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# CAUSTIC STRESS CORROSION TESTS FOR THE LLTR

M. E. Indig



PREPARED UNDER CONTRACT E(04-3)-893
TASK 10





GENERAL ELECTRIC

## DISCLAIMER

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# CAUSTIC STRESS CORROSION TESTS FOR THE LLTR

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Task 10

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GENERAL ELECTRIC

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*ABSTRACT*

*A series of tests have been performed in order to determine the effects of the caustic resulting from the Na/$H_2O$ reaction on the materials used in the LLTR-MSG series of testing. Stainless steel, 2 1/4Cr-1Mo and carbon steel have been evaluated. Stress corrosion cracking susceptibility and general corrosion are reported. Over the range of temperature, caustic concentration and heating rate tested the stainless steel stressed to 90% of yield or above suffered cracking. Whereas, the 2-1/4Cr-1Mo and carbon steel were not cracked.*

## *ACKNOWLEDGEMENTS*

*The author wishes to extend his appreciation to Mr. A. N. Bornstein and Mr. J. E. Weber for performing the experiments described in this report.*

# CAUSTIC STRESS CORROSION TESTS FOR THE LLTR

## 1. INTRODUCTION

The introduction of a large amount of water in the sodium side of the LLTR-MSG system is planned at 600°F. In order to determine the effects of the resulting caustic on the materials of the LLTR-MSG system, a series of stress corrosion experiments were performed at VNC. Various heat-up rates from 9 to 35°F/h. were used to simulate actual system cooldown or heat-up rates that could be used following the planned sodium-water-metal experiment. In the LLTR experiment the cool-down would occur at one atmosphere and under a nitrogen purge. All laboratory experiments at VNC were performed under those same environmental conditions that would be expected in the LLTR. The main purpose of the tests was to determine the susceptibility of the vessel material, 2¼Cr-1Mo, and the piping materials (Type-304 stainless steel) to caustic cracking over the range of expected temperatures. A second purpose was to determine general corrosion rates or any other specific corrosion attack over the temperature range of interest; room temperature was held to 600°F.

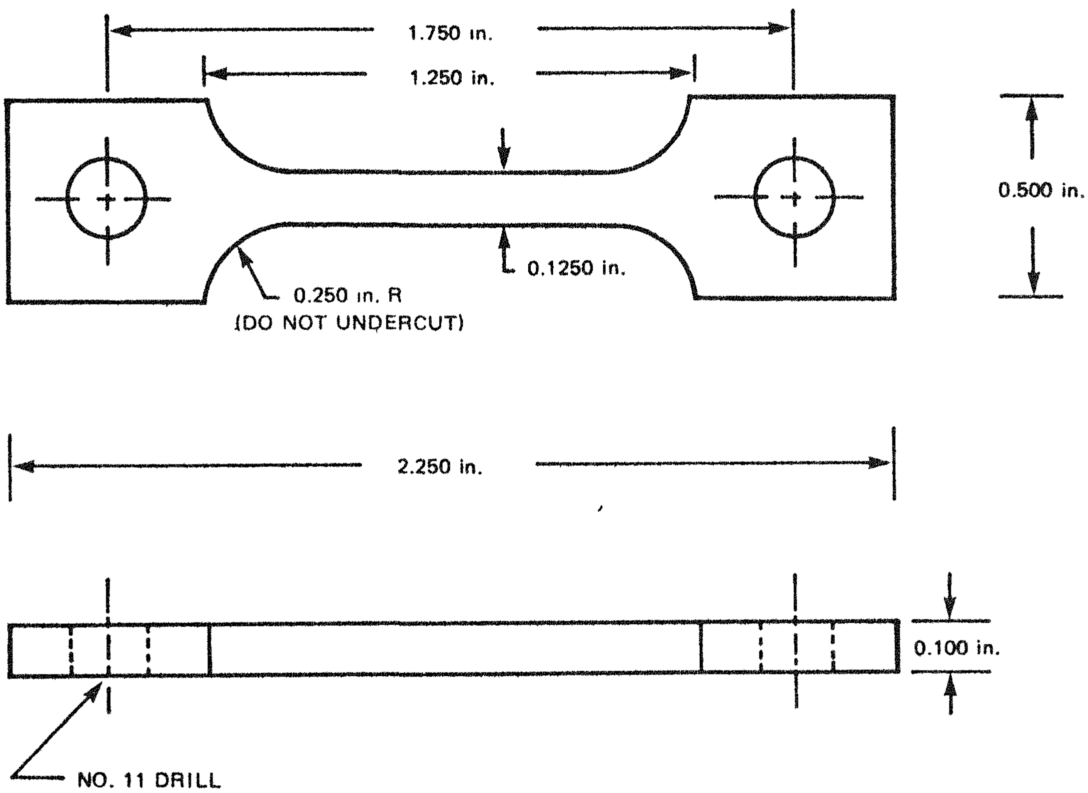


*Figure 1. Corrosion Tensile Specimen*

# 2. EXPERIMENTAL METHODS

## 2.1 MATERIALS

Dog-bone tensile samples were exposed to caustic solutions in all the tests performed. A drawing of the tensile samples is given in Figure 1. Three materials were used in the stress corrosion testing: Type-304 stainless steel, 2¼Cr-1Mo, and carbon steel (ASTM-A516 Grade 70). The carbon steel in plate form is similar to the replacement piping steel that could be used in the LLTR. The heat numbers, significant mechanical properties, and chemical compositions of the alloys are given in Table 1. The alloys investigated were used in several metallurgical conditions. Type-304 stainless steel was tested in the mill-annealed, solution-annealed and furnace sensitized condition; 2¼Cr-1Mo was tested in the as-received (normalized and tempered) and annealed conditions, and the carbon steel was tested in the as-received condition. The details of the heat treatments are given in Table 2.

## 2.2 TESTING ARRANGEMENT

Tensile samples of Type-304 stainless steel, 2¼Cr-1Mo and carbon steel (ASTM-A516 Grade 70) were loaded in a stressing facility and inserted into a 2-gallon, Type-316 stainless steel autoclave. The autoclave was protected from the test caustic solution by a nickel liner. Figure 2 shows a schematic of the experimental arrangement with one sample coupled to one piston. In an actual run eight samples are used which are connected to eight pistons. The pistons are pressurized individually so that a predetermined stress is maintained on each sample during the experiment. All internal fixtures of the stressing facility were fabricated from nickel or high nickel alloys for protection against caustic cracking. The pull rods were fabricated from Inconel X-750. A complete description of the testing arrangements is given in Reference 1.

Table 1

ALLOY COMPOSITIONS

| Material | Heat No. | Yield Point P.S.I. | Tensile Strength P.S.I. | % C | % Mn | % P | % S | % Si | % Ni | % Cr | % Mo | % Co | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 304 S.S. | X 11224 | 38,000 | 85,100 | 0.06 | 1.36 | 0.023 | 0.028 | 0.74 | 8.36 | 18.69 | 0.37 | 0.14 | 0.27 |
| 2¼Cr-1Mo | 88541 | 59,500 | 83,200 | 0.12 | 0.47 | 0.017 | 0.025 | 0.39 | 0.12 | 2.25 | 0.97 | | 0.14 |
| A516-70 | D 1923A4 | 51,700 | 80,300 | 0.23 | 1.05 | 0.012 | 0.023 | 0.18 | | | | | |

In the first two runs, D001 and D002, no attempt was made to electrically insulate the tensile samples from the stressing fixture. In our experimental arrangement the samples are connected to pins, clevices, and pull-rods which could cause galvanic coupling between samples or other internal portions of the stressing facility. Data obtained from N. Hoffman of LMEC indicated that carbon steel coupled to Type-304 stainless steel would prevent the stainless steel from cracking in caustic. Thus in the runs following D002, the specimens were electrically insulated from the retaining plate and clevices by using pre-oxidized Zr-2.5Nb retaining pins, bottom shims of pre-oxidized Zircaloy-4 and strips of Teflon.

