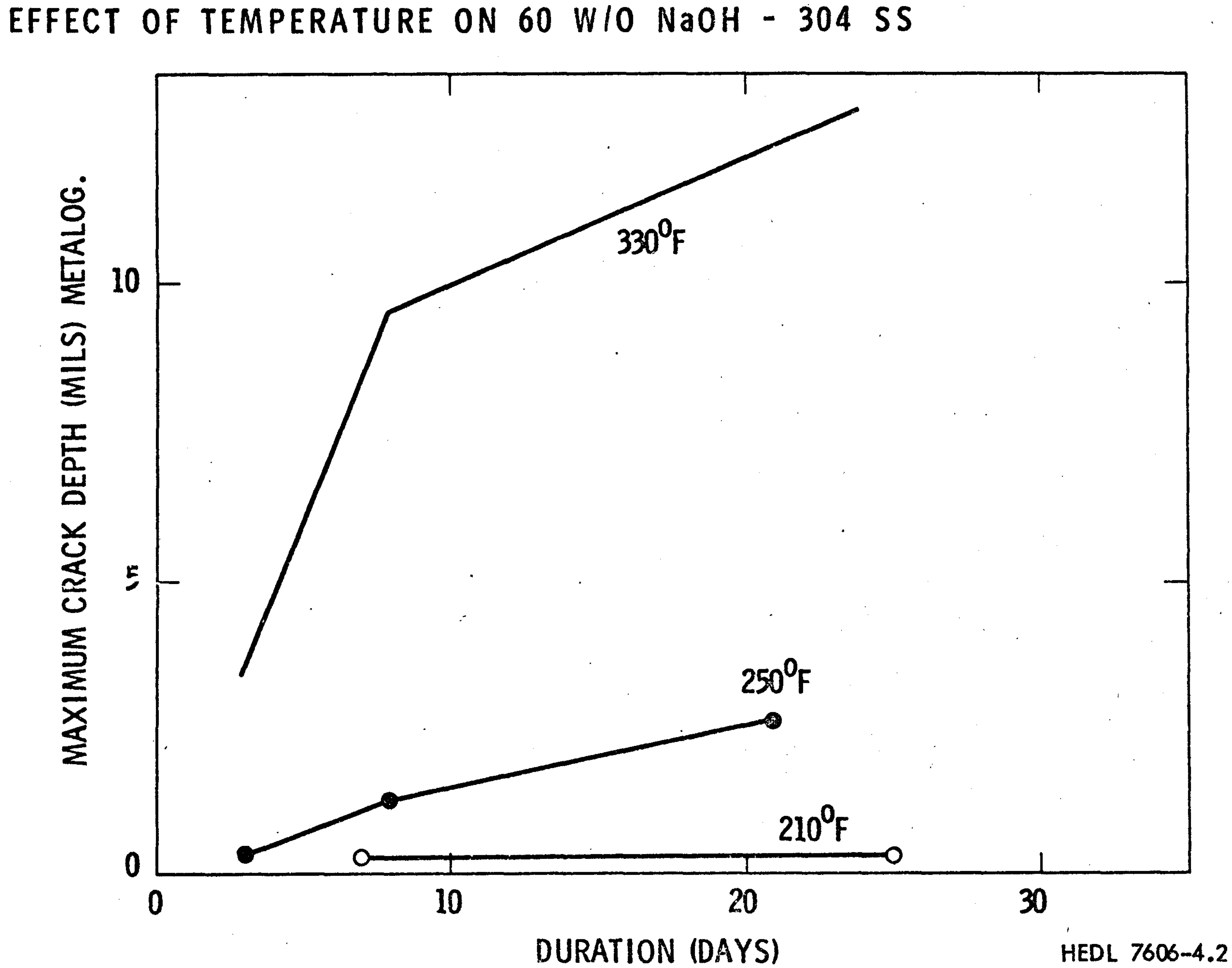


Figure 3. Effect of Temperature and Time on Depth of Crack Penitration in 60 w/o NaOH

