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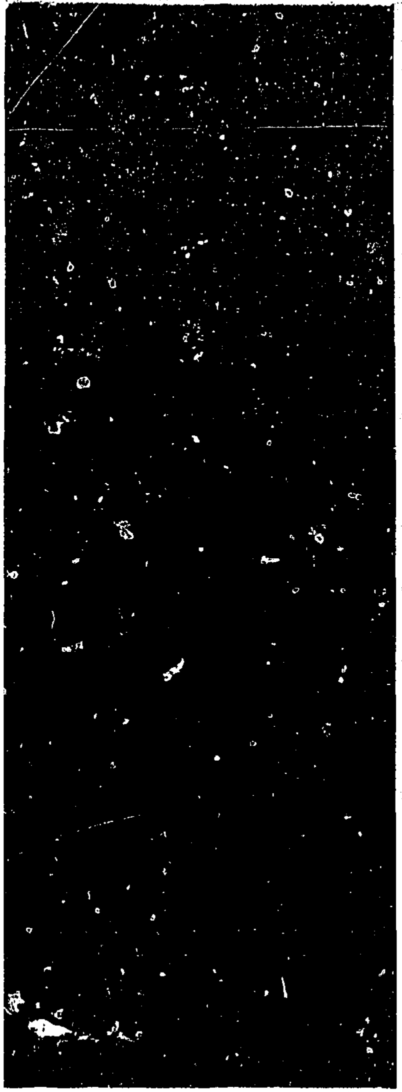

Corrosion of Alloy 800H in Caustic-Contaminated Superheated Steam at 538° C (1000° F)