Table 2

HEAT TREATMENT*

| Material | Type | Temperature ($^{o}$F) | Time | Quench |
|---|---|---|---|---|
| Type-304 SS | Solution Annealed | 1900 | 1 h | $H_2O$ |
| Type-304 SS | Furnace Sensitized | 1150 | 24 h | Argon |
| 2¼Cr-1Mo | Annealed | 1695 | 20 min | |
| | | Cool to: | | |
| | | 1350 | 45 min | Air |

*All other conditions were as-received

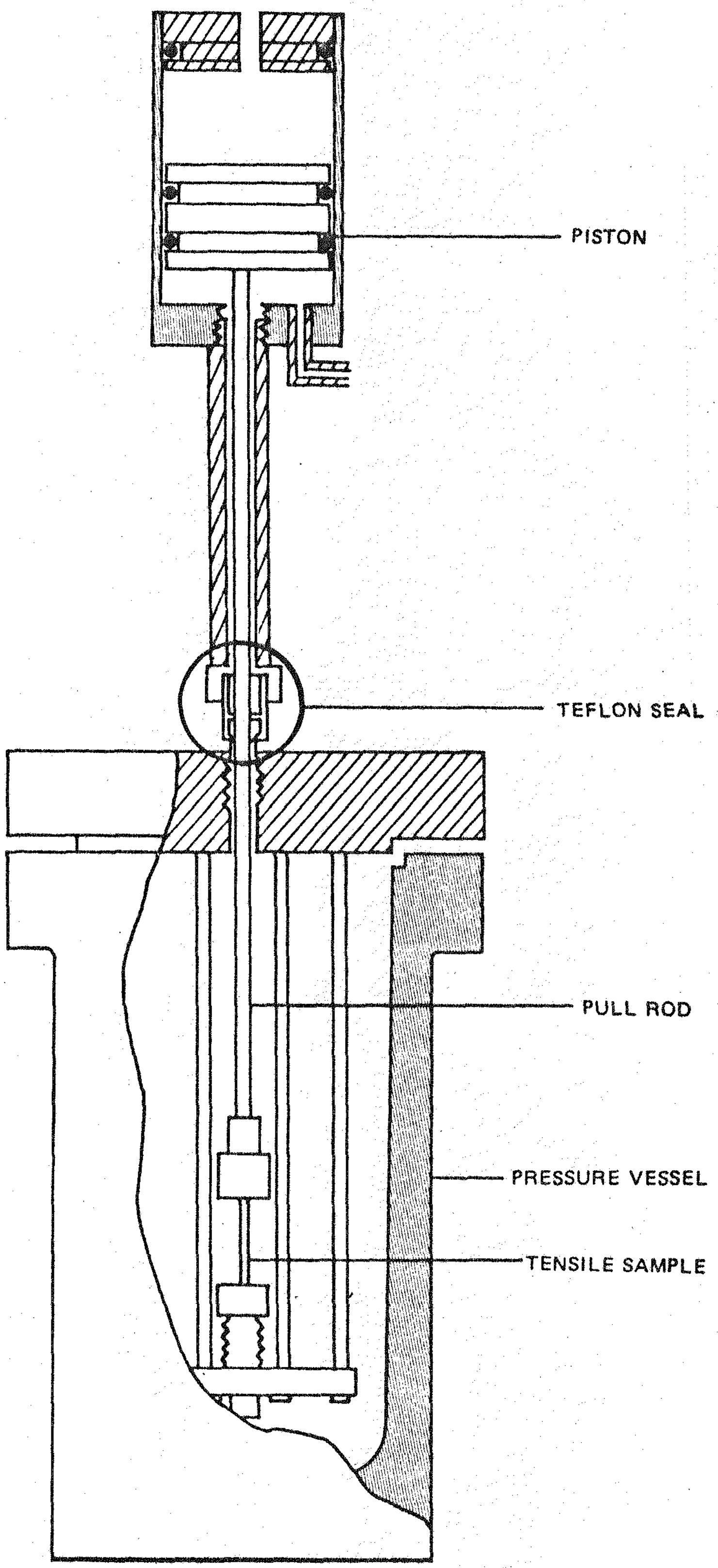


*Figure 2. Schematic Drawing of the Test Apparatus*

2.3 METHOD OF PERFORMING TESTS

The general experimental method used was to fill the nickel liner in the autoclave body with proper volume and concentration of NaOH solution, seal the autoclave head containing the samples and stressing facility to the autoclave body and evaluating the autoclave. The autoclave was then purged with one atmosphere of nitrogen and the purge maintained during the entire heating period. The pistons were then pressurized which stressed the samples, and the heating was initiated at a predetermined rate. During the heating period, the solution concentrated according to the NaOH-$H_2O$ boiling point curve shown in Figure 3. At 600$^{o}$F, the heaters were shut off, the pistons de-pressurized, the autoclave head unbolted and the head containing the samples was quenched in a bucket of water. After cooling, the samples were removed from the stressing facility, dimensionally analyzed, and examined with an optical stereoscope up to 140X. Selected samples were also examined non-destructively with a scanning electron microscope and eventually sectioned for metallographic examination.

In the first experiment, D001, a starting solution of 16% NaOH was used and heating rate of 18$^{o}$F/h. was desired. The heating rate shown in Figure 4 was considerably below the required rate especially in the 220-240$^{o}$F range. In this temperature range large amounts of steam must be formed and vented in order to increase the temperature and concentration of the internal solution. In this run the solution level eventually dropped below the gage section of the stressed samples. By calculation and experimental measurements, it is believed that the samples were covered with solution until 320 $\pm$ 10$^{o}$F. Run D001 was terminated at 500$^{o}$F. All subsequent runs were conducted with a starting solution of 35% NaOH and the solution could concentrate to 95% without uncovering the samples.

Runs D002 and D003 were conducted at the 18$^{o}$F/h. heating rate. Run D003 was conducted in order to determine whether the use of electrically conducting sample retaining pins had influenced the stress corrosion behavior by galvanic coupling as discussed previously.

Run D004 was conducted at nominal heating rates of 36$^{o}$F/h. However, as shown in Figure 5 the heating rate achieved was below the required rate in the lower temperature regime. Thus, the run was repeated (D005, shown in Figure 6), in order to obtain an adequate heating rate in the temperature range where the caustic solution undergoes the greatest change in concentration.

Run D006 shown in Figure 7 was conducted at the slowest heating rate, $9^{0}F/h$ and was the final experiment of the present phase.

