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Report No. COO-2018-23 (Q-7)

STRESS CORROSION CRACKING OF Fe-Cr-Ni ALLOYS IN CAUSTIC ENVIRONMENTS

A. K. Agrawal and R. W. Staehle
Department of Metallurgical Engineering

July 16, 1970 - October 14, 1970

U. S. Atomic Energy Commission
Chicago Operations Office
Argonne, Illinois

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To U. S. ATOMIC ENERGY COMMISSION
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On STRESS CORROSION CRACKING OF Fe-Cr-Ni ALLOYS IN CAUSTIC ENVIRONMENTS

For the period July 16, 1970 - October 14, 1970

Submitted by A. K. Agrawal and Roger W. Staehle

Department of Metallurgical Engineering

Date April, 1971

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1.0 ABSTRACT

Results from stress corrosion and electrochemical studies are reported for Fe-Cr-Ni alloy exposed to NaOH-H_2O solutions at temperatures below 200°C. The corrosion potential of Type 430 stainless steel in caustic solutions (< 60% NaOH) is considerably more active than that of Type 304 stainless steel. The stress corrosion cracking of 430 stainless steel as compared with 304 stainless steel occurs rapidly and in low concentrated caustic solutions (30% NaOH). The attack on 430 stainless steel is predominantly intergranular with some pitting. Design of an electrochemical cell suitable for electrokinetic investigation of metals at high temperatures in fused NaOH is given.

2.0 CONCLUSIONS

1. Stress corrosion cracking of annealed 430 and 304 stainless steels was studied in boiling caustic solutions (20-80% NaOH). The lower limit of caustic concentration at which failures occurred under 100% yield stress was 30% NaOH for Type 430 and 50% for Type 304. The failure time for 430 was considerably lower, 5.5-18.5 hours as compared to 37-102 hours for 304. The corrosion potentials of both stressed and unstressed specimens of 430 were 100-500 mV more active (cathodic) than that for 304 in solutions < 60% NaOH. The mode of attack was intergranular, with some pitting in the first alloy and transgranular in the second alloy.

2. Literature on corrosion of alloys at high-temperature in Na-NaOH environment is reviewed. Design is given of a zirconium oxide-coated all-nickel autoclave cell suitable for high-temperature electrokinetic corrosion studies in fused caustic environment.

3.0 INTRODUCTION

This work is being conducted in support of the LMFBR activities to identify the possible incidences and extent of caustic stress corrosion cracking which could cause premature equipment failure. The most likely sites where such SCC is possible are (1) in the steam generator at the Na-H_2O interface and (2) on exterior surfaces where Na spills or leaks can hydrolyze to form NaOH solutions in the presence of moisture.

Caustic SCC is a serious consideration in iron base alloy systems and becomes generally more serious with increasing iron concentrations in the alloy as shown in COO-2018-4.

This program is approaching the problem by conducting both direct SCC studies and fundamental studies aimed at understanding the phenomenon. The work is outlined in a series of tasks. Work performed on a given task is described. Note that work is not performed each quarter on all tasks owing to the schedule for starting the respective task and also to vagaries in academic schedules for graduate students.

4.0 PROGRESS IN INDIVIDUAL TASKS

Task 1 - Tests of Engineering Geometries

A. Aims

The purpose of this work is to conduct experiments which simulate possible failure modes in engineering geometries to find what kind of corrosion phenomena might occur in the event of a sodium leak. From this information more specific definitions could be given to fundamental studies.

B. Results to Date

None

Task 2 - General Effects of Alloy and Environmental Composition in Aqueous Solvents on Stress Corrosion Cracking (D. V. Subrahmanyam)

A. Aims

The purpose of this task is to assess the general effects of environment and alloy chemistry on the incidence of caustic stress corrosion cracking. Variables will include alloy chemistry, temperature, concentration of OH^-, identity of cation, dissolved gases including oxygen, and electrochemical potential.

B. Results

1. Introduction

In this report the caustic stress corrosion cracking behaviors of Types 304 and 430 stainless steels are compared.

Alloying elements exert a strong influence on the resistance of an alloy. Type 430 stainless steel is a ferritic type alloy containing 14-18% chromium and no nickel. An addition of 8% nickel to this alloy results in Type 304 stainless steel. Hence, it was of interest to undertake a comparison in sodium hydroxide environment.

2. Experimental

The composition limits and yield stresses of Types 430 and 304 stainless steel are given in Table I.

Table I

	Composition, wt.%								Yield Stress
Alloy	C	Mn	Si	P	S	Cr	Ni		psi × 10^{-4}
430	0.12	1.00	1.00	0.04	0.03	14.0 -18.0		Bal. Fe	3.50
304	0.08	2.00	1.00	0.045	0.03	18.0- 20.0	8.0- 12.0		1.74

The following heat treatment procedure was adopted for the 430 and 304 stainless steels:

(1) Type 430: Heated for 2 hr. at 2100°F, furnace-cooled to 1450- 1500°F and held there for 1 hr., and then furnace-cooled to room temperature.

(2) Type 304: Heated for 2 hr. at 2100°F and then air-cooled.

The heat-treated wires (15 mil dia.) were degreased and then subjected to constant load tests in boiling NaOH solutions of 10-80% strength. The failure times, corrosion potentials, and crack morphologies of the specimens were determined. Details of the experiments are given in a previous report.

3. Results

a. The effect of NaOH concentration on the failure times

The effect of caustic concentration on the failure times of specimens is shown in Fig. 1. The minimum NaOH concentration required to produce cracking in alloy 430 was 30%, while that in alloy 304 was 50%. In the concentration range 60-80% NaOH the failures were rapid for alloy 430, (5.5-18.5 hr) as compared to that for alloy 304 (37-102 hr). Thus, it appears that the addition of Ni improved the resistance of alloy 430. In a previous report [COO-2018-18 (Q-5)], it was mentioned that the sensitized 304 stainless steel has poor resistance to caustic SCC because of the depletion of Cr from and around the grain boundaries.

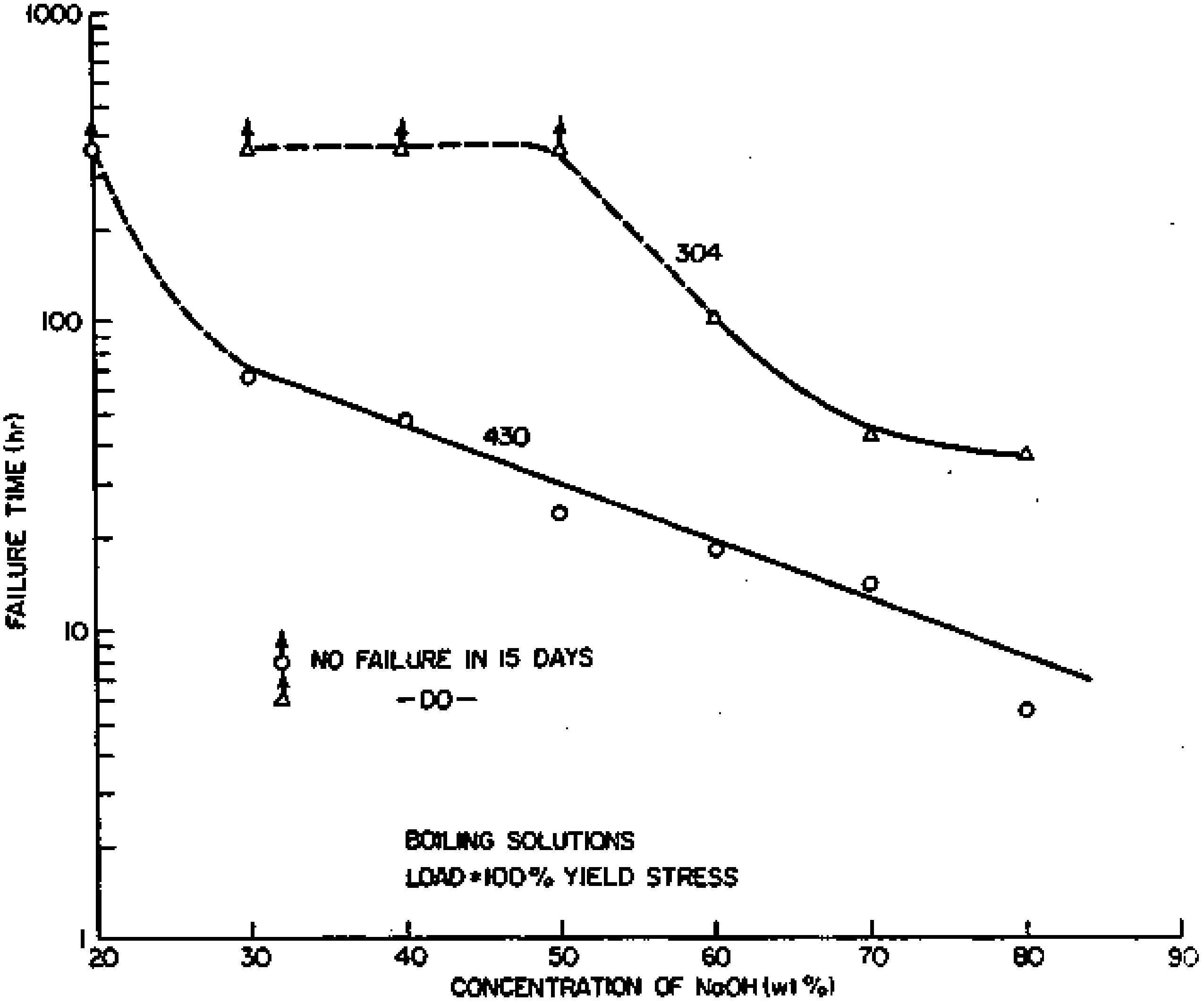


Fig. 1 - Effect of sodium hydroxide concentration on failure times

This indicates that the absence of either Ni or Cr lowers significantly the resistance of iron-base alloys to caustic stress corrosion cracking.

b. The effect of NaOH concentration on crack morphologies

The effect of NaOH concentration on the crack morphologies is shown in photomicrographs (Fig. 2). In this figure, photos 1 and 2 show the structures of the heat-treated 430 and 304 stainless steels, respectively. The 430 stainless steel shows a ferritic structure with chromium carbide precipitate along the grain boundaries. On the other hand, the 304 stainless steel shows a larger-grained austenitic structure free of any precipitates.