J. C. Griess
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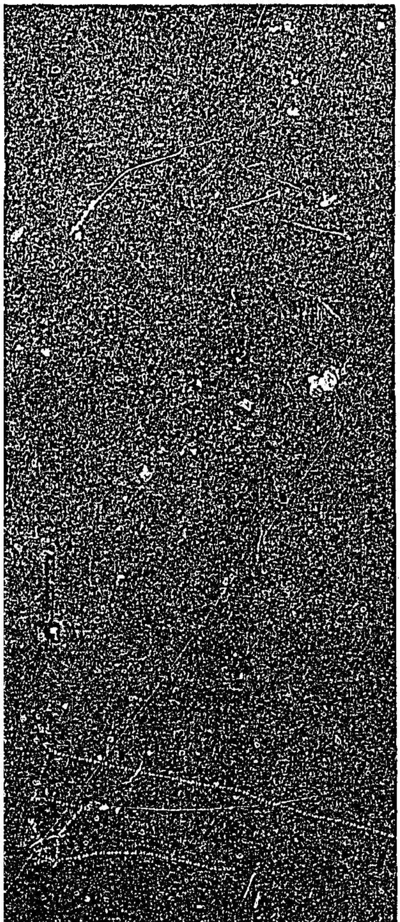

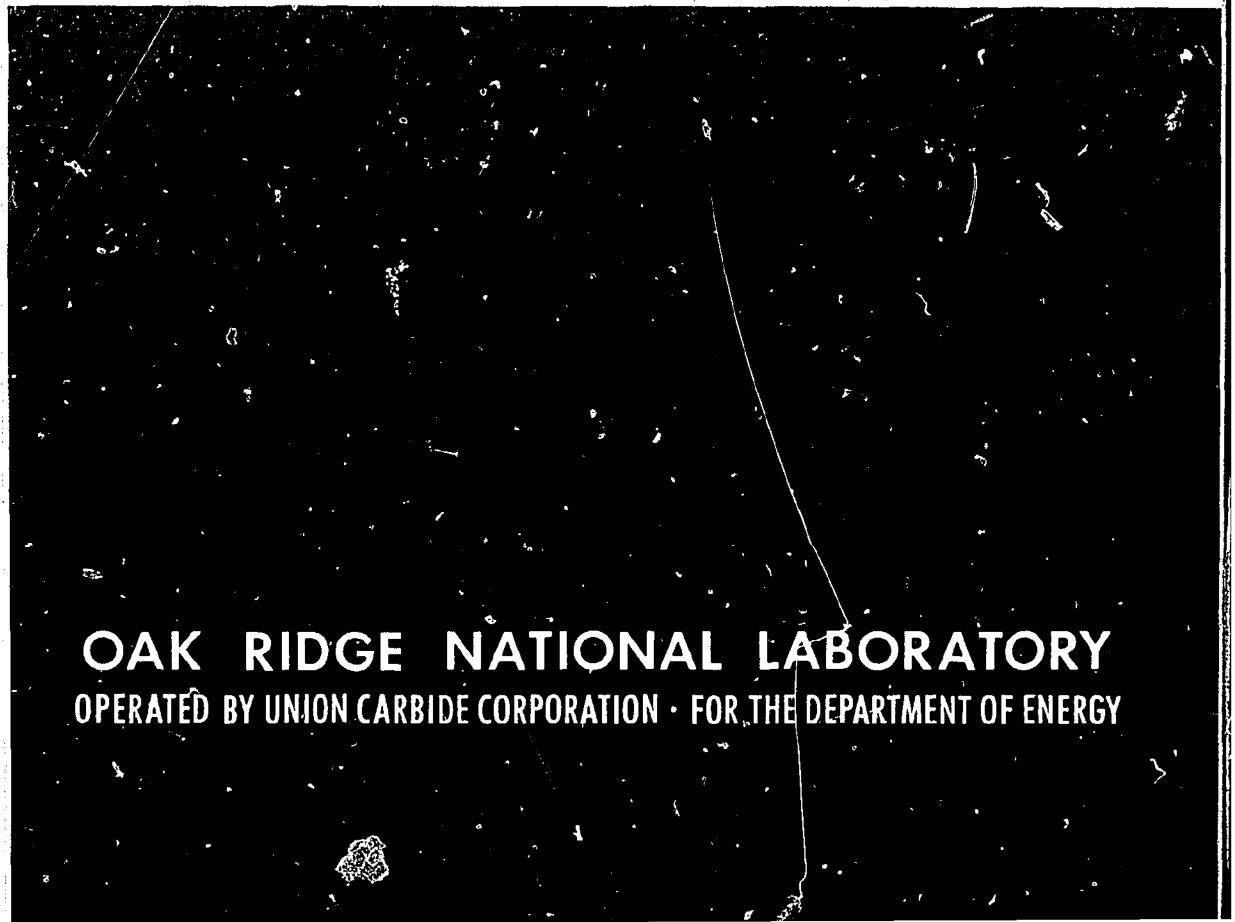

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CORROSION OF ALLOY 800H IN CAUSTIC-CONTAMINATED SUPERHEATED STEAM AT 538°C (1000°F)

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CORROSION OF ALLOY 800H IN CAUSTIC-CONTAMINATED SUPERHEATED STEAM AT 538°C (1000°F)

J. C. Griess and W. A. Maxwell*

ABSTRACT

Alloy 800H has very high corrosion resistance to high-temperature steam and is a promising material for superheater tubes in high-temperature gas-cooled reactors. The material, however, is susceptible to stress-corrosion cracking in some caustic environments. Experience at fossil-fired power plants has shown that excursions in the sodium concentration of the boiler feed water brought about by load changes can result in sodium concentrations of 20 to 30 ppb in the steam for short times. Consequently, we conducted this experimental program to determine if sodium dissolved in steam at this level adversely affects corrosion of Alloy 800H.

The corrosion resistance of four heats of Alloy 800H was determined in superheated steam containing 20 to 30 ppb Na as sodium hydroxide at 538°C (1000°F). Two of the heats contained the specified minimum carbon content (0.05%), and two contained near the maximum (0.10%). The test was conducted in a once-through loop at an operating power plant and used plant steam into which a dilute solution of sodium hydroxide was injected. Specimens stressed to 90% of the ASME design yield stress showed no signs of stress-corrosion cracking or other forms of localized attack during a 3991-h test. All four heats of the alloy corroded at 6.1 μm/year (0.24 mil/year), which though higher than in pure stream was still low.

INTRODUCTION

Alloy 800H is a prospective superheater tube material for high-temperature gas-cooled reactors (HTGRs). It is similar in composition to Alloy 800 but has a narrow range of carbon content (0.05–0.10%) and is solution treated at least at 1150°C (2100°F) to produce a relatively coarse grain size. The ASTM designation of the alloy is B 163-74; the

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*NUS Corporation, Clearwater, Florida.

UNS designation is N-08800. Both Alloys 800 and 800H have excellent resistance to steam at temperatures well above those expected in the superheaters of HTGRs; however, both materials are subject to caustic and chloride stress-corrosion cracking in aqueous solutions under certain conditions.

The purpose of our experiment was to determine if different heats of Alloy 800H would resist stress-corrosion cracking in superheated steam containing very low concentrations of dissolved sodium hydroxide. Experience has shown that, even with very efficient feedwater purification systems, excursions of the sodium concentration of the feedwater brought about by sudden load changes can result in sodium concentrations in the steam of 20 to 30 ppb for short periods.[1] Accordingly, our initial plan was to expose stressed specimens of Alloy 800H to superheated steam that had 20 to 30 ppb Na as sodium hydroxide dissolved in it. If failures were not apparent after 4000 h, the temperature of the steam was to be cycled every 24 h so that the environment would alternate between saturated and superheated steam. If cracking still did not occur, the plan was then to increase the sodium hydroxide concentration and repeat the test. However, the test program was terminated after completion of the first phase. The remainder of our report includes details of the test procedure and test results.