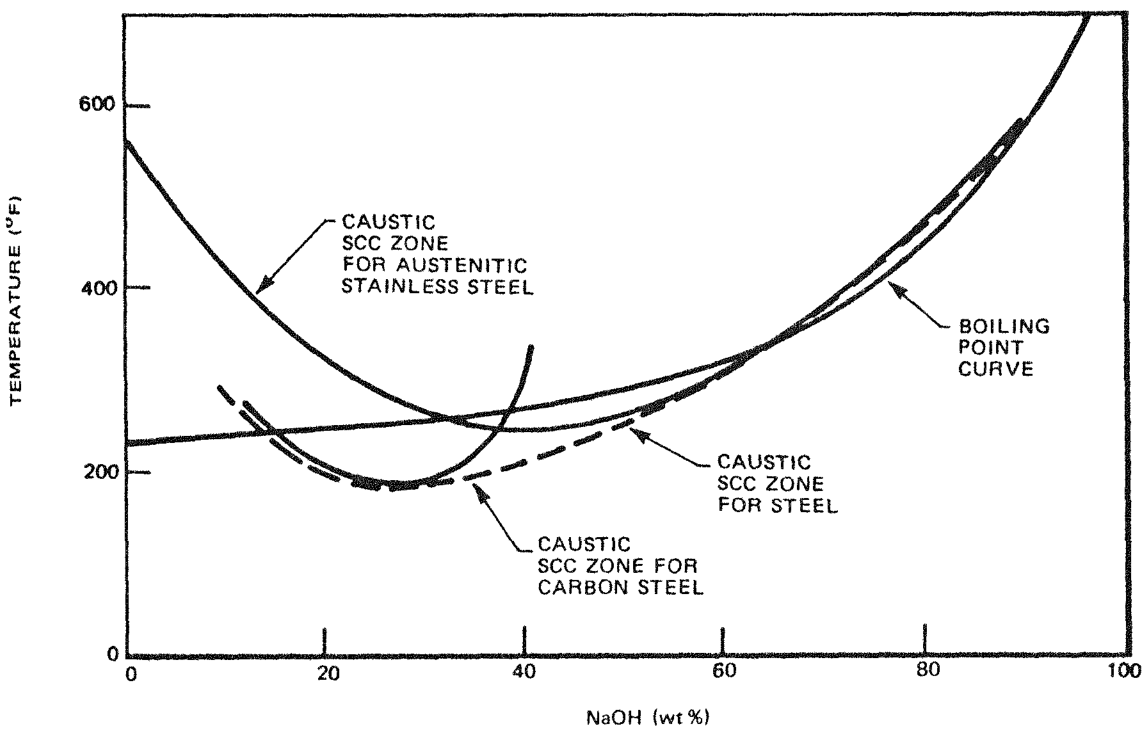


*Figure 3. Boundaries of Caustic SCC Danger Zones*

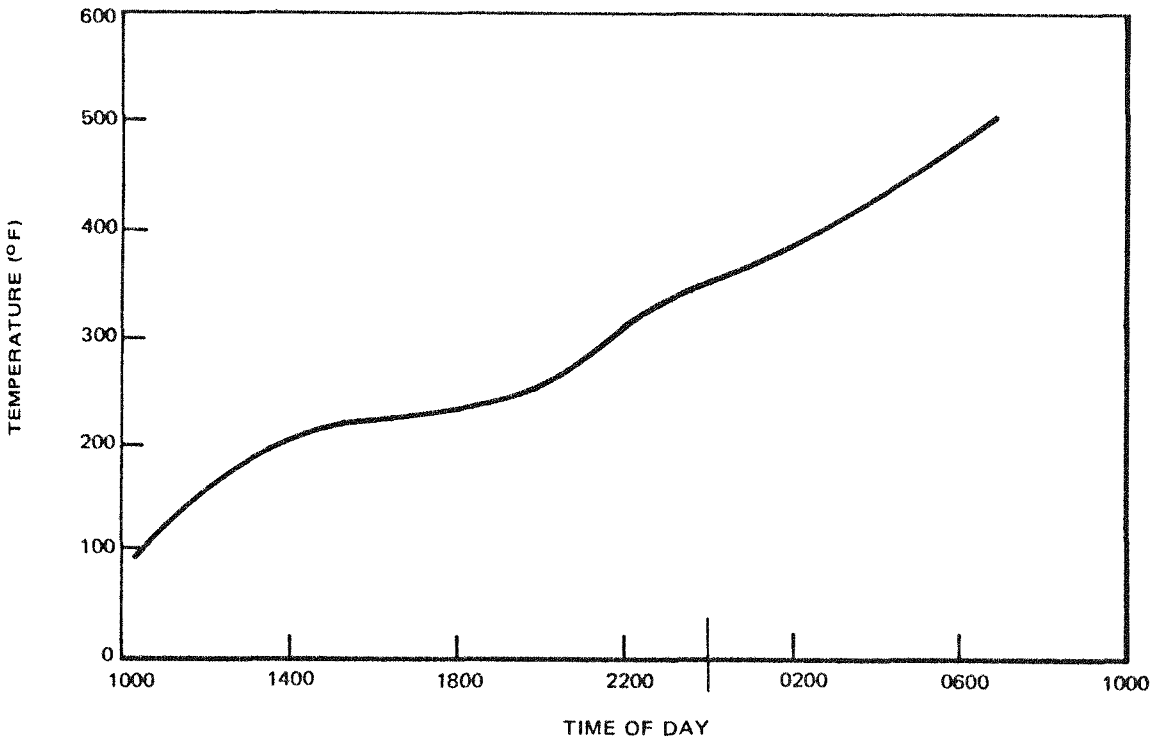


*Figure 4. Time – Temperature Curve (Run D001)*

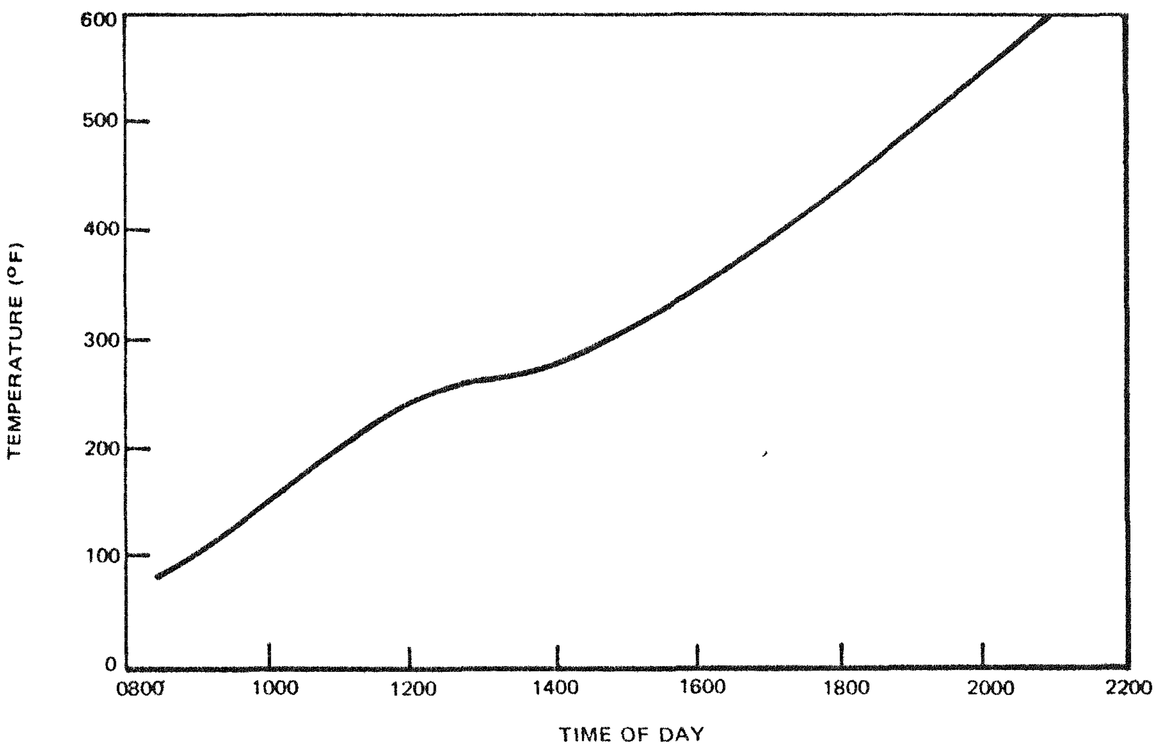


*Figure 5. Time – Temperature Curve (Run D004)*

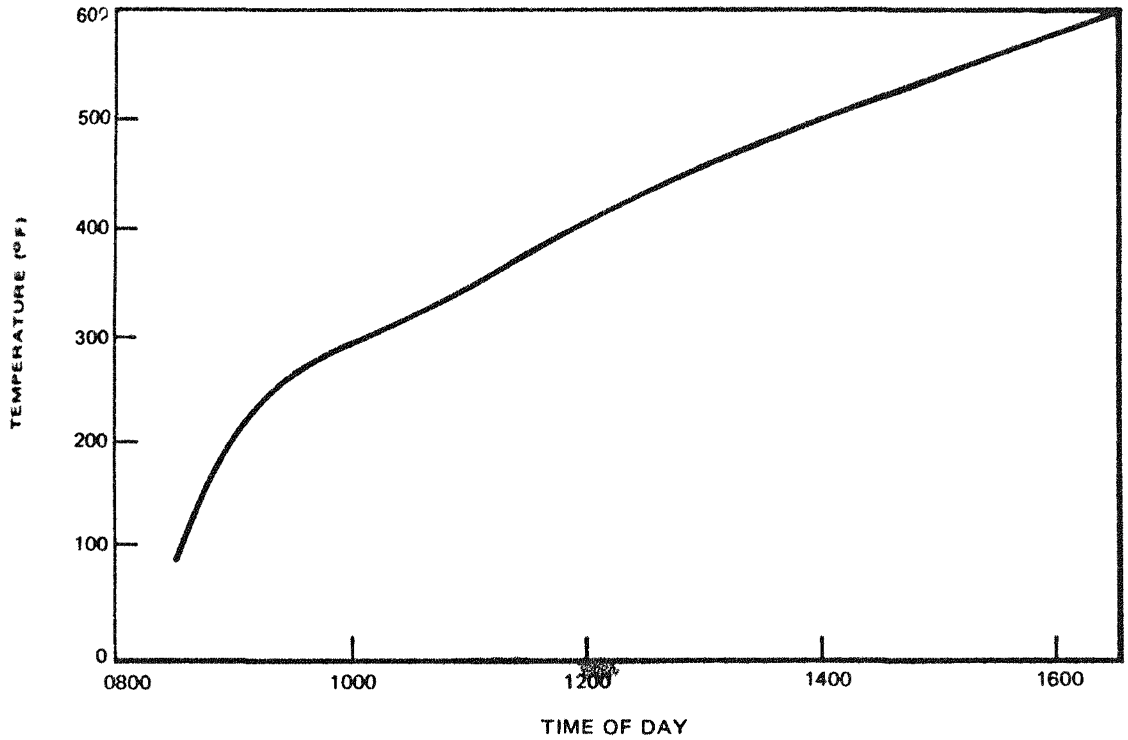


*Figure 6. Time — Temperature Curve (Run D005)*

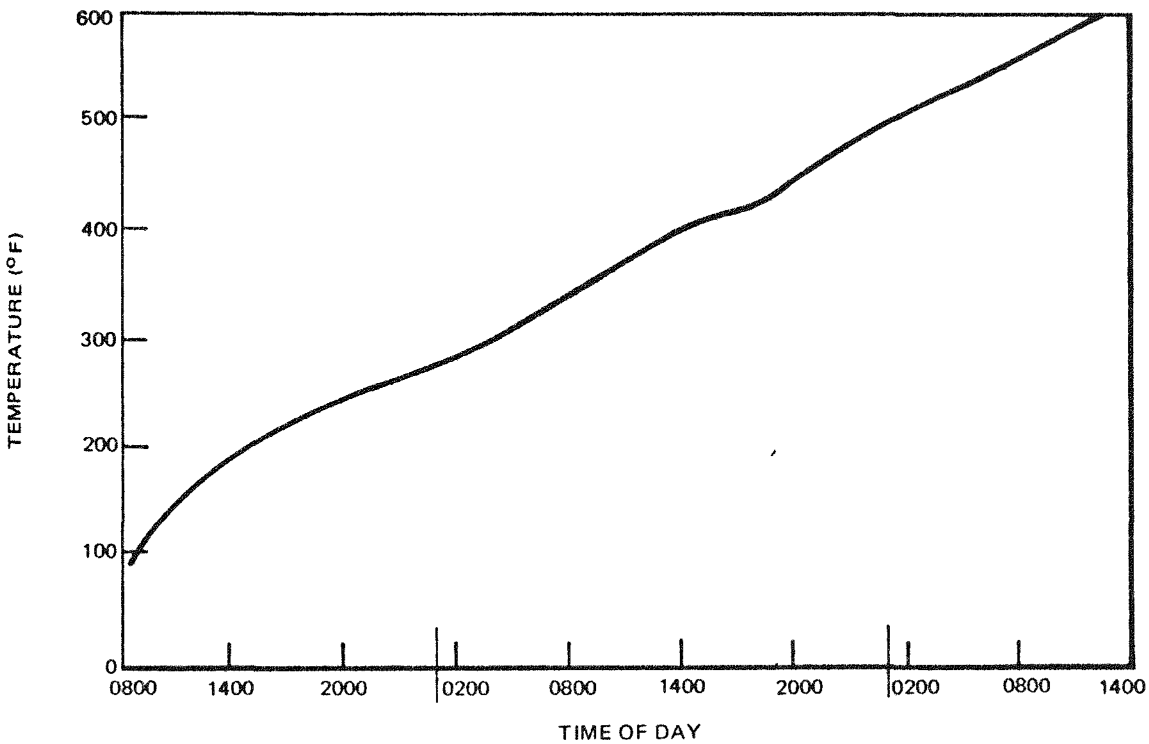


*Figure 7. Time — Temperature Curve (Run D006)*

## 3. STRESS CORROSION RESULTS

Tables 3 to 7 list the samples, metallurgical conditions, applied stresses and stress corrosion results. No stress corrosion occurred on the 2¼Cr-1Mo and carbon steel at any applied stress regardless of the heating rate. On the other hand the stainless steel was found quite susceptible to stress cracking. The degree of cracking depended on the applied stress and the heating rate. In runs D001 and D002, at 18$^{O}$F/h, the stainless steel samples stressed to 75% of yield strength (based on the 300$^{O}$F yield strength) did not show any obvious cracking by examination up to 140X. However those stressed to 100 and 150% of the yield were cracked. In run D003 also at 18$^{O}$F/h. the stainless steels stressed at 90, 100 and 150% of yield cracked.

In our experiments there appears to be no galvanic effects between samples or the test facility. Thus no difference in the stress corrosion behavior or stainless steel was noted in run D003 where the samples were electrically insulated, compared to runs D001 and D002 where there was no attempt to insulate the specimens.

Figures 8, 9 and 10 are scanning electron micrographs of a mill-annealed stainless steel sample from run D003 stressed at 100% of the 300$^{O}$F yield strength. The edge cracks are clearly intergranular while surface cracks appear to be mixed mode. Some cracks appear to initiate at pits.

The morphology of the cracking of both solution-annealed and furnance sensitized Type-394 stainless steel is especially interesting in run D004. The sensitized and solution annealed samples show the networks of continuous carbides at the grain boundaries as well as transgranular cracks as shown in Figures 11 and 12. Non-metallic inclusions appear to be initiation sites for some transgranular cracks.