Photos 3, 5, 7-9, and 11-18 are of the unstressed failed specimens of alloy 430. These indicate pitting features and significant intergranular type of attack. The cracked tips of the specimens from the solutions of 60, 40, and 30% NaOH show some ductile features relieved by elongated grain boundaries (photos 9, 13, and 16, respectively). The mode of failure of alloy 304 was of mixed type with predominantly transgranular character [photos 4 (80% NaOH) and 10 (60% NaOH)]. The unstressed specimen of alloy 304 in 80% NaOH shows some generalized type of corrosion (photo 6).

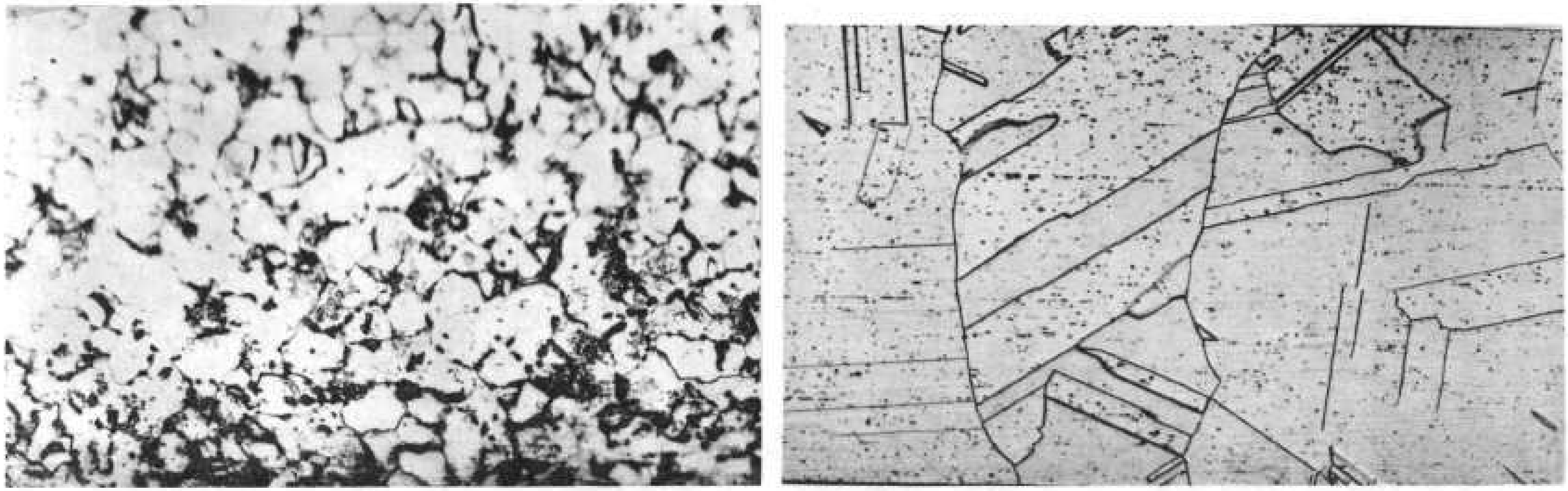
c. Corrosion Potentials

The corrosion potentials of the alloys as a function of NaOH concentration are shown in Fig. 3. The corrosion potentials of 304 stainless steel, both the stressed and unstressed, are more anodic than the corresponding potentials of 430 stainless steel. This difference is quite significant in solutions of low (< 60% NaOH) caustic concentrations. However, at concentrations of 60% NaOH and more the difference is reduced to marginal (see Fig. 3). The stressing had nominal effect on both the alloys. The slight shift in potentials was toward noble values for alloy 430, but, it was toward active values for alloy 304.

The negative shift of potentials is due to the accelerated dissolution kinetics, while the possitive shift is due to the filming process.

4. Discussion

The possible reactions causing failure of the 430 and 304 stainless steels are discussed here.



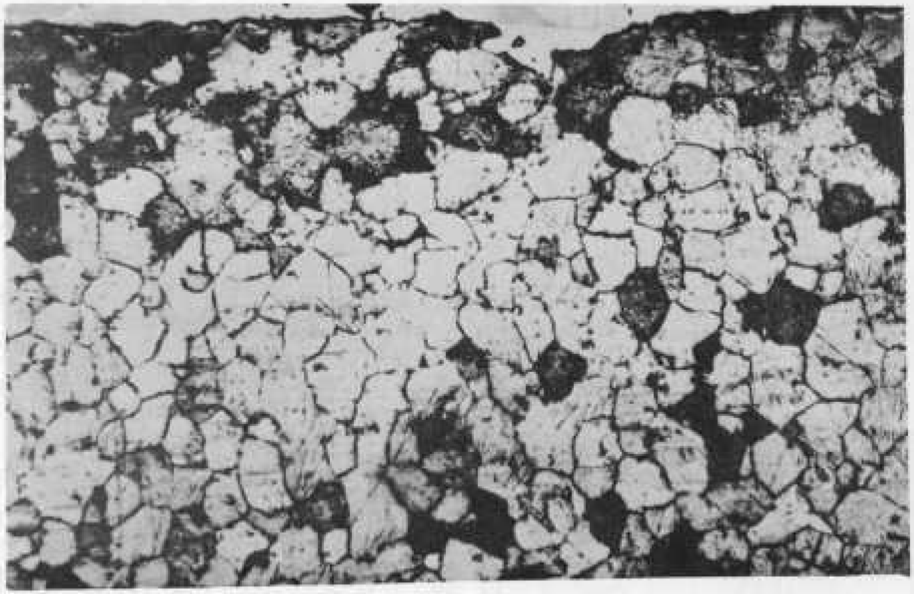
1. 430 Stainless steel annealed at 2100°F for 1 hr, furnace cooled to 1450-1500°F, held in the above range for 1 hr, and furnace cooled 250X

2. 304 Stainless steel annealed at 2100°F for 1 hr and air-cooled 150X

Fig. 2 - Effect of sodium hydroxide concentration on the crack morphologies of 430 and 304 stainless steels (structure of bare surfaces after heat treatment)