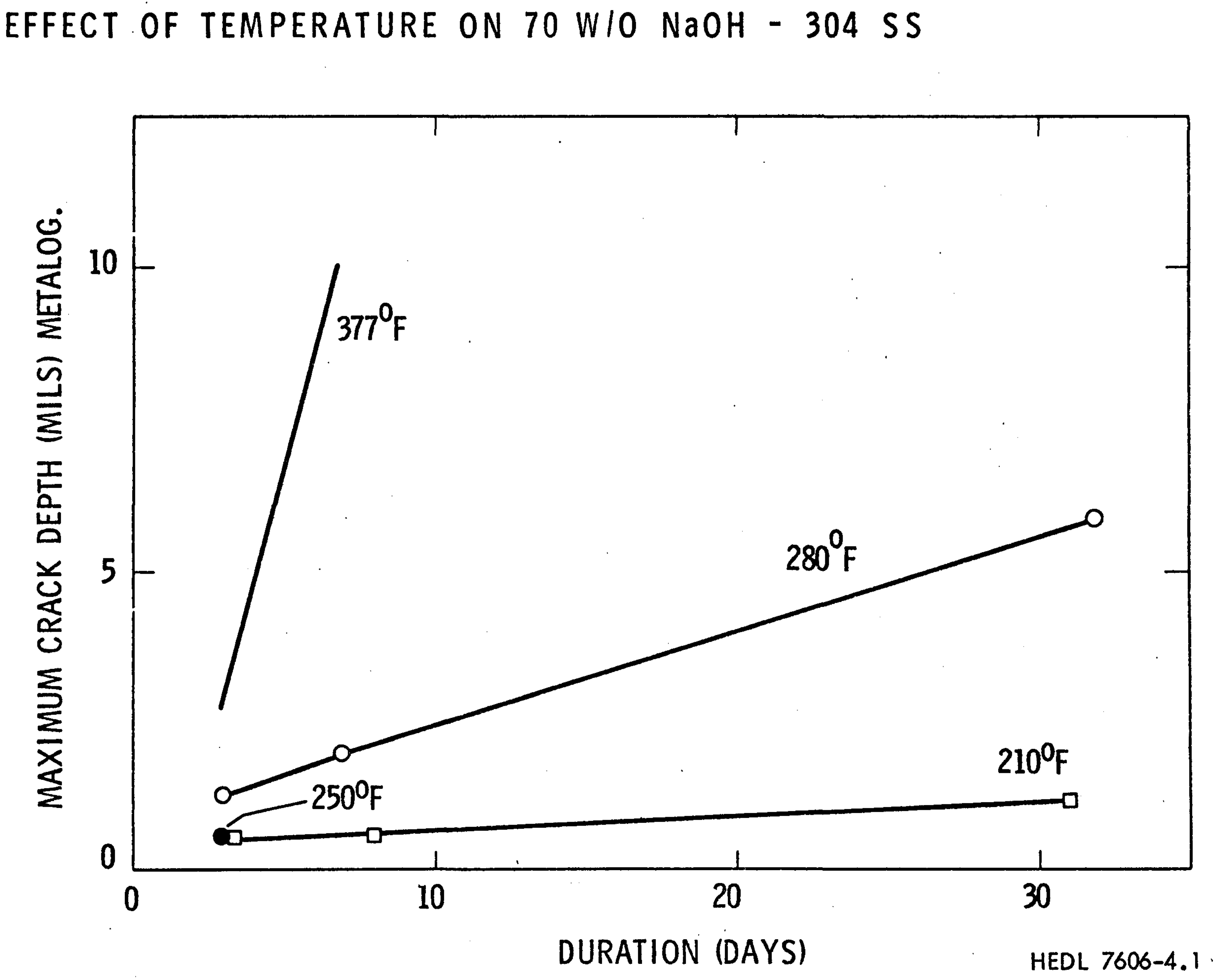


Figure 4. Effect of Temperature and Time on Depth of Crack Penitration in 70 w/o NaOH