Table 3

RUN D001 MATERIALS STRESSES AND OBSERVATIONS

| Alloy | Metallurgical Condition | Stress (ksi) | Observation[a] |
|---|---|---|---|
| $2\frac{1}{4}$Cr-1Mo | Normalized and Tempered | 35 | No SCC[b] |
| $2\frac{1}{4}$Cr-1Mo | Normalized and Tempered | 52.5 | No SCC |
| Type-304 SS | Mill Annealed | 23.3 | No SCC |
| Type-304 SS | Mill Annealed | 31 | Slight Cracks, SCC |
| Type-304 SS | Mill Annealed | 46 | Deep Cracks, SCC |
| Carbon Steel[c] | As Received | 34.5 | No SCC |
| Carbon Steel[c] | As Received | 46 | No SCC |
| Carbon Steel[c] | As Received | 69 | No SCC |

Table 4

RUN D002 MATERIALS STRESSES AND OBSERVATIONS

| Alloy | Metallurgical Condition | Stress (ksi) | Observation |
|---|---|---|---|
| $2\frac{1}{4}$Cr-1Mo | Normalized and Tempered | 35 | No SCC[b] |
| $2\frac{1}{4}$Cr-1Mo | Normalized and Tempered | 52.5 | No SCC |
| Type-304 SS | Mill Annealed | 23.3 | No SCC |
| Type-304 SS | Mill Annealed | 31 | Edge Cracks, SCC |
| Type-304 SS | Mill Annealed | 46 | SCC over entire gage length |
| Carbon Steel[c] | As Received | | No SCC |
| Carbon Steel[c] | As Received | | No SCC |
| Carbon Steel[c] | As Received | | No SCC |

[a] Initial sample examinations at 140X
[b] Stress corrosion cracking
[c] ASTM-A516 Grade 70

Table 5

RUN D003 MATERIALS STRESSES AND OBSERVATIONS

| Alloy | Metallurgical Condition | Stress (ksi) | Observation[a] |
|---|---|---|---|
| $2\frac{1}{4}$Cr-1Mo | Annealed | 30 | No SCC[b] |
| $2\frac{1}{4}$Cr-1Mo | Annealed | 40 | No SCC |
| $2\frac{1}{4}$Cr-1Mo | Annealed | 60 | No SCC |
| Type-304 SS | Mill Annealed | 27.9 | Minor Edge SCC |
| Type-304 SS | Mill Annealed | 31 | Minor Edge SCC |
| Type-304 SS | Mill Annealed | 46.5 | Edge SCC |
| Carbon Steel[c] | As-Received | 51.7 | No SCC |
| Carbon Steel[c] | As-Received | 70 | No SCC |

Table 6

RUN D004 MATERIALS STRESSES AND OBSERVATIONS

| Alloy | Metallurgical Condition | Stress (ksi) | Observation[a] |
|---|---|---|---|
| $2\frac{1}{4}$Cr-1Mo | Annealed | 30 | No SCC |
| $2\frac{1}{4}$Cr-1Mo | Annealed | 40 | No SCC |
| $2\frac{1}{4}$Cr-1Mo | Annealed | 60 | No SCC |
| Type-304 SS | Sol'n Annealed | 27.9 | No SCC |
| Type-304 SS | Sol'n Annealed | 31 | Minor Edge SCC[d] |
| Type-304 SS | Sol'n Annealed | 46.5 | Minor SCC |
| Type-304 SS | Furnace Sensitized | 46.5 | Edge SCC |
| Carbon Steel | As-Received | 69 | No SCC |

[a] Initial sample examination at 150X
[b] Stress Corrosion Cracking
[c] ASTM-A516 Grade 70
[d] Appears to be some grain dropping

Table 7

RUN D005 (36°F/h) MATERIALS STRESSES AND OBSERVATIONS

| Alloy | Metallurgical Condition | Stress (ksi) | Observation[a] |
|---|---|---|---|
| 2¼Cr-1Mo | Annealed | 30 | No SCC |
| 2¼Cr-1Mo | Annealed | 40 | No SCC |
| 2¼Cr-1Mo | Annealed | 60 | No SCC |
| Type-304 SS | As-Received | 27.9 | Minor SCC |
| Type-304 SS | As-Received | 31 | SCC at edges |
| Type-304 SS | As-Received | 62 | SCC |
| T pe-304 SS | Furnace Sensitized | 62 | SCC |
| Carbon Steel | As-Received | 70 | SCC |