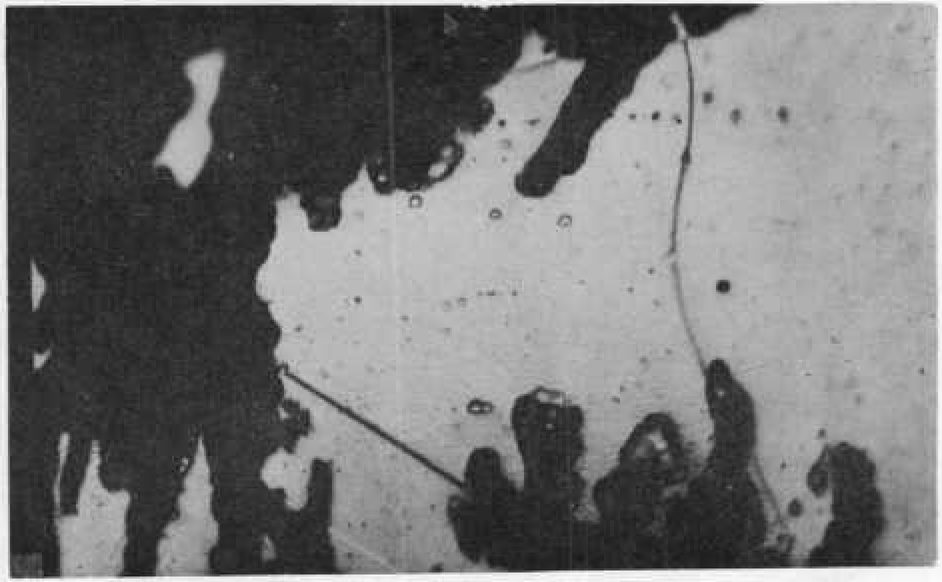
80% NaOH

430 Stainless Steel



3. Stressed; failure time = 5.5 hr
E_{corr} = -979 mV_H 150X

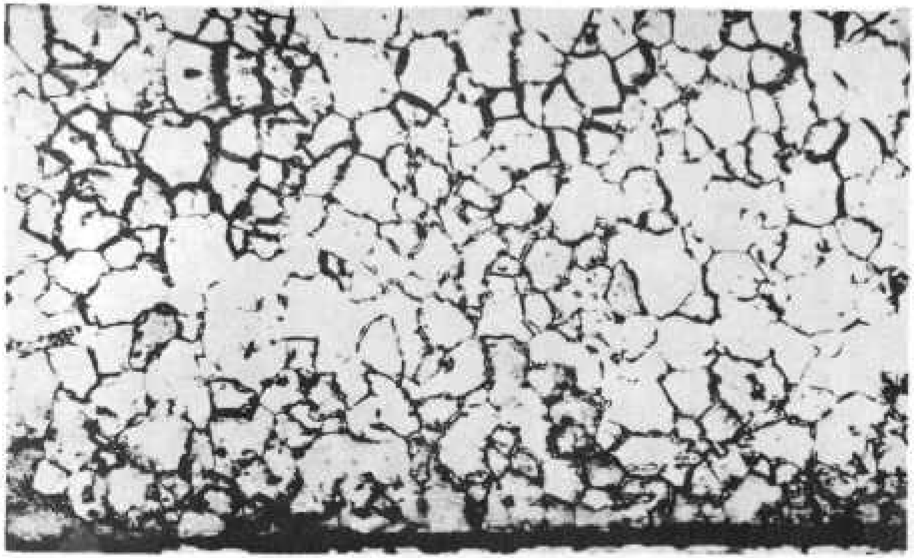
304 Stainless Steel



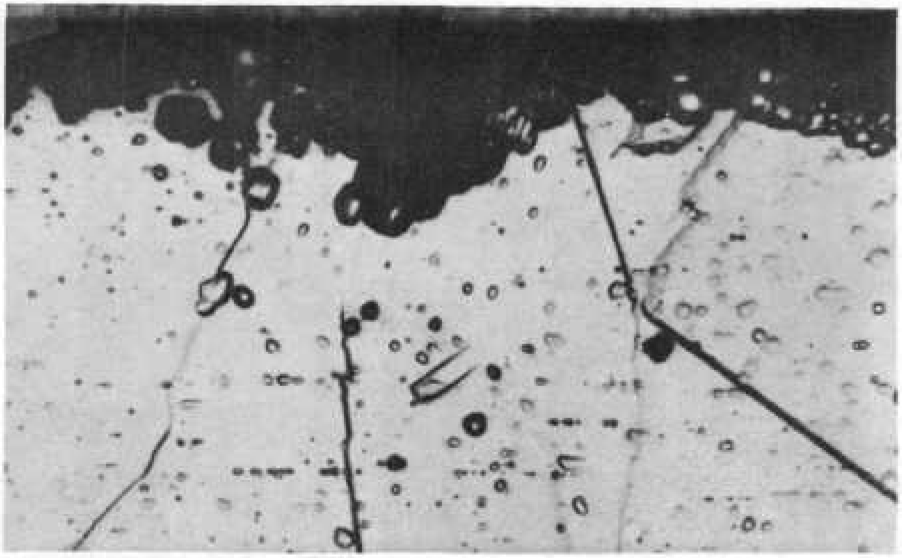
4. Stressed; failure time = 36 hr
E_{corr} = -970 mV_H 700X

Fig. 2 - (continued)

430 Stainless Steel 80% NaOH 304 Stainless Steel



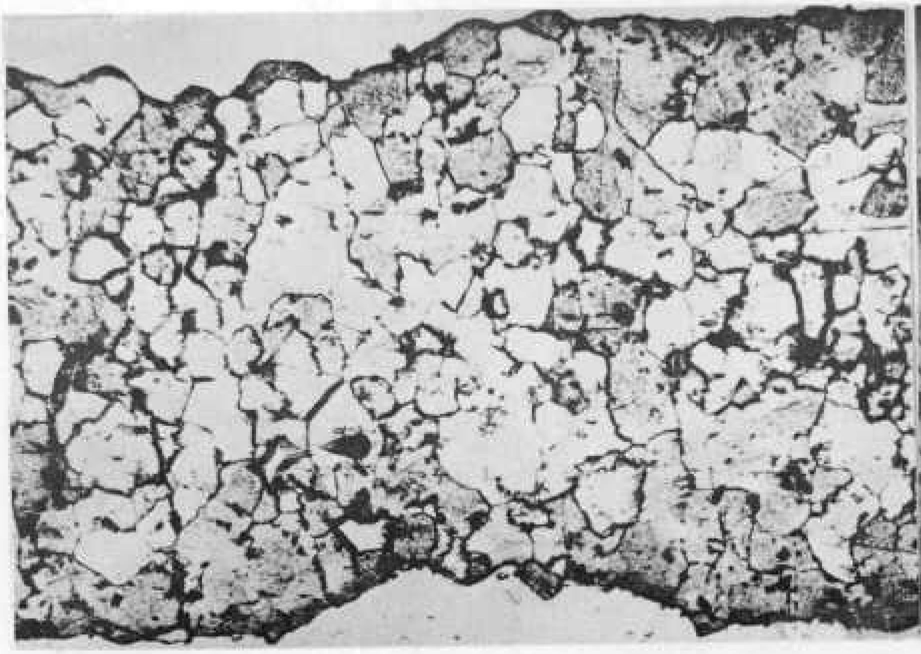
5. Unstressed; exposure time = 5.5 hr
E_{corr} = -980 mV_H 150X



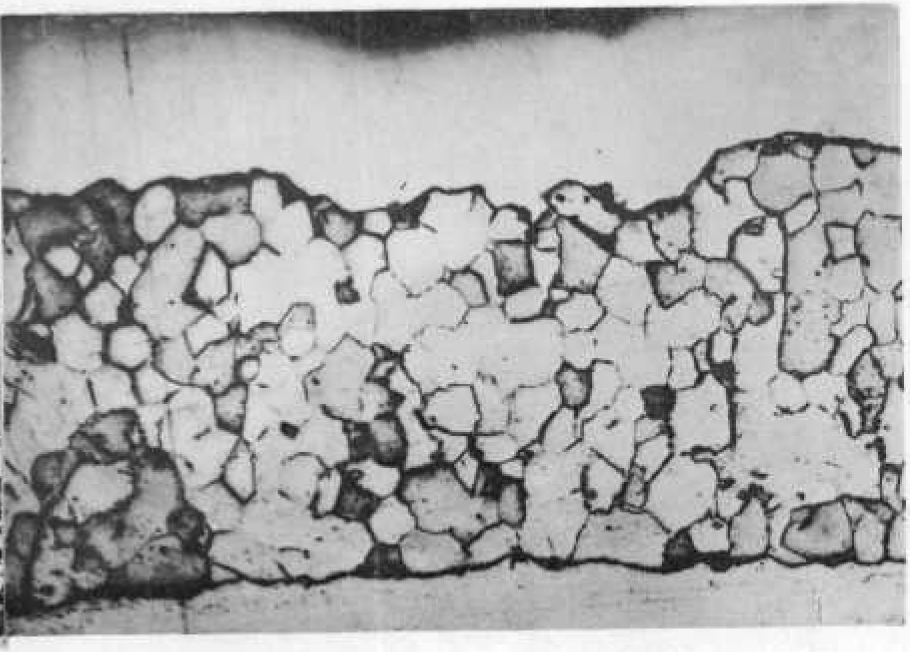
6. Unstressed; exposure time = 36 hr
E_{corr} = -955 mV_H 700X

Fig. 2 - (continued)

430 Stainless Steel 70% NaOH



7. Stressed; failure time = 14 hr
E_{corr} = -999 mV_H 150X



8. Unstressed; exposure time = 14 hr
E_{corr} = -979 mV_H 150X

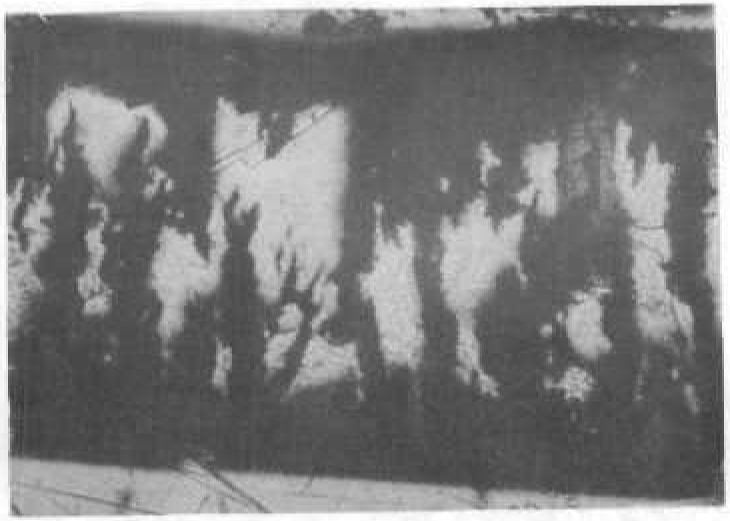
Fig. 2 - (continued)

430 Stainless Steel

60% NaOH
(stressed)