EXPERIMENTAL DETAILS

Four heats of Alloy 800H were tested. Two were at the minimum carbon level (0.05%), and two were near the maximum (0.10%). Table 1 shows the composition of the four alloys.

Three-point-loaded beam-type and C-shaped stressed specimens supplied by the General Atomics (GA) were used. The C-shaped specimens were machined from the wall of large diameter pipes. They were 15.9-mm (0.625 in.) OD, 13.3-mm (0.525 in.) ID, and 12.7 mm (0.50 in.) wide. The specimens also had a 5-mm (0.20-in.) gap machined along the tube axis; a nut and bolt arrangement was used to decrease the gap width

Table 1. The Elemental Composition of the Four Heats of Alloy 800H Used in the Test Program

Element	Composition, %			
	HH6260A	HH6746A	HH6918A	HH7385A
Carbon	0.05	0.05	0.09	0.10
Manganese	0.81	0.90	0.82	0.69
Iron	42.70	44.32	44.08	46.83
Sulfur	0.004	0.004	0.002	0.003
Silicon	0.43	0.27	0.33	0.30
Copper	0.36	0.49	0.61	0.60
Nickel	33.81	33.19	33.88	31.06
Chromium	21.20	20.09	19.33	19.58
Aluminum	0.25	0.30	0.43	0.41
Titanium	0.37	0.37	0.43	0.43

to produce a tensile stress on the outer surface. Figure 1 shows one of the two sets of these specimens in the loop. The maximum tensile stress was 98.6 MPa (14,300 psi), which was 90% of the ASME design yield strength at 538°C (1000°F). The maximum stress was opposite the gap of the "C" and required a 55-μm (0.0022-in.) deflection of the gap. These specimens were already stressed when supplied to us by GA. Ten specimens from each of two heats — HH6918A and HH7385A — were tested.

Three-point-loaded beam-type stressed specimens were 95.3 by 6.35 by 1.27 mm (3.75 by 0.25 by 0.050 in.) and were mounted in slots in a stainless steel holder. A set screw at the middle of the holder deflected the beam 0.74 mm (0.029 in.) to produce a maximum tensile stress of 98.6 MPa (14,300 psi), as specified by GA. These specimens had their surfaces ground and were weighed both before mounting and at the end of the test. Ten specimens were made from heat HH6746A and eleven from heat HH6260A.

In addition to the stressed specimens three coupons (unstressed) from each of the four heats in Table 1 were exposed throughout the test.