[a]Initial sample examination at 140X

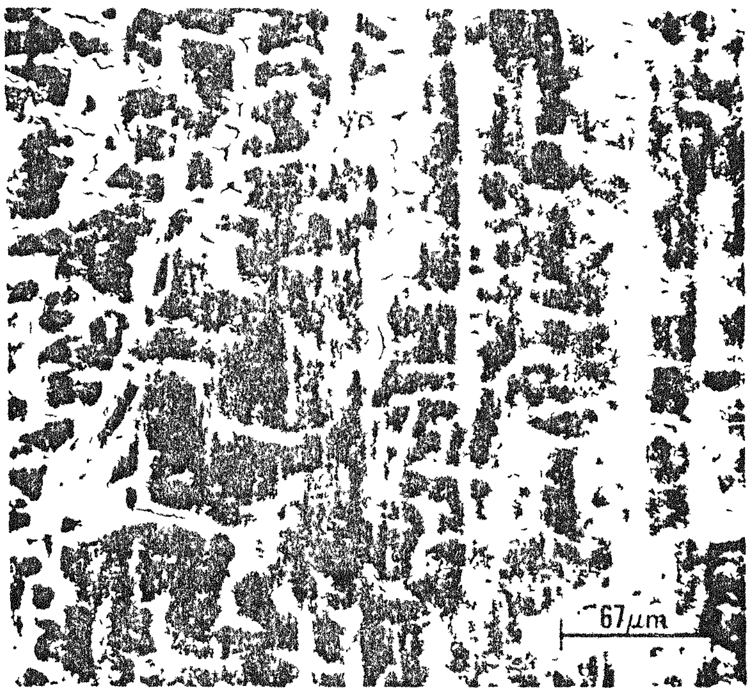


*Figure 8. SEM of Cracked Type-304 Stainless Steel (Run D003)*

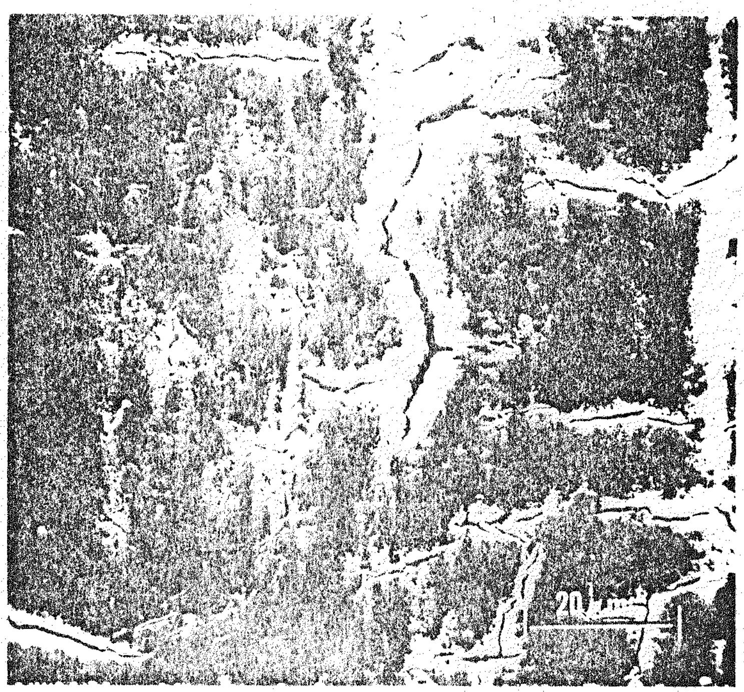

*Figure 9. SEM of Cracked Type 304 Stainless Steel (Run D003)*

*Figure 10. SEM of Cracked Type 304 Stainless Steel (Run D003)*

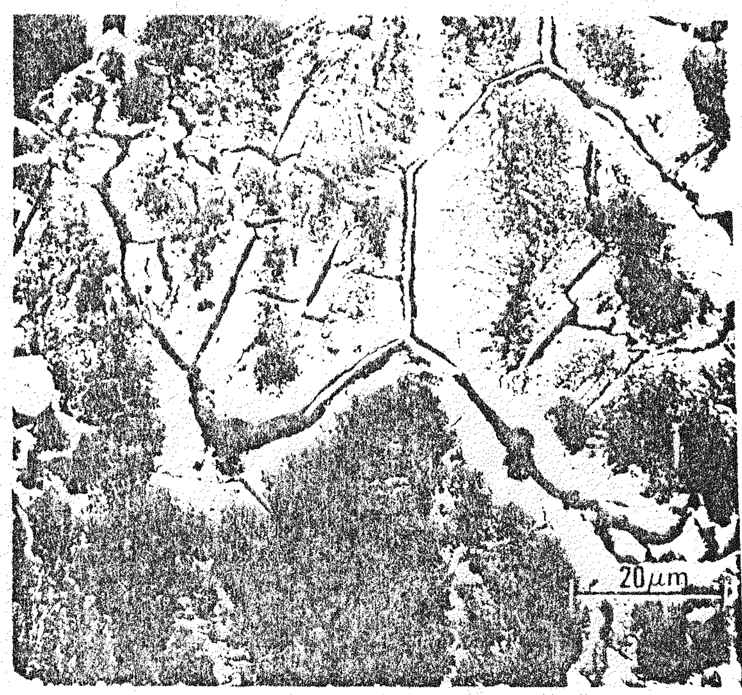


*Figure 11. SEM Cracked, Solution Annealed Type-304 Stainless Steel (Run D004)*

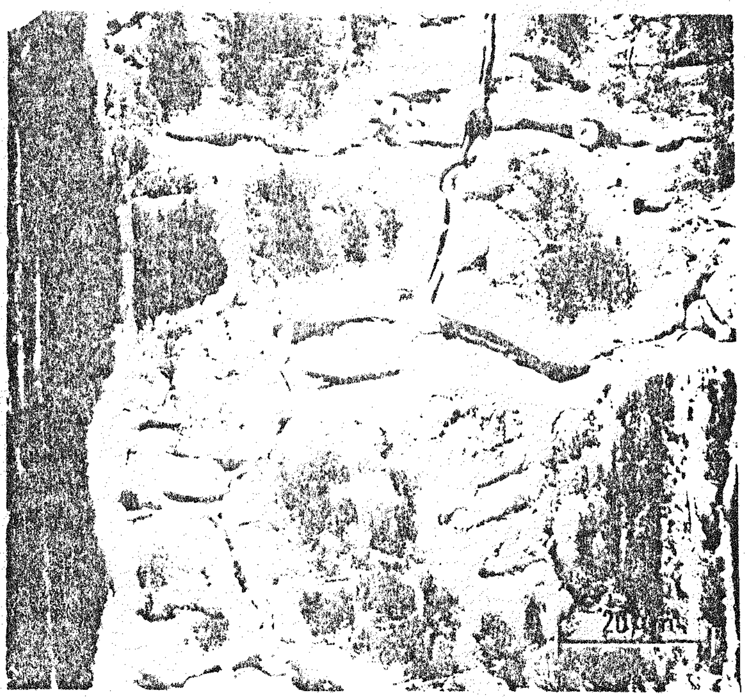


*Figure 12. SEM, Cracked Furnace Sensitized Type-304 Stainless Steel (Run D004)*

Figures 13 and 14, from run D005, compares a surface scanning electron micrograph (SEM) and a metallographic micrograph of a mill-annealed stainless steel. Crack initiation sites can be seen with the SEM and the very shallow, mostly transgranular cracks are evident with the metallographic section. This sample was stressed at 100% of the yield strength and heated at 36°F/h. At 200% of the yield strength, the cracking depth increases significantly as shown in Figure 15. Run D006, at 9°F/h heating rate — the slowest heating rate studied — had the most severe cracking. In this run, Type-304 stainless steel samples stressed at 200% of the yield strength completely parted.

In comparison, the highly stressed $2\frac{1}{4}$Cr-1Mo and carbon steel samples showed no evidence of stress corrosion. Figures 16 and 17 show the general metallographic sections of the highly stressed samples after exposure to the caustic solution.

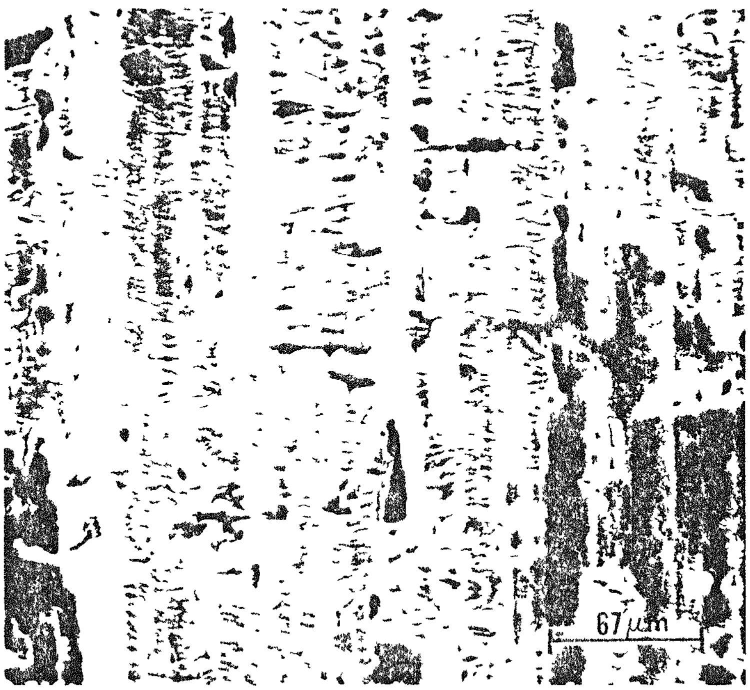


*Figure 13. SEM, Cracked Mill Annealed Type-304 Stainless Steel (Run D005) Stressed to 100% of Yield Strength*