9. Stressed; failure time = 18.5 hr
E_{corr} = -974 mV_H 150X

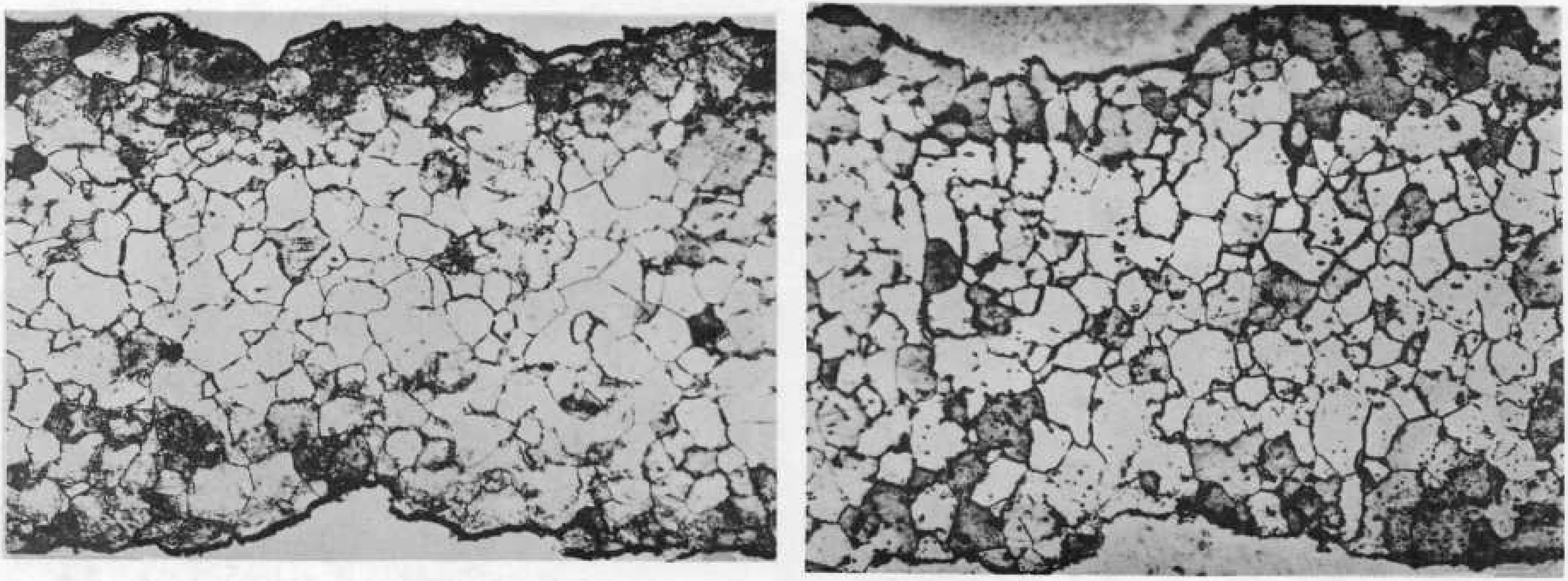
304 Stainless Steel



10. Stressed; failure time = 102 hr
E_{corr} = -925 mV_H 150X

Fig. 2 - (continued)

430 Stainless Steel - 50% NaOH

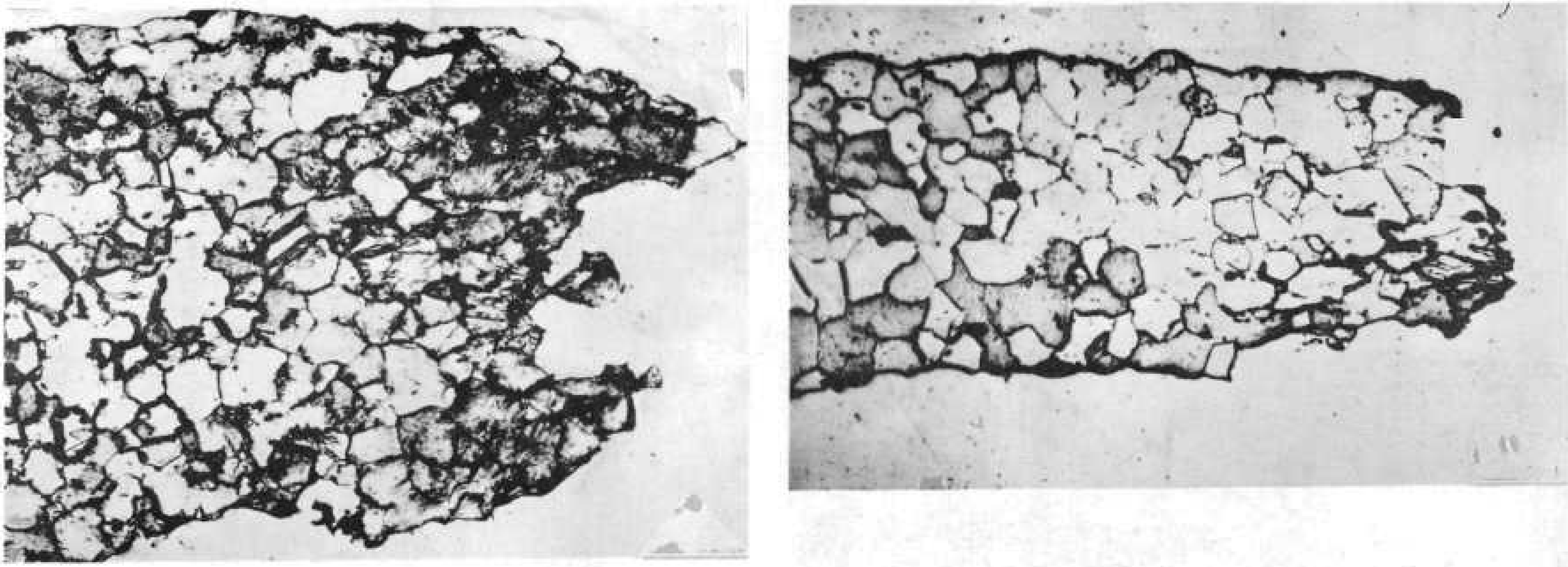


11. Stressed; failure time = 26.5 hr
E_{corr} = -929 mV_H 150X

12. Unstressed; exposure time = 26.5 hr
E_{corr} = -929 mV_H 150X

Fig. 2 - (continued)

430 Stainless Steel - 40% NaOH

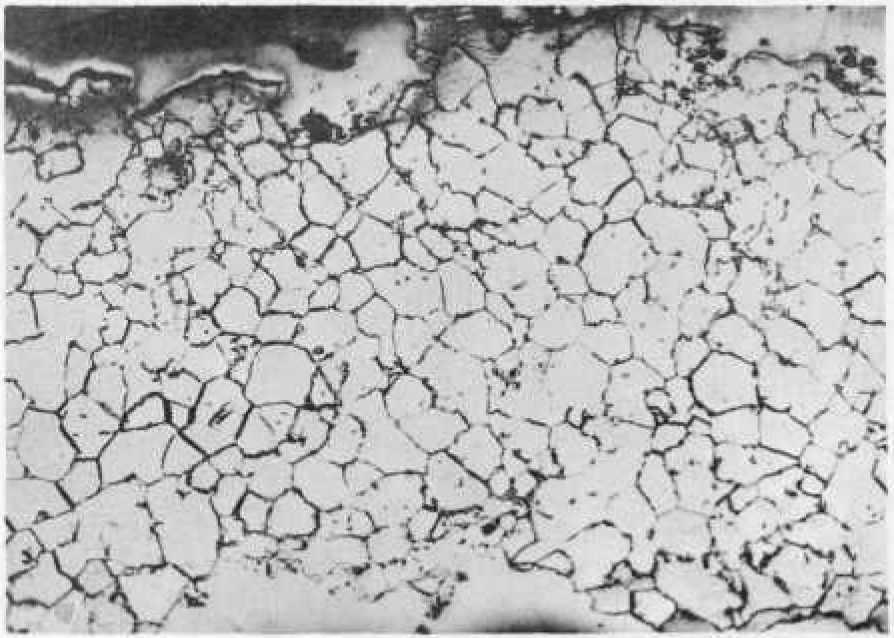


13. Stressed; failure time = 48 hr
E_{corr} = -909 mV_H 150X

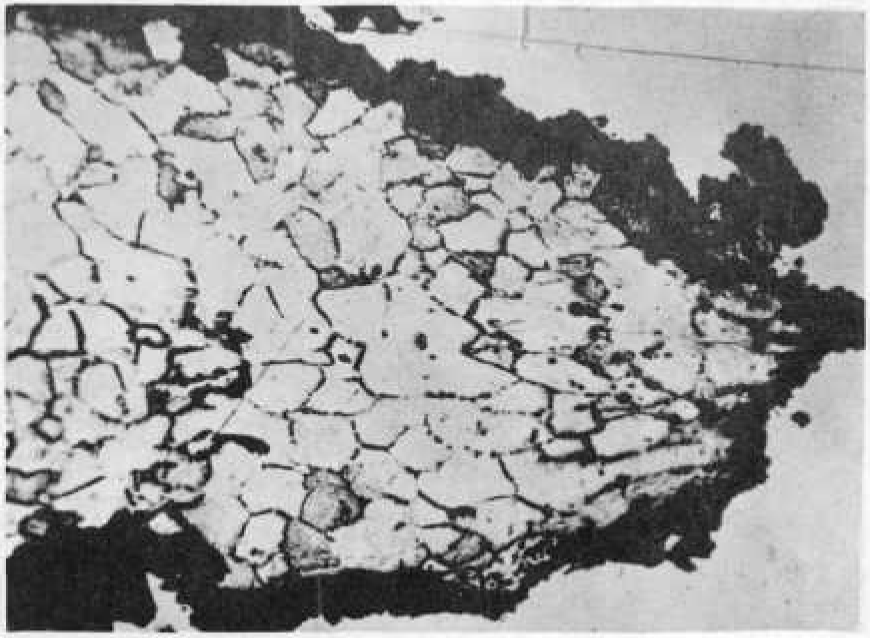
14. Unstressed; exposure time = 48 hr
E_{corr} = -914 mV_H 150X

Fig. 2 - (continued)