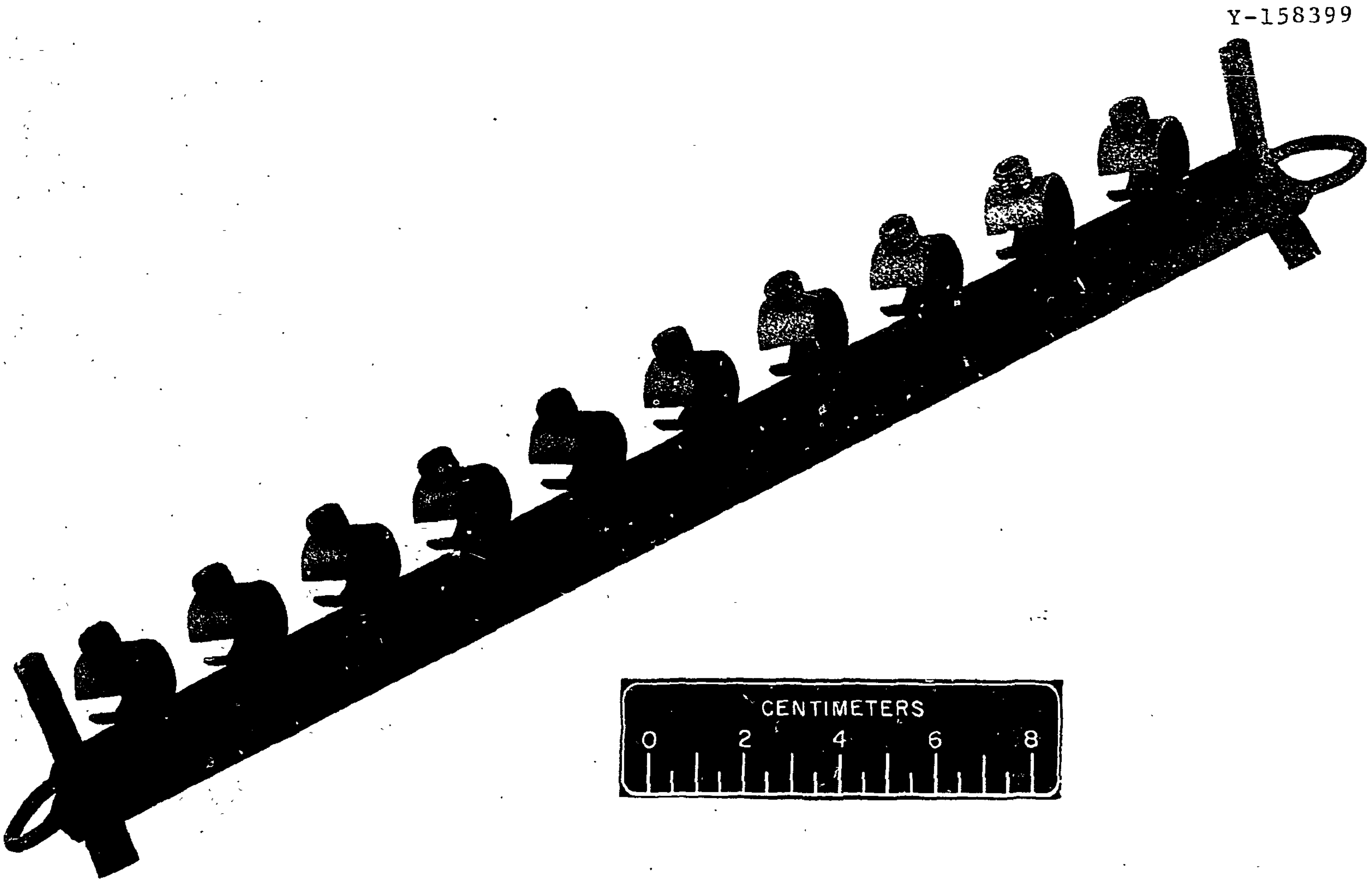

Fig. 1. Set of C Specimens That Had Been Stressed to 90% of the ASME Design Yield Stress, Shown After Removal From Test.

The dimensions of these specimens were 64 by 12.5 by 1.3 mm (2.5 by 0.50 by 0.050 in.) with a 5.2-mm-diam (13/64-in.) hole near each end. These specimens were mounted on stainless steel screws and were separated from each other by aluminum oxide washers. All specimens had a milled finish. After cumulative exposure times of 500, 1004, and 1968 h and at the end of the test (3991 h) these specimens were weighed. After the final weighing representative specimens were descaled in boiling 10% NaOH containing 5% $KMnO_4$ to establish that the weight gains were proportional to the actual amount of the alloy oxidized.

All specimens were tested in a once-through loop made of Inconel Alloy 625, which was located at the Bartow Plant of the Florida Power Corporation, St. Petersburg, Florida. The loop is shown schematically in Fig. 2. Pure steam was fed from the Bartow Plant superheater to the loop at a rate of 45 kg/h (100 lb/h). A solution containing 2 to 3 ppm Na as sodium hydroxide was injected into the incoming steam at a rate of 0.45 kg/h (1.00 lb/h); no other additions were made. The steam pressure was 10.5 MPa (1525 psi). The feed tank containing the dilute sodium hydroxide solution was blanketed with nitrogen to prevent absorption of CO_2 from the air. The tank was closed with a "breather" arrangement, which consisted of a column of lithium hydroxide (for CO_2 removal) through which any incoming or outgoing gas would have to pass. At the entrance to the loop the steam temperature was slightly less than 538°C (1000°F), but by the time it reached the first test section, where all specimens were located, the temperature was 538°C (1000°F). The test section of the loop had a 48-mm (1.9 in.) ID, was 3.7 m (12 ft) long, and was flanged on one end for insertion and removal of the specimens. After the steam passed through the second test section, it was condensed. The sodium ion concentration of the condensate was determined at least once daily with a sodium ion analyzer (Milton Roy model 626.03). The sodium ion analyzer was calibrated at least once weekly against a standard sodium hydroxide solution.

The total test time was 3991 h. The test was interrupted after 500, 1004, and 1968 h for specimen examination. Unscheduled shutdowns of the loops occurred eight times during the test as a result of either plant outages or malfunctioning of an instrument on the test equipment.