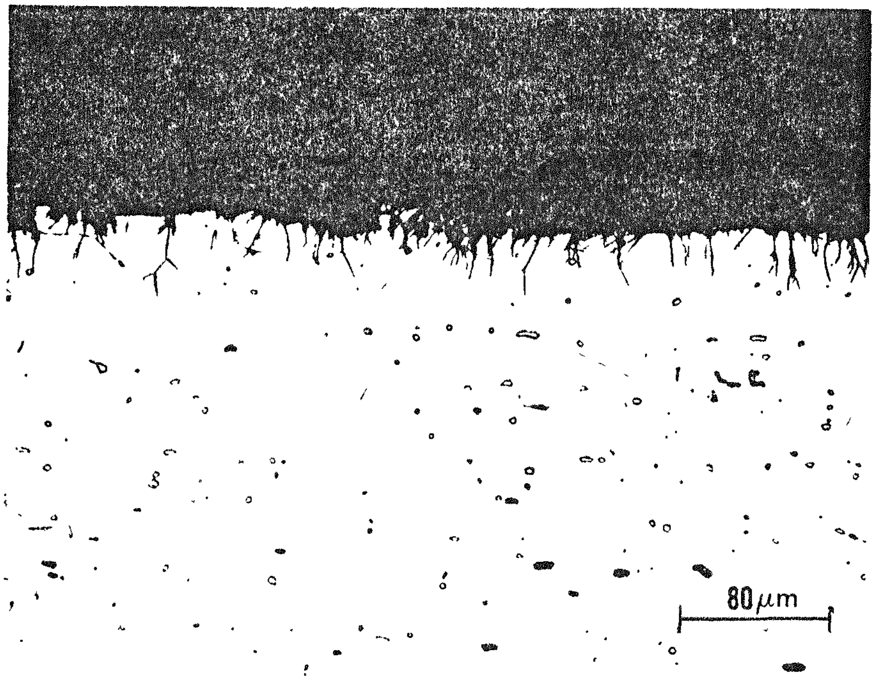


*Figure 14. Metallography of Figure 11*

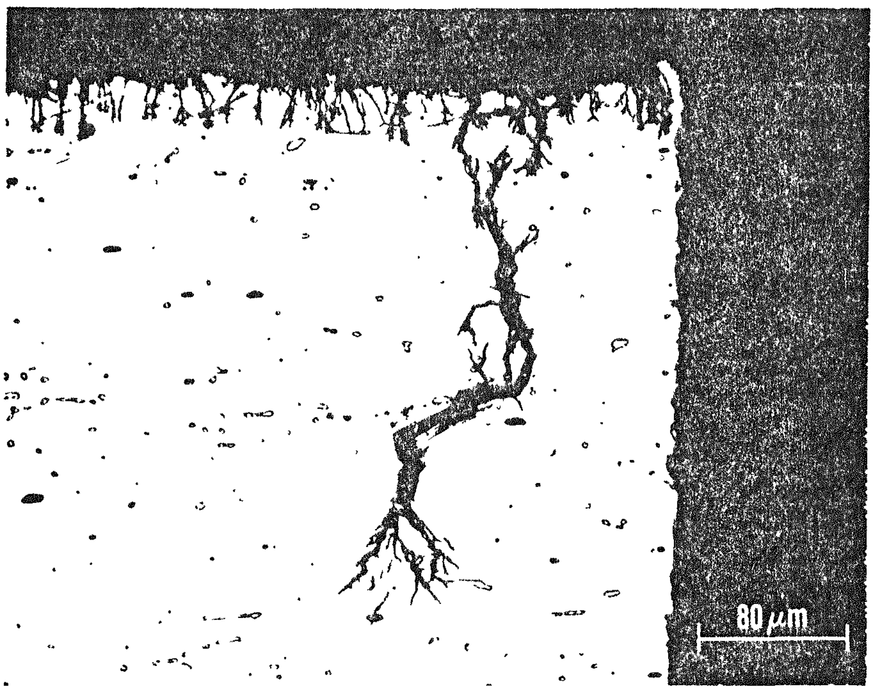


*Figure 15. Cracking of Type-304 Stainless Steel Heated at 36$^{o}$F/h, Stressed at 200% of Yield Strength*

Table 8

RUN D006 ($9^{o}F/h$) MATERIALS STRESSES AND OBSERVATIONS

| Alloy | Metallurgical Condition | Stress (ksi) | Observation[a] |
|---|---|---|---|
| 2¼Cr-1Mo | Annealed | 30 | No SCC |
| 2¼Cr-1Mo | Annealed | 40 | No SCC |
| 2¼Cr-1Mo | Annealed | 60 | No SCC |
| Type-304 SS | As-Received | 27.9 | Minor SCC |
| Type-304 SS | As-Received | 31 | SCC |
| Type-304 SS | As-Received | 62 | Fractured |
| Type-304 SS | Furnace Sensitized | 62 | Fractured |
| Carbon Steel | As-Received | 70 | No SCC |

[a]Initial sample examination at 140X

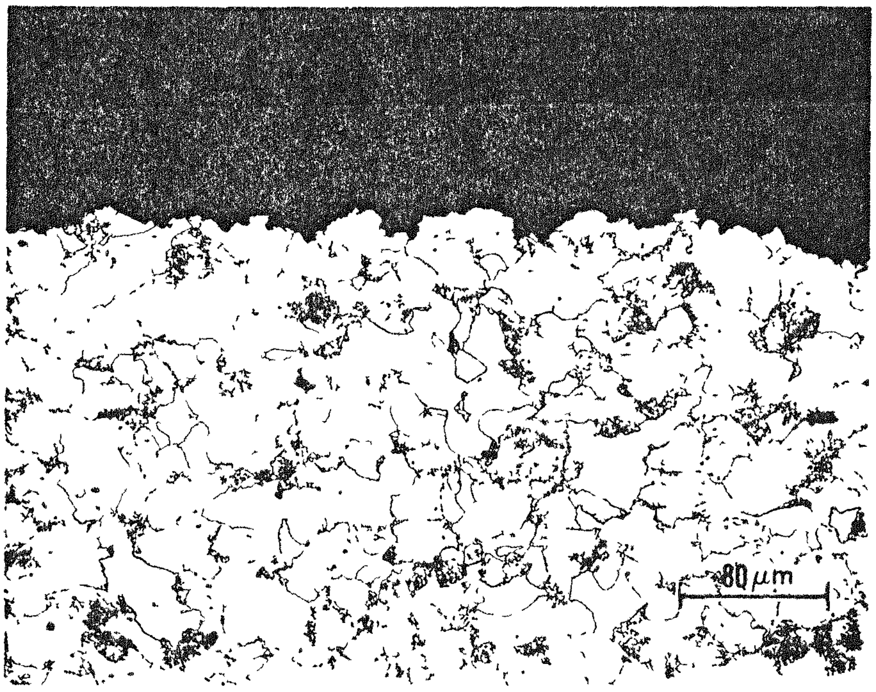


*Figure 16. Metallography of Highly Stressed and Corroded 2-1/4Cr-1Mo (Run D003)*

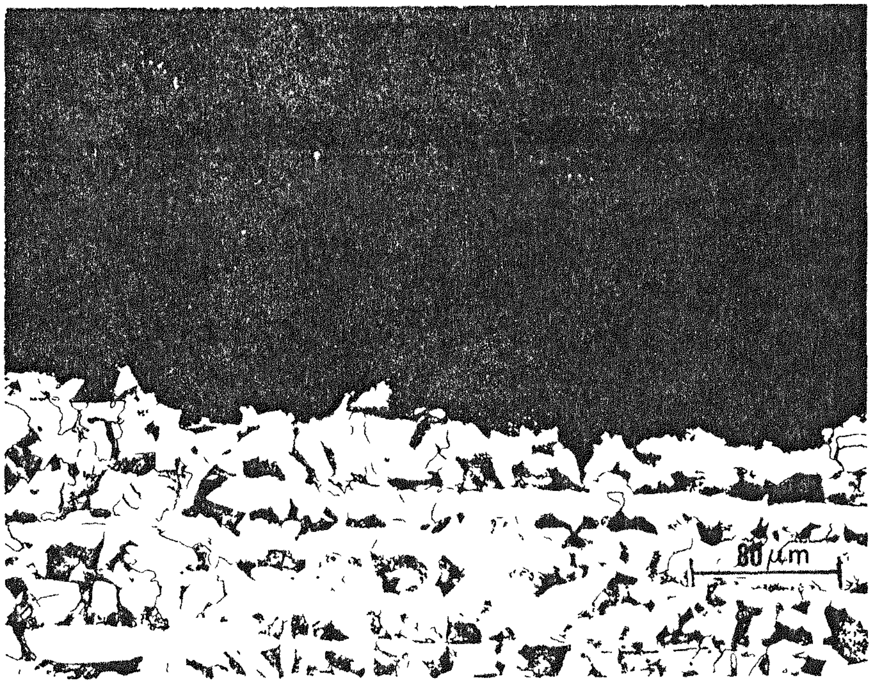


*Figure 17. Metallography of Highly Stressed and Corroded Carbon Steel (Run D006)*