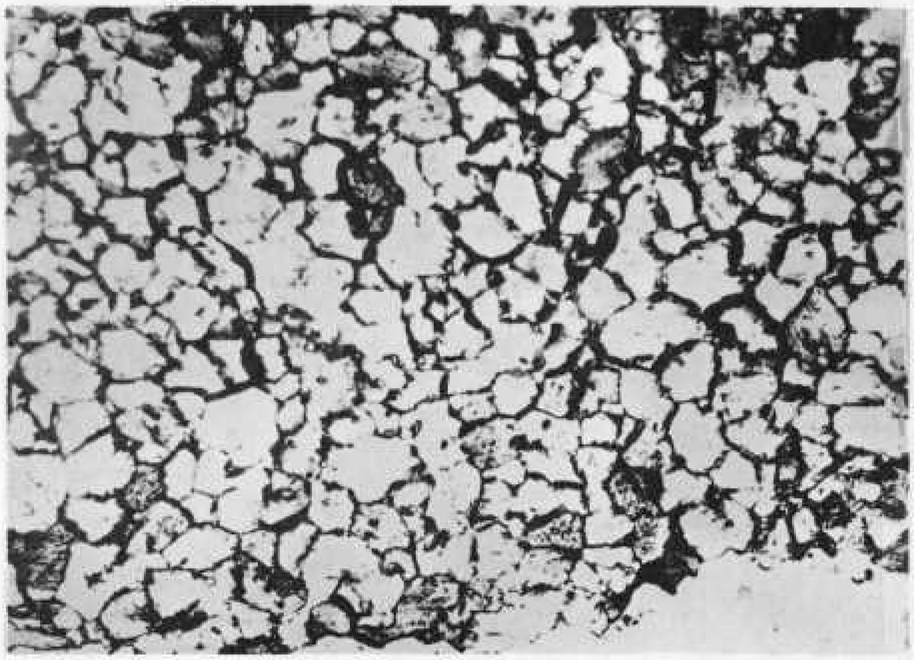
430 Stainless Steel - 30% NaOH



15. Stressed; failure time = 67.4 hr; pitting failure far from failed end.
E_{corr} = -912 mV_H 150X



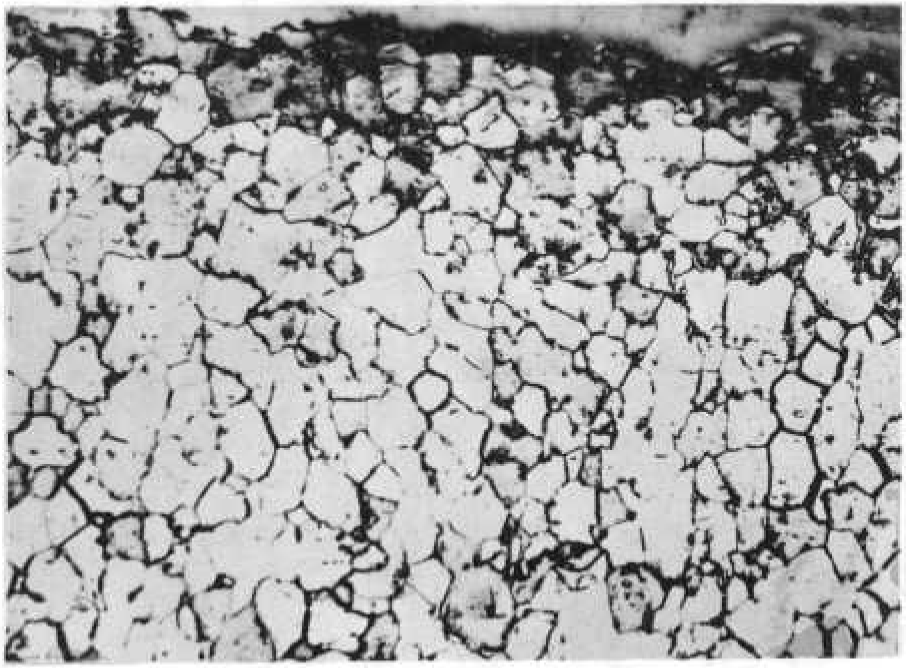
16. Stressed; failure time = 67.4 hr; plastic deformation near the crack tip.
E_{corr} = -912 mV_H 150X



17. Unstressed; exposure time = 15 days
E_{corr} = -930 mV_H 150X

Fig. 2 - (continued)

430 Stainless Steel - 20% NaOH



18. Stressed; no failure in 15 days
$E_{corr} = -565\ mV_H$ 150X

Fig. 2 - (continued)

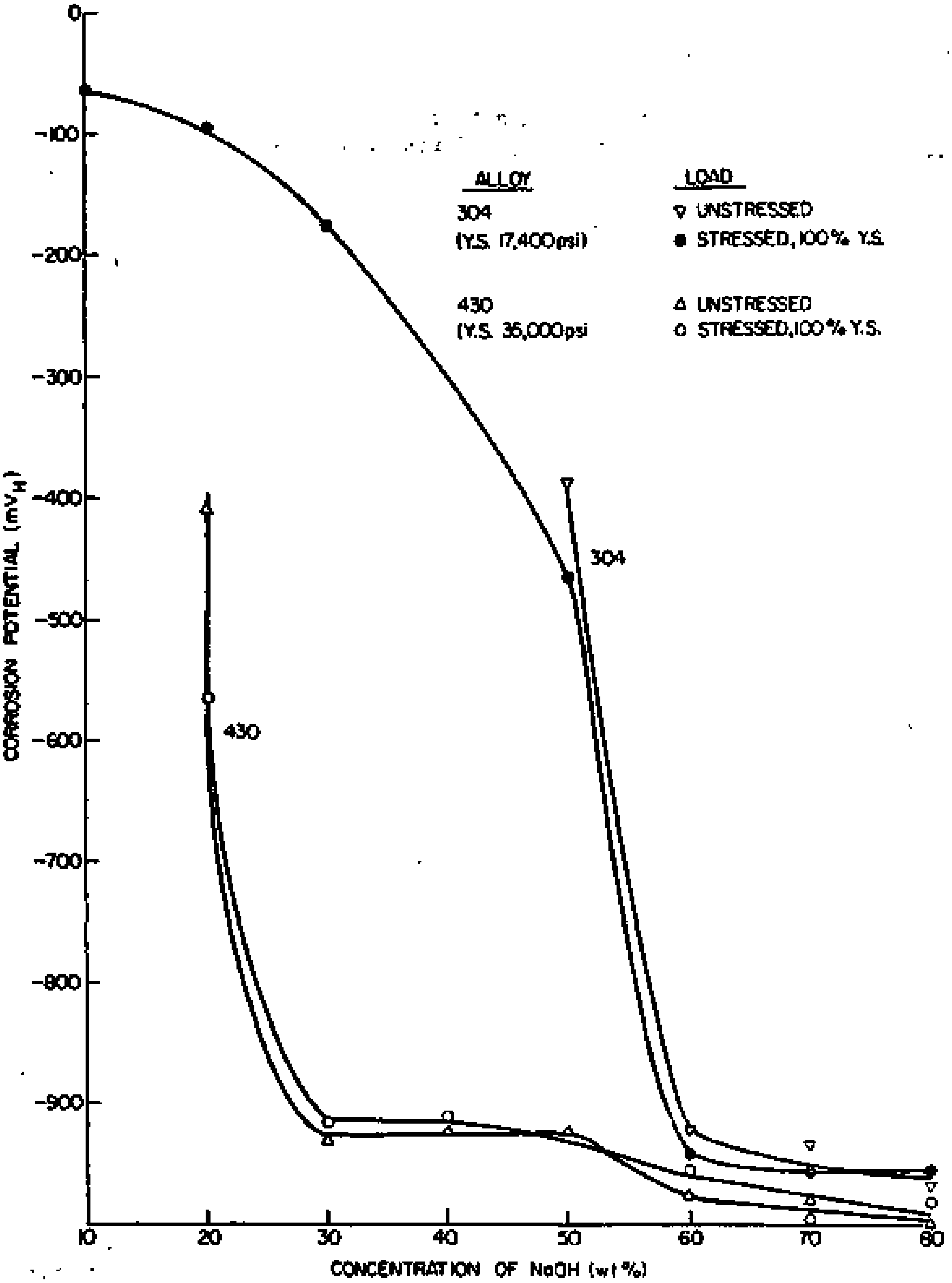


Fig. 3 - Effect of sodium hydroxide concentration on corrosion potentials

The reactions that might be occurring in NaOH solution with iron and chromium carbide of alloy 430 are as follows:

$$2Cr_7C_3 + 21H_2O = 7Cr_2O_3 + 6C(s) + 42H^+ + 42e \qquad (1)$$

$$Fe + 2H_2O = HFeO_2^- + 3H^+ + 2e \qquad (2)$$

$$3HFeO_2^- + H^+ = Fe_3O_4 + 2H_2O + 2e \qquad (3)$$

Reactions (1) and (3) would be responsible for the formation of thick films and lead to pitting attack, while dissolution reaction (2) would be responsible for intergranular cracking. In a situation where both pitting and intergranular cracking were observed all three reactions might be occurring.

The annealing at 2100°F does not leave any carbide precipitates in 304 stainless steel. Hence, in this case, the cracking process probably involves the formation of anionic species $HNiO_2^-$, in addition to $HFeO_2^-$. The pitting occurs in the presence of stable oxide films on the surface, which are formed at higher potentials. At steady state corrosion potential of alloy 304 there might not be such films on the surface. This possibly was the reason for the predominant transgranular attack on alloy 304.

Task 3 - General Effect of Alloy and Environmental Composition in Sodium Base Environments Containing NaOH on Stress Corrosion Cracking

(F. O. Du)

A. Aims

The purpose of this task is to perform a parallel program to that in Task 2 except for the environment being a sodium base.

B. Results

1. Introduction

Literature pertinent to SCC of alloys in aqueous NaOH environments was reviewed in report COO-2018-4(Q-1). Here, literature pertinent to SCC of alloys in fused NaOH is reviewed. Literature on corrosion studies done to date in fused NaOH environments is meager, especially SCC studies.

Since data on fused NaOH are not readily available but scattered in obscure literature, another aspect of this review was to make available such data which might be required in carrying out this task. The data sought were physical properties, thermodynamic properties, heat transfer properties, fluid flow properties, solubilities, and electrochemical interaction with Fe-Cr-Ni alloys. To avoid unnecessary verbiage, only references to these are given here.

2. Corrosion in fused NaOH

Cragihead and Smith[1] conducted corrosion tests on 30 elemental metals and 62 alloys in fused NaOH environments. At 1500°F only five metals (silver, nickel, zirconium, copper, and monel) showed any degree of resistance to corrosion. In these five cases the nature of attack was intergranular. Tests performed by Gregory and Wace[2] showed that at high temperature in fused NaOH, platinum and zirconium have some degree of corrosion resistance but silver and nickel are the most corrosion-resistant metals.