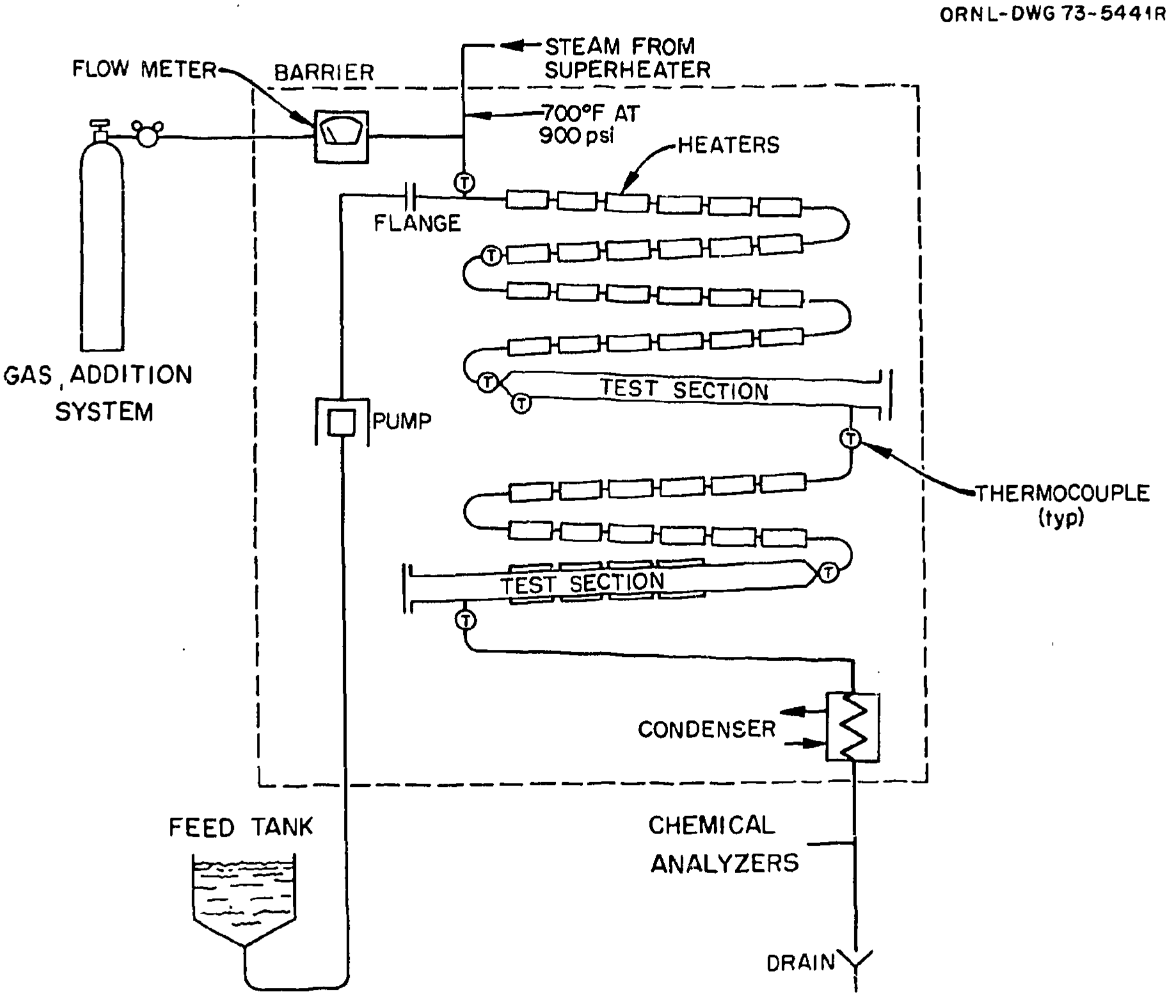

Fig. 2. Inconel Alloy 625 Test Loop.

There was one unscheduled shutdown between the start of the test and the 500-h inspection, two between the 500- and 1004-h inspections, two between the 1004- and 1968-h inspections, and three in the 1968- and 3991-h interval. During an unscheduled interruption steam containing sodium hydroxide probably condensed and wetted the specimens and the loop walls. When the loop was restarted the condensate evaporated, and briefly until the sodium hydroxide dissolved in the steam the specimens were presumably in contact with a solution containing more than 20 to 30 ppb Na. Since the sodium hydroxide concentration in the steam during operation was well below saturation,[2] any sodium hydroxide remaining after evaporation of the water would rapidly dissolve in the steam.

RESULTS

All the stressed specimens were examined microscopically at intermediate times and at the end of the test. All were covered with black scales and no cracks were visible. Measurements showed that all specimens were elastically stressed at the end of the test, although the springback of the C-specimens was not measured quantitatively. After release of the load on the beam specimens, all appeared to be flat; there was no significant creep of any of the specimens.

One C-specimen from each heat was mounted and metallographically polished to look for evidence of intergranular attack or cracks in the region of maximum stress. Figure 3 shows an as-polished section that reveals the only nonuniform attack found on any examined; furthermore, the penetration was only 10 μm deep. All other surfaces were covered with thin uniform films. Figure 4 shows the large grain size of etched specimens from heats HH6918A and HH7385A.