## 3.1 GENERAL CORROSION

In order to evaluate the general corrosion rate of the materials studied, all the cross-sections of all specimens tested were measured before and after the test. Because samples stressed over the yeild strength have reduced gage sections due to strain as well as corrosion, their net dimensional changes are expected to be the greatest. For this reason the only dimensional measurements given in Table 9 are for samples stressed at or below the yield strength. Samples from run D001 may be expected to have lower corrosion rates because these samples were uncovered above 320°F. Because of the formation of general surface oxides which are included in the measurements, a few selected samples were measured destructively by obtaining metallographic cross-sections. In the metallographic sections, the oxide can readily be distinguished from metal. It was found that surface oxides were <0.001 inch and thus too thin to significantly affect the measurements.

Table 9

DIMENSIONS OF SAMPLE GAGE SECTIONS BEFORE AND AFTER TEST - SAMPLES STRESSED AT OR BELOW YIELD STRENGTH

| Run | Sample | Alloy | Cross-Sections (in.) Before Test | After Test |
|---|---|---|---|---|
| D-001 | 1048 | $2\frac{1}{4}$Cr-1Mo | 0.120 x 0.097 | 0.116 x 0.094 |
| | 1049 | $2\frac{1}{4}$Cr-1Mo | 0.120 x 0.098 | 0.116 x 0.093 |
| | 1314 | Carbon Steel | 0.122 x 0.095 | 0.122 x 0.095 |
| | 1315 | Carbon Steel | 0.122 x 0.095 | 0.120 x 0.093 |
| | 15 | Type-304 SS | 0.123 x 0.098 | 0.123 x 0.098 |
| | 16 | Type-304 SS | 0.123 x 0.099 | 0.124 x 0.099 |
| D-002 | 1050 | $2\frac{1}{4}$Cr-1Mo | 0.121 x 0.097 | 0.115 x 0.091 |
| | 1051 | $2\frac{1}{4}$Cr-1Mo | 0.120 x 0.098 | 0.113 x 0.091 |
| | 1316 | Carbon Steel | 0.123 x 0.096 | 0.118 x 0.091 |
| | 11 | Type-304 SS | 0.121 x 0.098 | 0.119 x 0.098 |
| | 12 | Type-304 SS | 0.123 x 0.098 | 0.121 x 0.097 |
| D-003 | 1045 | $2\frac{1}{4}$Cr-1Mo | 0.119 x 0.098 | 0.115 x 0.092 |
| | 1046 | $2\frac{1}{4}$Cr-1Mo | 0.119 x 0.098 | 0.115 x 0.092 |
| | 1320 | Carbon Steel | 0.122 x 0.096 | 0.122 x 0.095 |
| | 8 | Type-304 SS | 0.122 x 0.098 | 0.121 x 0.098 |
| | 9 | Type-304 SS | 0.120 x 0.097 | 0.118 x 0.097 |
| D-004 | 1055 | $2\frac{1}{4}$Cr-1Mo | 0.119 x 0.097 | 0.116 x 0.092 |
| | 32 | Type-304 SS | 0.121 x 0.097 | 0.119 x 0.098 |
| | 33 | Type-304 SS | 0.123 x 0.096 | 0.120 x 0.095 |
| D-005 | 1058 | $2\frac{1}{4}$Cr-1Mo | 0.120 x 0.097 | 0.119 x 0.096 |
| | 1340 | Type-340 SS | 0.123 x 0.095 | 0.123 x 0.096 |
| | 1341 | Type-340 SS | 0.124 x 0.095 | 0.122 x 0.095 |
| D-006 | 1062 | $2\frac{1}{4}$Cr-1Mo | 0.120 x 0.098 | 0.114 x 0.091 |
| | 1343 | Type-304 SS | 0.124 x 0.096 | 0.123 x 0.095 |
| | 1344 | Type-304 SS | 0.124 x 0.097 | 0.122 x 0.096 |

From Table 5, it appears that the corrosion rates for $2\frac{1}{4}$Cr-1Mo and carbon steel are comparable and about a factor of six higher than Type-304 stainless steel. The amount of general corrosion increased with decreasing heat rate. Thus at $18^{\circ}$F/h, $2\frac{1}{4}$Cr-1Mo and carbon steel had about 0.0025 inch of corrosion on any surface. At $9^{\circ}$F/h the corrosion was about 0.0035 inch for the same materials while at the fastest heating rate $36^{\circ}$F/h the corrosion on a surface for the ferritic alloys was about 0.001 to 0.0015 inch.

# 4. DISCUSSION

It has been established previously by H. Isaacs of ORNL that 2¼Cr-1Mo steel is susceptible to stress corrosion in boiling caustic solutions.[2] It is also well known that carbon steel will crack in the same environment. However, in our tests no cracking of these ferritic alloys occurred. Apparently the amount of time spent in the susceptible temperature regions is too short to initiate cracking. The obvious implication is that with any reasonable cooling or heating rates following a sodium-water reaction in the LLTR, the 2¼Cr-1Mo will not crack. In addition, the amount of general corrosion attack does not appear severe in the time spent in heating to 600°F at heating rates of 9 to 36°F/h.

The Type-304 stainless steel test showed significant susceptibility to caustic cracking over the range of heating rates tested. Unlike the ferritic steel, it was not possible to heat the austenitic steel fast enough to avoid crack initiation. The only apparent exception was those samples loaded to 75% of the yield strength in run D001 and D002. However these samples were only examined on their surfaces up to 140X. While cracking was observed in samples stressed at 90 to 100% of the yield strength, the cracking was not severe in 18°F/h and 36°F/h heating rates. Of course higher stress levels and slower heat rates resulted in severe cracking. The results in run D001 and D002, nominal heating rates of 18°F/h appear similar. If any difference occurred, it was that the cracks in run D001 appeared deeper. Since the level of electrolyte dropped below the samples above 320°F, it appears that most of the stainless steel cracking is initiated below 320°F.

# 5. SUMMARY

Over the range of concentrations and temperatures indicated by the Na-$H_2O$ boiling point curve, from room temperature to $600^{O}F$, $2\frac{1}{4}$Cr-1Mo and carbon steel (ASTM-A516 Grade 70) do not appear to be susceptible to caustic cracking as long as the samples are continuously heated at rates between 9 to $36^{O}F/h$. The lowest safe heating rate at which caustic cracking of the ferritic steels can be avoided was not determined.

Type-304 stainless steel samples stressed at least to 90% of their yield strength cracked in the concentrating caustic solution of the range of heating rates tested. It was not possible to avoid caustic cracking even at the highest heat rate that was used. The severity of cracking increased with applied stress and decreasing heating rate.

## REFERENCES

1. A. N. Bornstein and M. E. Indig, "High Temperature Aqueous Stress Corrosion Testing Device", U.S. Patent 3, 922, 903.
2. M. E. Indig, "Environmental Corrosion Effects on CRBRP Materials in the Steam Generation Circuit", GE-FBRD, Internal Conference for Nuclear Steam Generator, Gaglinburg, Tenn., September 9-12, 1975.