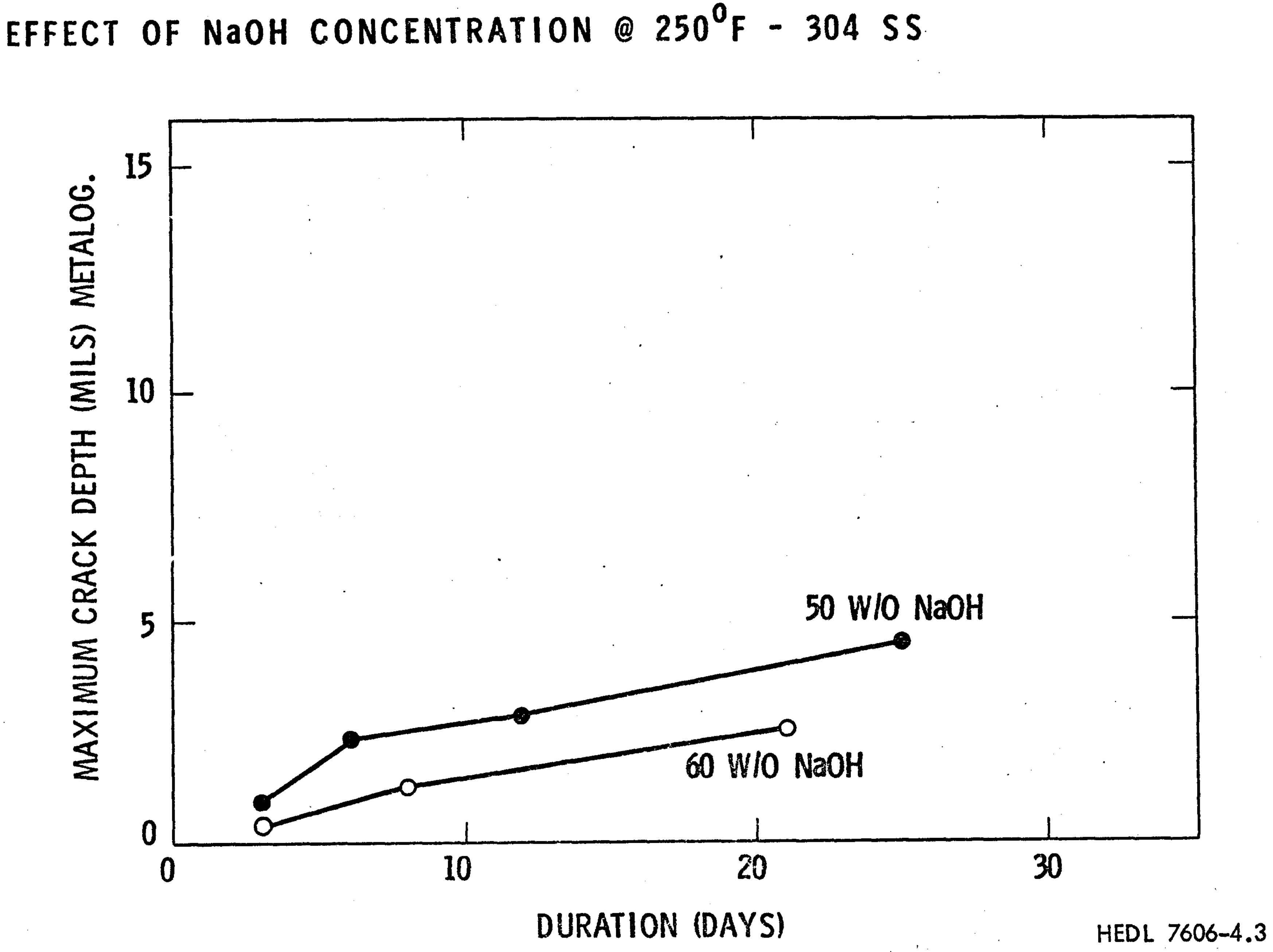