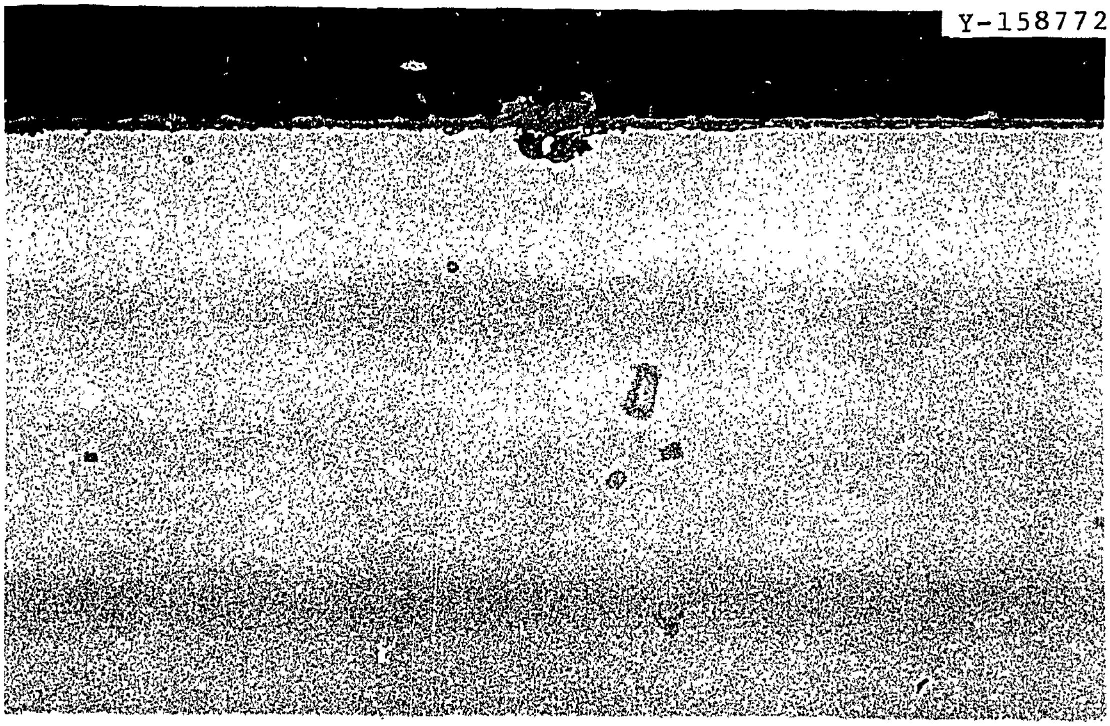

Fig. 3. As-Polished Section of Alloy 800H (Heat HH6918A) After 3991h in Superheated Steam Containing 20 to 30 ppb Na at 538°C (1000°F). 500×.