A few corrosion tests on ceramic materials have also been reported. In fused NaOH alundum, zirconium oxide stabilized with lime, mixtures of aluminum oxide and magnesium oxide, and thoria show some degree of corrosion resistance. Smith[3] performed corrosion tests on ceramic and ceramic-related substances in fused NaOH. He noticed that several other ceramics are sufficiently resistant to be useful, but observed magnesium oxide as the most corrosion resistant of the ceramics. Corrosion in the fused NaOH was observed to occur both by solution and by chemical reaction. A few ceramics were noted to react by oxidation-reduction reactions, but most have been found to be attacked by oxide-ion-donor-acceptor reaction.

Corrosion literature is reviewed under the following headings: corrosion mechanisms, influence of additives, mass transfer corrosion, dynamic corrosion, and stress corrosion cracking.

a. Corrosion mechanisms

Chemical reaction between fused NaOH and a metal occurs in two steps; i.e., primary reaction and secondary reaction.[4] Regardless of metal (M), with Au as an only exception, the primary reaction is

$$2NaOH + M \rightarrow M\text{oxide} + Na_2O + H_2.$$

The sequence and nature of the secondary reactions which may occur depends on various factors, such as whether the atmosphere is static or flowing, reducing, neutral, or oxidizing, and which metal is involved. Possible reactions which have been substantiated by experimental evidence are:

$$\text{Moxide} + H_2 \longrightarrow M + H_2O$$

$$M + Na_2O \longrightarrow \text{Moxide} + 2Na$$

$$Na_2O + 1/2\ H_2 \longrightarrow NaOH + Na$$

$$H_2O + Na \longrightarrow NaOH + 1/2\ H_2$$

$$2Na + NaOH \longrightarrow Na_2O + NaH$$

$$NaH \longrightarrow Na + 1/2\ H_2$$

Corrosion by oxidation of the metals is caused either by the hydroxyl ions, alkali metal ions, or impurities dissolved in the fused NaOH system.

(1) Corrosion by hydroxyl ions: The hydroxyl ions are reduced to hydrogen and oxide ions, while the metal is oxidized to form metal ions. The metal ions may in turn dissolve and act as oxide-ion acceptors and form an oxide or an oxysalt.

For a metal of valence x, the corrosion by hydroxide ions may be represented as

$$M + xOH^- \longrightarrow M^{x+} + xO^= + \frac{x}{2} H_2 \quad .$$

The above reaction occurs from most reactive metals to the most inert. Sometimes this hydroxyl ion reaction produces a hydride of the metal. If the hydride is volatile it may escape; if the hydride is not volatile it may react with the hydroxide as do the alkali metal hydrides. This side reaction does not seem to be important in the corrosion of most metals. Water may also form at times; e.g.,

$$NiO + H_2 \longrightarrow Ni + H_2O \quad .$$

Corrosion of elemental metals can be divided into 2 groups. The first group consists of those metals which are strongly attacked by hydroxyl ions at 500°C; i.e., alkaline earth metals, antimony, arsenic, berryllium, cerium, niobium, magnesium, manganese, molybdenum, tantalum, titanium, tungsten, and vanadium. The second group consists of metals which have some corrosion resistance in fused NaOH at 500°C; i.e., aluminum, bismuth, chromium, cobalt, copper, gold, indium, iron, lead, nickel, palladium, platinum, silver, and zirconium.

The second group of metals appears to be corrosion resistant because of protective film formation, and, in some cases, small thermodynamic driving force. For instance, aluminum seems to be protected by film formation, whereas nickel can be maintained almost in thermodynamic equilibrium in the melt under isothermal conditions.

The corrosion rate of nickel at high temperature has been found to depend on the partial pressure of hydrogen over the melt. Under hydrogen cover in fused NaOH up to 815°C, nickel has insignificant corrosion for 100 hours provided that thermal gradient is absent.[4] In the absence of hydrogen cover, the corrosion rate is slow below 400°C but, increases with temperature; above 800°C it is exceedingly high.[5] The general reaction is

$$Ni(s) + 2NaOH(\ell) \longrightarrow Na_2NiO_2(s) + H_2(g)$$

At 950°C if the hydrogen formed is evacuated from the system slowly, so that a significant partial pressure exists over the melt, considerable water vapor is evolved.[6] It was suggested that the corrosion process consists of two steps; i.e.,

$$Ni + 2NaOH \longrightarrow NiO + Na_2O + H_2$$

and

$$NiO + 2NaOH \longrightarrow Na_2NiO_2 + H_2O,$$

with the overall reaction being,

$$Ni + 4NaOH \longrightarrow Na_2NiO_2 + Na_2O + H_2O + H_2 \quad .$$

An additional source of water was postulated from the reduction of oxide ions by hydrogen when the latter is present in sufficient concentration.[3,7]

As mentioned above the reaction between fused NaOH and Ni was inhibited by H_2, but no such effect was observed in case of Fe.[5] A series of reactions between fused NaOH and Fe, Cr, Mn, Ti, Ta, and Be is listed by Walker <u>et al</u>.[8]

(2) Corrosion by alkali metal ions: After OH^- ions have been reduced and consumed, Ni reacts with Na^+ ions. Sodium ions are reduced and sodium nickelate is formed.

It is also postulated that hydroxyl and sodium ions are simultaneously reduced by all metals. Sodium ion reduction may be represented as

$$Ni + 2Na^+ \longrightarrow Ni^{++} + 2Na \quad .$$

The sodium thus generated can react with hydroxyl ions as follows:

$$2Na + 2OH^- \longrightarrow 2Na^+ + 2O^{--} + H_2 \quad .$$

If the second reaction proceeds as rapidly as sodium is generated, the net result is as though only hydroxyl ions had been reduced.

(3) Corrosion by Oxidizing Solutes: Dissolved oxygen and the peroxide ions are known to be powerful oxidizing agents in fused hydroxides. Using such solutions, investigators were able to cause very rapid corrosion of nickel with the production of oxysalts in a valence state greater than two.[9]

Water at sufficient concentration seems to act as a weak oxidizing agent.[6] A small addition of water to the blanketing atmosphere over fused NaOH has little effect on the corrosion rate of nickel, but substantial amounts of water made the corrosion much more severe.

(4) Corrosion of Alloys: The corrosion of alloys by fused NaOH is not clearly understood; however, there is as yet no evidence to support the assumption that its mechanism is different from that encountered with elemental metals.

Microstructure reveals two phenomena distinctive of alloys. First, the formation of pores or voids beneath the surface of the corroded alloy, and second, the formation of complex two-phase corrosion products at the surface and along the grain boundaries.

Qualitatively, Brasunas[10] has proposed the following:

> At the early stage of corrosion the Fe atoms at the surface of the metal specimen are oxidized much more rapidly than the Ni atoms. As a result, the surface becomes depleted in Fe. This depletion establishes a concentration gradient and causes diffusion of Fe from the interior of the specimen to the surface, where reaction continues. The diffusion of iron is presumed to occur by a vacant-lattice site mechanism, so that there is a flux of vacancies diffusing from the surface into the interior of the specimen. Since the crystal lattice cannot maintain more than a certain concentration of vacant lattice sites, the excess vacancies which accumulate from inward diffusion "precipitate" as voids. These voids continue to grow as long as the inward flux is maintained.

The second kind of corrosion phenomenon is related to the inhibition by formation of oxide film on surface of the metal. A protective coating can be formed on a metal surface even by exposure to the vapor of NaOH at about 750-800°C.

Corrosion of Inconel, stainless steels, and Croloy in fused NaOH environment is discussed below.

Inconel: When Inconel was exposed to fused NaOH at 450-815°C for up to 400 hours, selective leaching of Fe and Cr occurred.[11,12] The corrosion product, a mixture of oxides and sodium oxysalts, was seen to have grown in a network of channels which started from the metal surface and penetrated into the bulk Inconel. The geometry of this network differed considerably with experimental conditions. Rate measurements were made and results reported.

Among the various metals which form complex corrosion product layers in fused NaOH, only Inconel has been extensively studied. Results obtained from tests under helium blanketing atmosphere were quite different from those obtained under hydrogen with regard to both corrosion rate and microstructure.

Under a hydrogen-blanketing atmosphere, Inconel showed a slight amount of corrosion after 100 hours at 600°C. From 600 to 800°C, corrosion increased rapidly. At all temperatures corrosion attack began at grain boundaries. Grain boundary corrosion products consisted of a metallic matrix within which were acicular particles of a nonmetallic phase. After grain boundary attack had advanced a few mils into the alloy, a massive two-phase corrosion product layer formed on the surface and thickened with time.

Under a helium-blanketing atmosphere, the corrosion rate of Inconel was significantly greater. A massive two-phase layer was formed but the microstructure was quite different.

Systematic studies at Oak Ridge of the corrosion of Inconel in KOH have revealed that attack is a function of temperature, time of exposure, and ambient atmosphere. Pitting type corrosion was noted at temperatures above 1000°F and was more pronounced under air or a vacuum than under a hydrogen atmosphere.

Stainless Steels: The microstructure of corrosion products formed in the reaction between fused sodium hydroxide and iron-rich Fe-Cr-Ni alloys were investigated.[13,14] Type 304 stainless steel and four other high-purity Fe-Cr-Ni alloys were exposed to fused NaOH at 815°C. Each corrosion product layer was found to contain a nonmetallic network threading through a metallic matrix, and which was similar to that in Inconel.

Nonsensitized Type 304 stainless steel specimens were exposed to high-temperature, high-purity water reactor environment.[15] Intergranular cracking was observed. Similar failures occurred in stressed 343 tubular capsule specimen exposed to a dilute solution of NaOH at 650°F, while exposure at 550°F caused mixed transgranular and intergranular cracking.