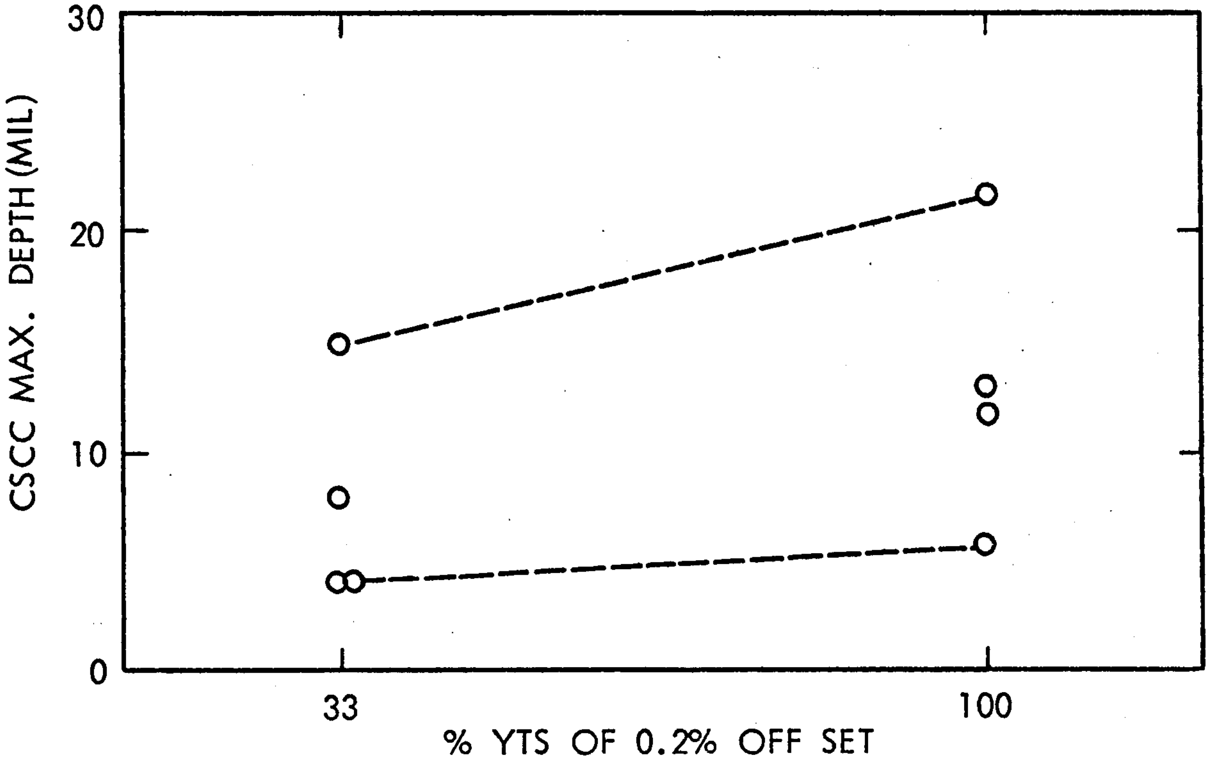


