Contract No. W-7405-eng-92

CORROSION OF STAINLESS ALLOYS IN HIGH-
TEMPERATURE NITROGENOUS
ENVIRONMENTS

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July 14, 1959

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CORROSION OF STAINLESS ALLOYS IN HIGH-TEMPERATURE NITROGENOUS ENVIRONMENTS

Donald L. Keller

On the basis of screening tests and favorable mechanical properties, AISI Type 318 stainless steel was selected as a fuel-element cladding material to operate in a coolant comprised essentially of gaseous nitrogen modified by the addition of oxygen and water vapor. Tests at atmospheric pressure confirmed calculations which indicated that small additions of oxygen to nitrogen would inhibit nitriding by the process of preferential oxidation. The tests at atmospheric pressure determined that the rate of oxidation of Type 318 stainless was generally at a minimum when 0.5 volume per cent oxygen was added to the nitrogen gas. Oxidation of this steel was more severe when additions of 0.1 and 5.0 volume per cent oxygen were made to the nitrogen. The rate of oxidation was primarily temperature dependent, but was also influenced by time. Oxidation during exposure periods of less than 1000 hr appeared to proceed at a parabolic rate. On longer exposures, however, there were indications of more rapid attack. A maximum depth of attack of 2.9 mils was observed on Type 318 stainless which had been exposed at 1650 F for 3658 hr.

Stress-corrosion studies indicated that unstressed and stressed specimens were attacked at about the same rate. Stresses as high as 1800 psi were applied to the stressed specimens. These studies also indicated that the rate of attack increased with an increase in the grain size of the metal and with an increase in the water-vapor content of the gaseous environment. The effect of grain size and water vapor was not as apparent in the studies in which stress corrosion was not a variable.

The results of high-pressure studies (200 psi) indicated that, on a qualitative basis, the rate of oxidation was not affected by pressure.

INTRODUCTION

The objective of this program of research on the Gas Cooled Reactor Experiment (GCRE) was to select a fuel-element cladding material and a compatible gaseous environment which would permit satisfactory operation for the life of the fuel element.

More specifically, the problem was to find a combination that would provide a cladding with satisfactory strength, oxidation, and corrosion resistance in the range 1400 to 1650 F, in addition to having suitable physical properties. Calculations indicated that the average surface temperature of the fuel elements would be 1400 F, although temperatures as high as 1650 F might be reached at hot spots. Nitrogen had been selected as the coolant for the system. The immediate problem posed by this selection was associated with the conversion of some molecular nitrogen to nascent nitrogen upon radiation. Nascent nitrogen would attack the metal cladding severely.

In the early part of this investigation, tests were run in mixtures of gaseous ammonia with nitrogen to simulate an irradiated nitrogen atmosphere. Cracking of the ammonia on the metal surface produced nascent nitrogen, thus simulating the production of nascent nitrogen from molecular nitrogen by radiation. All metals and alloys under

consideration were attacked or "nitrided" by such atmospheres. Although nickel-base alloys were found to be most resistant to nitriding, none was entirely satisfactory.

To overcome this difficulty, small additions of oxygen to the nitrogen atmosphere had been tried at the Engineering Research and Development Laboratories at Fort Belvoir, Virginia.⁽¹⁾ The metal surfaces reacted with these oxidizing additions in preference to nitrogen, with the result that nitriding was prevented. The metal surface oxidized instead. Attention was then turned to the search for a cladding material which had the necessary high-temperature mechanical properties and which, while oxidizable, would not be severely attacked by the modified nitrogen atmospheres. Screening tests indicated that iron-base alloys possessed the best combination of high-temperature strength and oxidation resistance. Nickel-base alloys had been eliminated from consideration because of high nuclear cross section and poor strength above 1500 F.

In the present investigation, three phases were carried on concurrently. The greater part of the effort comprised experimental work at atmospheric pressure to study the effects of time and temperature of exposure and of oxygen content of the nitrogen atmosphere on the severity of oxidation on unstressed specimens. In a second phase some of these variables were studied on specimens under stress. The third phase of the work was conducted at higher gas pressures, mainly at 200 psi. Because the gas coolant was to be at a pressure of 200 psi, it was desirable to determine if there were pressure effects, and, if so, to correlate any such pressure effects to the results of the work at atmospheric pressure.

STUDIES AT ATMOSPHERIC PRESSURE

James G. Hoag, Charles J. Slunder, and A. M. Hall

This section of the report covers oxidation studies of AISI Type 318 stainless steel and certain other alloys in atmospheres of nitrogen containing small amounts of either oxygen, or oxygen plus water vapor, at temperatures of 1500, 1650, 1750, and 1800 F. In addition, limited tests were conducted in nitrogen atmospheres containing small amounts of carbon monoxide.

Initially, the test specimens were preannealed at 2150 F in order to duplicate the maximum temperature expected in the fabrication of a fuel-element assembly. Later in the program it was learned that fabrication techniques might be changed; therefore, the preannealing temperature was raised to 2450 F in order to correspond with the new conditions.

X-ray diffraction studies and fluorescence analyses of the oxidation products were made in the course of the investigation.

^{*}References at end of text.