Croloy: The corrosion rate of croloy in an aqueous solution of NaOH was observed to be very dependent on temperatures.[16] Preliminary investigation indicated a corrosion rate of 1 ipy in 98% NaOH at 660°F. In general, the corrosion rate in aqueous NaOH was very high above 200°F, reaching a maximum of 2.67 ipy at 900°F. The rate in fused NaOH was of the same order, reaching a maximum of 2.67 ipy at 900°F; however, the corrosion rate in sodium containing approximately 90 ppm Na_2O was comparatively low at temperatures up to 1250°F. For the system NaOH-Na, the corrosion rate increased as the concentration of NaOH increased, but it was lower than that in the aqueous NaOH at the same temperature. Plots of corrosion rate of Croloy 2-1/4 in aqueous NaOH and in Na containing NaOH are given in reference 17. The corrosion rate in a sodium hydroxide sodium hydride sodium system was lower than the rate in the sodium hydroxide-sodium system.

Examination of specimens removed from a model steam generator test loop after 1000 hours of exposure to 1000°F sodium showed no significant decarburization of Croloy or Type 316 stainless steel.[18,19] Although there is slight evidence of a beginning stage of decarburization at the Croloy sample surface, no change in the microstructure was evident other than the normal effects due to exposure at these temperatures.

In other studies partial decarburization of Croloy exposed to 980°F sodium and the precipitation of carbides in Type 316 stainless steel exposed to 1100°F sodium are reported.[20,21] The corrosion rate of Croloy in Na-10% NaOH at 900°F was found to be approximately three times the rate in Na-5% NaOH at the same temperature.[20,22] Recent reviews of investigations on corrosion of possible reactor metals are given by Simon et al. of Battelle Memorial Institute.

b. Effect of Additives

The effect of additive agents on corrosion was investigated at Oak Ridge National Laboratory. Addition of 50% NaCN to NaOH was found to minimize the attack on Inconel. However, none of the additives tested to date seems to reduce corrosion by any significant level. Several corrosion inhibitors evaluated in static capsule experiments at Battelle Memorial Institute also failed to depress the corrosiveness of 1500°F NaOH.[23] One additive, MgO, appeared to inhibit attack noticeably, but its effect was far from enough to eliminate the problem.

c. Mass Transfer

Mass transfer is normally referred to as the corrosion-related phenomenon where metal is removed from the hot parts of a loop system and deposited in the cool parts of the system. This phenomenon is particularly encountered in fused NaOH with nickel, iron, copper, silver, gold, and their alloys.

The reaction between nickel and molten sodium hydroxide was investigated for its mass transfer effect.[5,24] The amount of mass transfer is noted to be strongly affected by variables such as temperature, temperature gradient, flow conditions, atmosphere, and the chemical composition of both the caustic and the nickel.

In the initial stages of deposition of nickel in the fused NaOH system, crystals grew as a dense deposit, forming an almost continuous plate over the cold leg surface. The crystal grains in this plate frequently continued in the orientation of the grains in the base metal. When this dense plate became several thousandths of an inch thick, very long dendrites began to appear. Because of the dendritic form of the thicker deposits, a relatively small amount of nickel was found to have a large effect in restricting flow through a pipe. When the flow of liquid was rapid dendrites became dislodged and they collected in irregular masses, which formed plugs that effectively stopped fluid flow altogether.

The mass transfer of iron in fused sodium hydroxide has been found to be more severe than that of nickel under comparable conditions. For instance, it was found that under hydrogen at 550°C the mass transfer of iron was worse than that of nickel at 800°C, other conditions being constant. However, iron was not observed to form the long dendrites that were found for nickel, rather, the crystals on the iron deposits remained somewhat equiaxed in habit.

Hastelloy B and the stainless steels have been observed to undergo mass transfer in fused sodium hydroxide under hydrogen. Monel showed mass transfer under both hydrogen and helium. Extensive studies of mass transfer have been made on Inconel. It was found that Inconel showed corrosion in fused sodium hydroxide at roughly the same rate, whether mass transfer took place or not, and that mass transfer took place at roughly the same rate as for pure nickel under the same conditions. Mass transfer deposits formed in an Inconel-NaOH system under an atmosphere of helium were virtually devoid of chromiu. Hydrogen suppressed mass transfer of Inconel with about the same effectiveness as it did for pure nickel.

The mechanism of mass transfer in fused NaOH is not known. Several possible mechanisms have been postulated, which are all possible in the sense that they do not violate known principles, otherwise, they are quite speculative.

d. Dynamic Corrosion

The dynamic corrosion of nickel in fused NaOH is approximately 10 times as great as static corrosion.[25] Addition of sodium uranate increased the corrosion rate by a factor of 3 at 600°C. However, at 500°C uranate did not show any effect.

e. Stress Corrosion Cracking

Stress corrosion cracking tests of Type 347 stainless steel were conducted at 636°F for periods up to 1800 hours with 1 and 4 molal NaOH. Capsules containing the solutions and stressed U-bend specimens were used. Time to failure was observed by deviation in measurements of high-temperature strain gages mounted on the outer wall of the capsules or by pressure gages. Transgranular cracking, in approximately 100 hours, was noted in nonstress-relieved materials in the welds and welded region. With stress-relieved welds, the welds failed in a thin-wall gage section at a stress level of about 22,000 psi. Corrosion in the specimens was predominately intergranular in nature. The results of this study indicate that an applied stress just below the yield point was not sufficient to cause stress corrosion cracking in a normally conducive environment. It was not until a specimen was plastically deformed that stress corrosion cracking occurred.[26]

In another experiment, tests were performed at 650-850°F in various NaOH mixtures to investigate the behavior of Type 347 stainless steel in simulation to the event of a water leak into the NaK-filled system. Capsules were used and the test showed stress corrosion cracking to be severe in 100% NaOH, and in NaOH solutions.[27] The addition of various additives to the NaOH showed that if the corrosion rate can be made to exceed 5000 mg/dm^2-mo the tendency to crack is reduced. A summary of promising additives to caustic solutions is presented in this paper.

Tests of U bend specimens, stress rupture specimens, and miniature boiler have shown that Type 347 stainless is subject to caustic stress corrosion cracking under a variety of conditions. Pure anhydrous NaOH will cause cracking at 850°F, but may not do so at a lower temperature. Concentrations of 16 to 60% NaOH in sodium will cause cracking at 850°F. Concentrated aqueous solutions of NaOH will produce cracking at 650°F with threshold stress below 2 or 3% of the yield strength. Dilute aqueous solutions containing 1 to 2% NaOH were also investigated. Stress corrosion cracking produced by caustics is metallographically indistinguishable from that produced by chlorides. Unlike chloride cracking in aqueous solutions, caustic cracking is not dependent on the presence of oxygen.[28]

Posey[29] tested Type 347 stainless steel with KOH, NaOH, LiOH, and NH_4OH to determine which are less conducive to stress corrosion and best suited for pH control of the water coolant. No cracks were observed in the specimens.

The general corrosion and behavior of stainless steels and high nickel alloys have been extensively studied. But, the stress corrosion cracking of alloys in fused NaOH have not been fully investigated. In the case of creep behavior of alloys in the system fused NaOH there appear to be no literature to date. It is therefore an open field and should prove challenging.

3. Properties of fused NaOH

Data were collected on various properties of fused NaOH. A handy reference to data sources is given below.

	Ref. No.*
Sodium Hydroxide Handling:	
Caustic soda, the most dangerous of all alkali to handle	30
Caustic soda poisoning, fume poisoning, eye burns	31,32
Skin and flesh burns, precaution and prevention, storage and handling	30
Physical Properties of Sodium Hydroxide:	
Melting and boiling point of pure NaOH	33,34
Boiling point of conc. solution of NaOH (Duhring and Ramsey Young rules)	35,36
Melting point and composition for several eutectic hydroxide system	35,36
Density of molten NaOH	34,37-41
Vapor Pressure of anhydrous molten NaOH	42
Water vapor pressure over molten NaOH	43
Thermal coefficient of expansion	33,38
Electrical conductivity	44,33
Specific conductivity	33
Equivalent conductance-single salt melts	45
Electrical resistivity	33
Thermodynamic Properties:	
Heat capacity, heat of formation, heat of vaporization, heat of fusion	46-49
Fusion point for $NaOH-Na_2CO_3$	50-54
Cooling curves	46,48-54
Entropies of phase transition and fusion	36,55-62
Entropy, Enthalpy, Heat capacity, Free Energy, Equilibrium constant	55-62
Heat Transfer Properties:	
Thermal conductivity	39,63,64
Heat transfer coefficient	39,45,65,66
Fluid Flow Properties:	
Viscosity	39
Surface tension	39

	Ref. No.*
Electrochemical Data:	
Electrode potential of anion at 700°C	67
Electrode potential of Nickel, Copper, Cobalt, Silver, and Platinum	67,68
Corrosion potential of stainless steels w/r to Gold	69
Emf of fused NaOH cell at 400°C	
Decomposition potential of NaOH	70,71
Solubilities:	
Solubility of metals in fused NaOH	72
Solubilities of Nickel in fused NaOH as a function of melt temperature	72
Solubility of sodium in NaOH	71,73-75
Solubility of H_2, O_2, and N_2 in NaOH	76
Solubility of NaOH in Na	77
Solubility of NaOH in Methanol and Ethanol at 28°C	78
Solubility of NaOH in water	78
Solubility relationship for NaOH + Na_2CO_3, NaOH + Na_2CO_3 + H_2O	50,79-84
Determination of the moisture contamination on pure NaOH	85
Evaporation procedure to produce anhydrous NaOH	
Phase diagrams of NaOH + other hydroxides	
Na-H_2O System:	
Reaction of Na with water	86
Reaction of Na with moist air, and other impurities	86
Analysis of Na-water reaction problem	16-22
Reactions resulting from leakage of water in sodium heat transf. system	87,88

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*Numbers refer to the listings under Section 5.0, References.