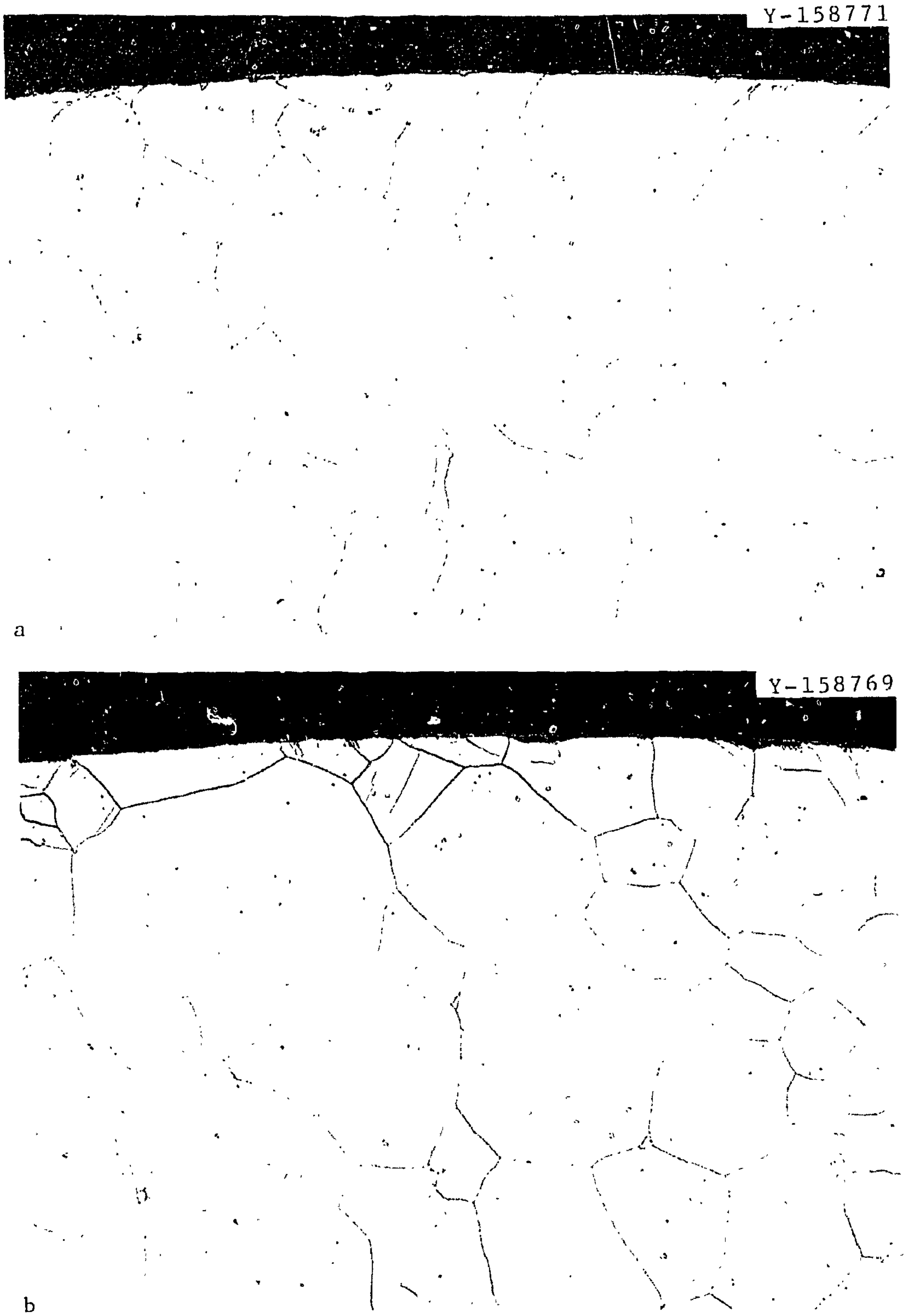

Fig. 4. Etched Specimens of Alloy 800H Illustrating Large Grain Size and Absence of Localized Attack. 100×. (a) Heat HH6918A. (b) HH 7385A.

The beam-type specimens were weighed both before and after test; and all specimens gained weight, as shown in Table 2.

Table 2. Weight Gains of Beam-Type Specimens
After 3991 h in Superheated Steam Containing
20 to 30 ppb Na at 538°C (1000°F)

Specimen (Heat HH6260A)	Weight Gain (g/m^2)	Specimen (Heat HH6746A)	Weight Gain (g/m^2)
1	5.4	1	5.8
2	5.3	2	5.6
3	5.6	3	5.8
4	6.3	4	6.1
5	5.8	5	5.9
6	5.7	6	6.3
7	5.8	7	6.6
8	5.9	8	5.9
9	5.9	9	6.4
10	5.7	10	6.4
11	5.9		

Weight gains among the individual specimens agreed well, and the two heats did not differ significantly. One specimen (3, HH6260A) was descaled to determine if the weight gain corresponded to that expected from the amount of metal oxidized. On the basis of the defilmed weight loss of the specimen and the assumption that the corrosion product was $(Fe_{0.7}Cr_{0.3})_2O_3 \cdot NiO$, the amount of oxide should have been 33.7 mg; 33.5 mg was actually found. Hence, we conclude that the weight gain of the specimens was directly proportional to the amount of metal oxidized, and that very little if any of the oxide was lost. The average weight gain of the specimens was 5.9 g/m^2 during the 3991-h test, which corresponds to a corrosion rate of 4.3 μm/year (0.17 mil/year). As with the C-specimens there was no visible evidence of any kind of localized attack.

The weight gains of the unstressed coupons from the four heats of Alloy 800H are shown in Table 3. All specimens at all weighings agreed excellently. A representative specimen from each heat was descaled, and the weight of corrosion product expected from the amount of metal oxidized was compared with the amount actually found. In each case the amount of oxide found was 99 to 102% of that expected, indicating that with these specimens as with the beam specimen the weight gain was directly proportional to the weight of metal oxidized.

The average weight gains of the specimens after each exposure correspond to corrosion rates of 8.1, 5.8, 9.7, and 6.1 μm/year (0.32, 0.23, 0.38, and 0.24 mil/year) after 500, 1004, 1968, and 3991 h, respectively.