Figure 5. Effect of NaON Composition and Time on Depth of Crack Penitration at 250°F

EFFECT OF STRESS ON CSCC OF 304 SS
(50 W/O NaOH AT 250°F FOR 21 DAYS)



CONCLUSIONS:

1. RESULTS SHOW WIDE VARIANCES
2. DEPTH OF MAXIMUM CSCC DECREASES WITH STRESS
3. FIVE MIL MAXIMUM CRACK DEPTH WOULD REQUIRE YTS < 33%

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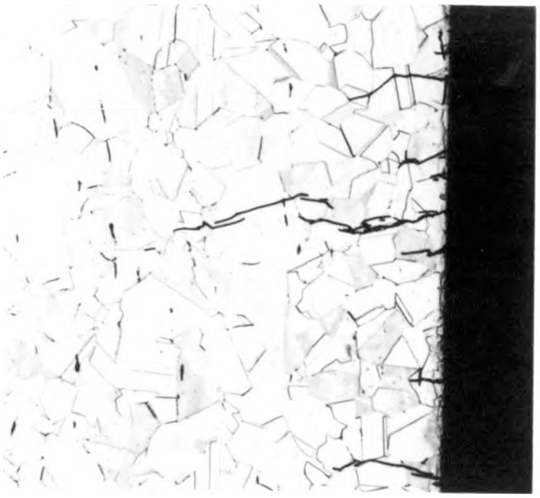
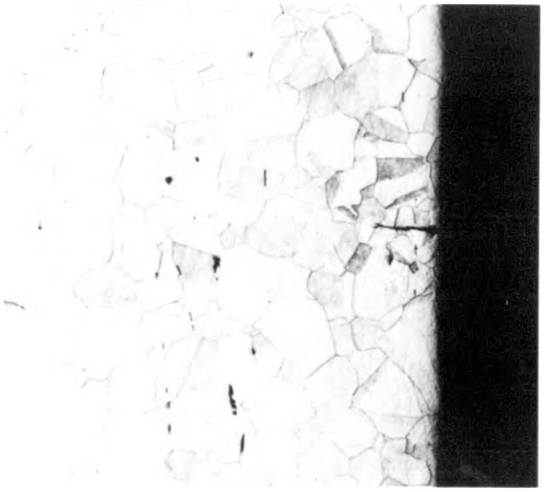
Figure 6. Effect of Stress State on Depth of Crack Penitration in 50 w/o NaOH at 250°F for 21 Days in 304 Type SS

EFFECT OF STRESS ON DEPTH OF CSCC
304 SS EXPOSED TO 50% NaOH AT 250°F FOR 21 DAYS



100% YTS
0.0163 INCH
(0.414 mm)



33% YTS
0.0038 INCH
(0.097 mm)

0.01 INCH
(0.254 mm)

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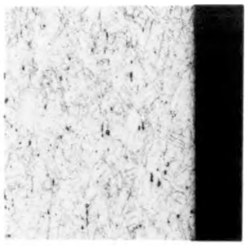
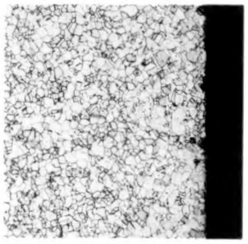
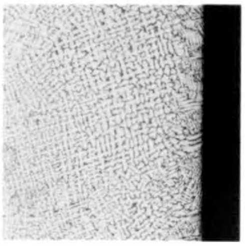
EFFECT OF ALLOY COMPOSITION ON CSCC
ALL SPECIMENS EXPOSED TO 50% NaOH AT 250°F FOR 21 DAYS



NO ATTACK
INCONEL 718
150 ksi YTS
Rc 45

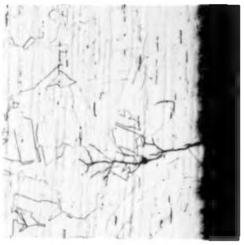


PITTING ONLY
A286 ALLOY
Rc 33
YTS 85 ksi

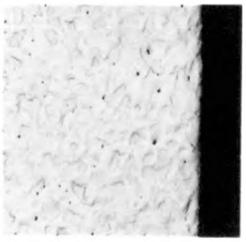


NO ATTACK
AS - CAST
STELLITE 6
WELD DEPOSIT

0.0037 INCH (0.094 mm)
DEPTH CSCC
TYPE 316 SS



0.0137 INCH (0.348 mm)
DEPTH CSCC
TYPE 304 SS



NO CSCC
SOLUTION ATTACK
NOT MEASURED
TYPE SA-36
CARBON STEEL

HEDL 7607-35.1