Task 4 - Dissolution and Passivation Behavior

(G. Theus)

A. Aims

This task is aimed at obtaining information on the kinetics of oxidation and reduction processes in electrochemically accessible environments. This includes aqueous and fused salt environments as opposed to liquid metals. This work will define those regions where activated dissolution and passivation occur as a function of alloy, temperature, and environmental composition. The definition of these regions provide guides to where stress corrosion might occur and also provide direct information on corrosion rates.

B. Results

1. Introduction

Results of the kinetic studies of Fe-Cr-Ni alloys in aqueous caustic solutions (1,5, and 10N NaOH) have been reported in the previous four reports. The present work concerns the kinetic studies of alloys in fused NaOH environments.

In this report design of an experimental cell suitable for use in fused NaOH environments is presented. Computer programs developed to construct Pourbaix type diagrams thermodynamic equilibrium diagrams for the behavior of metals in fused NaOH solutions are also presented.

a. Design of the cell (autoclave) is shown in Fig. 4. The cell will be made of pure nickel and coated with zirconium oxide stabilized with lime. These materials are most resistant to attack by fused NaOH. A reversible gold-oxygen electrode will serve as reference electrode. The cell will be heated and maintained at fused NaOH temperature or above in a crucible furnace.

A noninductively wound Lindberg Hevi-Duty crucible furnace Model No. 56622, dimensions 5" I.D. and 8" depth, along with Lindberg furnace controller Model No. 59344, will be used. A dry box will be required for storage and handling of pure NaOH.

Purchase orders have been issued for the furnace and accessories. Arrangements are being made for construction of the cell.

b. Thermodynamic equilibrium diagrams are useful means of estimating the stability of various phases (i.e., metal and corrosion products) in an environment. In construction of such a diagram (Pourbaix diagram) the fundamental relation used is the Nernst equation;

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_R}{a_o} \quad ,$$

where

E = reduction potential,

$E^\circ = \frac{\Delta G^\circ}{nF}$,

ΔG° = standard free energy change for the reaction, and

a_R, a_o = activities of the reduced and the oxidized species, respectively.

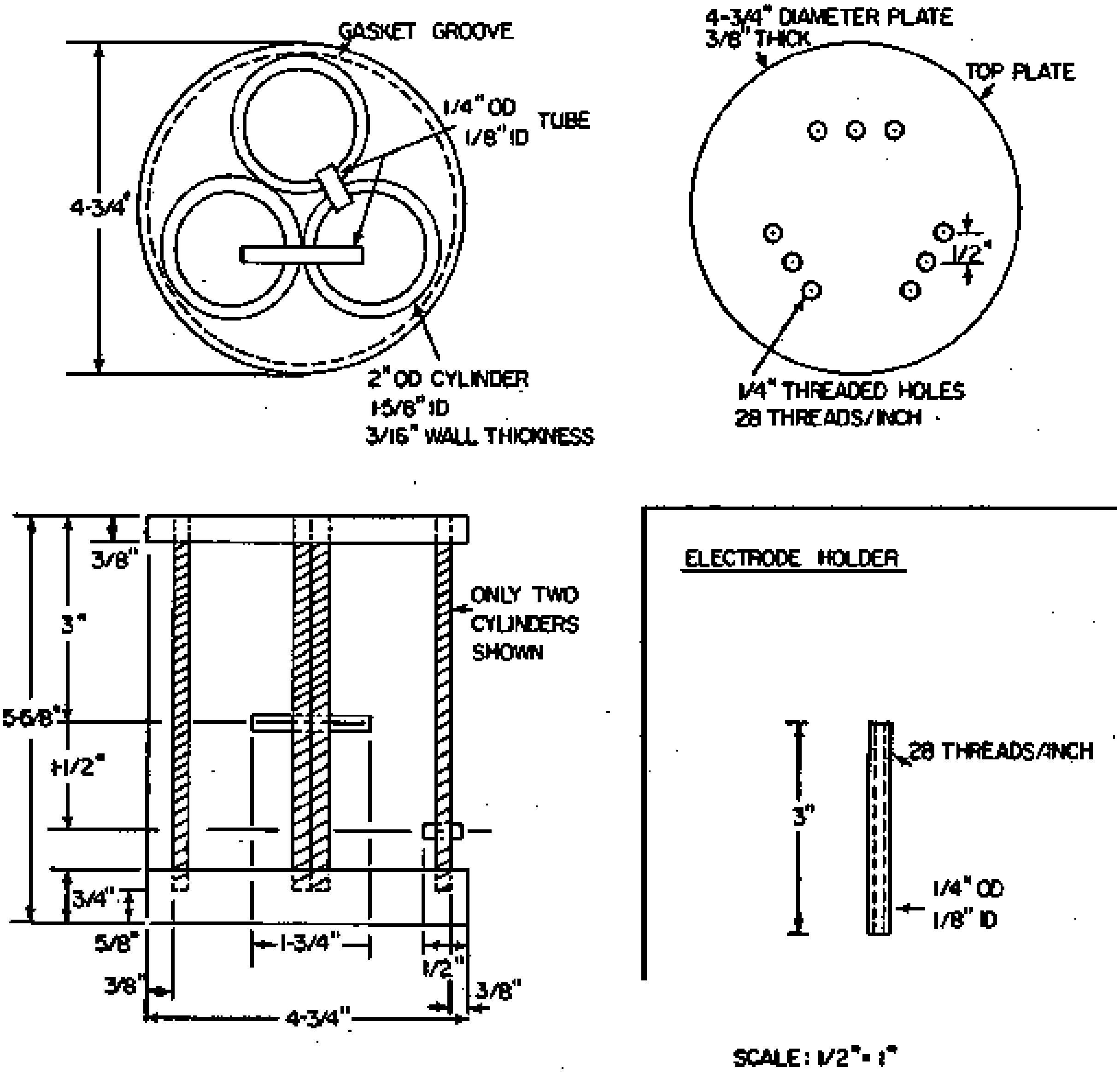

Fig. 4 - Nickel autoclave

It is therefore necessary to know the standard free-energy changes for the various reactions in the system as a function of temperature.

ΔG° vs. T correlations for various reactions of Fe, Cr, and Ni in fused NaOH in the temperature range 600°-1400°K are being attempted from published thermodynamic data. Correlations for two reactions of Fe; i.e.,

$$2Fe + NaOH + 5/4\ O_2 \rightarrow Na + Fe_2O_3 + 1/2\ H_2O \qquad (1)$$

and

$$3Fe + NaOH + 7/4\ O_2 \rightarrow Na + Fe_3O_4 + 1/2\ H_2O \qquad (2)$$

were found to be

$$\Delta G^\circ = -123.79 + 3.32 \times 10^{-2}\ T$$

and

$$\Delta G^\circ = -187.94 + 4.44 \times 10^{-2}\ T,$$

respectively. The respective correlation coefficients for (1) and (2) were 0.990 and 0.996. A correlation coefficient of 1.0 means a perfect fit.

Task 5 - Effect of Environment on Mechanistic Behavior
(F. O. Du)

A. Aims

The aim of this work is to find the effects of environmental variables on the course of mechanistic processes associated with caustic SCC. This work emphasizes effects of environmental chemistry as opposed to Task 7 which emphasizes effects of metallurgical variables. This work also helps to interpret work in Task 6.

B. Results

The apparatus is being fabricated.

Task 6 - The Straining Electrode and Transient Dissolution

A. Aims

In other work at OSU it has been shown that the straining electrode provides a good method for identifying those regions of electrochemical potential where SCC is most likely. The purpose of this task is to extend this understanding to caustic systems.

B. Results

None this quarter.

Task 7 - Initiation and Propagation of Cracks

A. Aims

The aim of this work is to study initiation and propagation processes in single crystals of Fe-Cr-Ni alloys. Special attention is to be paid to the crystallography of initiation and fracture processes. This work emphasizes metallurgical variables.

B. Results

None this quarter.

Task 8 - Corrosion Processes in Crevices

A. Aims

The aim of this work is to define electrochemical processes in crevices associated with caustic environments. Crevice effects include accelerated corrosion as well as the formation of insoluble corrosion products which expand and exert substantial forces. Both of these processes can be very destructive.

B. Results

None this quarter.

Task 9 - Dissolution at Grain Boundaries

A. Aims

Caustic SCC frequently occurs intergranularly and substantial intergranular attack is observed frequently when alloys are exposed to caustic environments. The purpose of this work is to define the amount and mechanism of intergranular corrosion and also that portion which is accelerated by stress.

B. Results

None this quarter.

Task 10 - Local Dissolution Processes on Caustic Environments

A. Aims

The aim of this work is to investigate initiation processes using thin foils which can be exposed to the environment, stressed, and subsequently examined in the electron microscope.

B. Results

None this quarter.

Task 11 - Metallurgical Structure

A. Aims

The susceptibility of many alloys to SCC can be drastically altered by changing the metallurgical structure. Such changes can be effected by cold work precipitation hardening, special heat treatments and changes in alloy composition to produce certain phases. This work will consider possibilities for applying these procedures for preventing SCC.

B. Results

None this quarter.

Task 12 - Detailed Nature of the Passive Film

A. Aims

The aim of this task is to define the detailed aspects of chemistry and structure of the protective film on the surface of Fe-Cr-Ni alloys in caustic environments. This effect is important because all chemical reactions and stress corrosion cracking are related directly to the chemical or mechanical breakdown of these protective films.

B. Results

None this quarter.

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