Table 3. Average Weight Gains on Unstressed Specimen in Superheated Steam Containing 20 to 30 ppb Na at 538°C (1000°F)

Heat	Specimen	Weight Gain, g/m^2			
		500 h	1004 h	1968 h	3991 h
HH6260A	1	1.3	2.5	6.3	7.9
	2	1.5	2.1	6.0	7.9
	3	1.5	2.1	5.8	8.7
HH6746A	1	1.5	2.1	6.7	8.1
	2	1.7	2.4	6.6	8.2
	3	1.7	2.5	6.8	8.2
HH6918A	1	1.3	2.2	7.0	8.2
	2	1.3	2.0	6.3	8.3
	3	1.4	2.0	6.6	8.3
HH7385A	1	1.4	2.0	6.4	7.2
	2	1.5	2.1	6.5	8.1
	3	1.3	2.0	6.5	7.8

DISCUSSION

Alloy 800 (and presumably Alloy 800H) is subject to caustic cracking in high-temperature aqueous solutions, but the concentration of caustic necessary to produce cracks is relatively high, and stress levels at least approaching the yield strength are required.[3,4] In such solutions cracking is an electrochemical process as shown by the fact that cracking can either occur or be prevented by adjustment of the electrochemical potential of the alloy. In our test stressed specimens were exposed to steam containing very low concentrations of sodium hydroxide. This gas is not an electrolyte in the usual sense. Furthermore, our specimens were stressed at 90% of the ASME design yield stress, which is substantially below the nominal yield point of the material. In view of these facts the absence of cracking was not expected. During start-up after a shutdown it is likely that a liquid phase existed on our specimens briefly, but the amount of caustic in the liquid was so small that after evaporation of the water the caustic rapidly dissolved in the steam.

It has been demonstrated[5] that the more the surface of Alloy 800 (and presumably also Alloy 800H) is cold worked, the less the corrosion in high-temperature steam. Our data agree with this observation. The beam-type specimens with ground surface had weight gains that averaged 5.9 g/m^2 during the 3991-h test, whereas the coupon, which had experienced less cold work (milling-machine finish), showed an average weight gain of 8.2 g/m^2.

However, the weight gains of both types of specimens were greater than for Alloy 800 specimens exposed at the same temperature in pure steam. For example, in another series of tests (still in progress at the Bartow Plant) specimens of Alloy 800 that had been ground on a 100-mesh belt grinder and exposed to superheated steam at 538°C (1000°F) showed average weight gains of 0.48, 0.55, and 0.64 g/m^2 after 504, 1621, and 3051 h, respectively; annealed and pickled specimens exposed for 2615 and 5551 h had average weight gains of 2.1 and 2.4 g/m^2, respectively. Comparison of these values with those in Table 3 illustrates the greater corrosion in the caustic-containing steam than in pure steam. The belt-ground specimens had a carbon content of 0.08% and the annealed ones, 0.05%. The only basic difference between the materials tested in pure steam and those tested in the caustic-contaminiated steam was that the latter materials had been solution annealed to produce a relatively large grain size. Since selective grain boundary attack was not noted in either case, we conclude that the presence of 20 to 30 ppb Na in the steam produced the increased attack.

Note that although the attack rate was greater in the presence of caustic, it was still quite low, averaging only 6.1 μm/year (0.24 mil/year) after 3991 h. In an operating reactor steam containing as much as 20 ppb Na would be expected seldom and then only briefly. Our data indicate that under such conditions corrosion of Alloy 800H superheater tubes would not be seriously affected.

Table 3 shows that the rate of weight gain was neither power dependent on time nor constant. The incremental weight gain between 1004 and 1968 h was significantly higher than for other incremental periods. We know no apparent reason for this. For about the first 2100 h of test we experienced no difficulty in maintaining the level of sodium in the steam at between 20 and 30 ppb, and the amount of sodium injected into the steam corresponded well with the sodium concentration of the condensate. Thus, abnormally high concentration of sodium in the steam did not exist during this period and could not account for the large incremental weight gain between the 1004 and 1968 h weighings. However, after about 2100 h the sodium content of the condensate decreased to 0 to 4 ppb, although the rate of injection into the steam as it entered the loop did not change. During the next four days the sodium content of the condensate increased to 35 ppb and on the following day it was 75 ppb. Then the feed to the loop was stopped. During the next four days the sodium concentration of the condensate gradually returned to normal, and the injection of feed solution to the loop was resumed. Thereafter, the caustic concentration in the condensate stayed at the expected level.

We know no reason for the lack of control of the sodium content during this period. However, since the weight gains of the specimens between 1968 h and the end of the test did not seem abnormal, it appears that the lack of control of the sodium for the few days produced no unusual corrosion.

SUMMARY

Exposure of four different heats of Alloy 800H to superheated steam containing 20 to 30 ppb Na as sodium hydroxide at 538°C (1000°F)

produced no signs of localized attack on specimens stressed to 90% of the ASME design yield stress. However, both stressed and unstressed specimens gained more weight than similar specimens of Alloy 800 exposed to pure steam for even longer times. Although the presence of caustic in the steam enhanced corrosion, even in the worst case the weight gain during the 3991-h test corresponded to an average penetration rate of only 6.1 μm/year (0.24 mil/year). Since steam in high-temperature gas-cooled reactor superheaters seldom and then only briefly would contain as much as 20 ppb Na, we conclude that such excursions would not compromise the integrity of Alloy 800H superheater tubes.

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