Experimental Techniques

Apparatus

The specimens were exposed in Vycor tubes heated by 18-in.-long horizontal Hevi-Duty tube furnaces; five of these furnaces were used in the program. The temperature of the furnaces was maintained by potentiometer controllers using Chromel-Alumel thermocouples. Originally, the thermocouples were placed in ceramic protection tubes; however, because of concern over the temperature lag with the ceramic sheathing, a change to closed-end Inconel-sheathed thermocouples was made. In earlier work, the test temperature was controlled within plus 15 and minus 5 F. The temperature control was later refined to be within plus 3 and minus 5 F of the test temperature at 1650 F. This was done by shunting resistance heaters across the potentiometer so that 80 per cent of the power was on at all times. The specimens were suspended in the muffle by means of platinum wires which were hung on a Nichrome frame.

The gas-flow rate in some of the earlier work was estimated to be approximately 150 cm³ per min. In later work, a rate of flow of 200 cm³ per min, measured by variable-area flowmeters, was maintained. The effluent gases were bubbled through mineral oil to prevent back diffusion of ambient air into the furnace.

In the tests conducted in atmospheres containing water vapor, the water was introduced by bubbling the nitrogen-oxygen mixtures through water maintained at the temperature calculated to give the desired dew point. During the experiments, the dew point was measured periodically with a General Electric dew-point meter.

Procedure

The specimens used were 1/2 in. square by 15 mils thick. These were cut to size and deburred prior to any surface or heat treatment. After the preparatory treatments the specimens were weighed and measured.

Four specimens were placed in the middle of the furnace, under the thermocouple and side by side. The plane of the specimens was parallel with the direction of flow of the test gas. The furnace was sealed with rubber stoppers and a water-soluble glue, and then purged for 2 hr with the test gas before heating to the test temperature. At the end of an exposure period, the furnace was cooled to room temperature before the specimens were removed.

At the end of each exposure period, the specimens were weighed and one specimen was removed from the test and examined metallographically. A new specimen was then inserted in the furnace to replace the specimen which was removed and exposure was continued. With this procedure, a number of specimens could be exposed and available for examination during the course of an experimental run.

During the test runs, temperatures and gas-flow rates were checked at least twice a day during the week, and once a day on the weekend. Dew points for tests having additions of water vapor to the test environment were determined about three times a week.

The depth of attack of a specimen was determined by measuring the difference between the original thickness, as measured with a micrometer, and the thickness of the unattacked metal after exposure, as determined metallographically. Scaling interfered with micrometer measurements after the test. Measurement of the unattacked metal after exposure was found to be more accurate than direct measurement of the attacked metal because it is independent of any loss of scale by flaking which might have occurred. Using this method, it is estimated that the measurement of attack was accurate to ± 0.1 mil. The attack was measured at its deepest point of penetration.

Screening Tests on Candidate Cladding Materials

During the period when tests were conducted in environments containing ammonia, many metals and alloys were investigated. It was found that high-nickel alloys were more resistant (although not fully resistant) to the nitriding reaction than iron-base alloys. Generally speaking, it may be said that the high nickel content dilutes the amount of nitridable alloy. However, because of their unfavorable nuclear cross section, the high-nickel alloys are not practical as claddings for fuel elements.

The severity of nitriding encountered in the early work made it mandatory that steps be taken to circumvent this difficulty. Results at the Engineer Research and Development Laboratories (ERDL) indicated that the addition of 0.5 volume per cent oxygen to nitrogen prevented AISI Type 347 stainless from absorbing nitrogen at 1600 F. With this information, thermodynamic calculations were made to ascertain the merit of exposing specimens in a slightly oxidizing nitrogenous environment. These calculations indicated that the oxides formed by the presence of oxygen or water vapor would be more stable than the nitrides. This meant that oxides should form preferentially to nitrides. However, for nitriding to be prevented, it is necessary that the oxide form initially at a rate which quickly forms a protective oxide.

When it became apparent that the introduction of small amounts of oxidizing gases to the gas coolant would probably inhibit the nitriding reaction, the potentialities of iron-base alloys were examined again, and five iron alloys believed to have the necessary high-temperature properties were chosen for evaluation. The five alloys selected for screening tests were AISI Types 316, 318, and 347 stainless steels, and two Timken alloys (16-25-6 and 16-15-6). The nominal compositions of these alloys are:

Alloy	Nominal Composition (Balance Iron), w/o					
	Cr	Ni	C	Mn	Mo	Nb
Type 316	17	12	0.10	2	2	--
Type 318	18	14	0.08	2	2	0.8
Type 347	18	10	0.08	2	--	0.8
16-15-6	16	15	0.07	7.5	6	--
16-25-6	16	25	0.08	1.5	6	--

The results of tests performed on these five alloys in several slightly oxidizing nitrogen atmospheres are shown in Tables 1 and 2.

TABLE 1. MAXIMUM DEPTH OF OXIDATION OF VARIOUS FERROUS ALLOYS EXPOSED FOR 100 HR
IN NITROGEN CONTAINING SMALL AMOUNTS OF OXIDIZING GASES^(a)

Alloy	Maximum Depth of Penetration After 100 Hr in Nitrogen Atmosphere Having Addition Shown, mils											
	0.07 Volume Per Cent H ₂ O			0.2 Volume Per Cent H ₂ O at 1650 F	0.05 Volume Per Cent Oxygen		0.1 Volume Per Cent Oxygen			0.5 Volume Per Cent Oxygen		
	1500 F	1650 F	1800 F		1650 F	1800 F	1500 F	1650 F	1800 F	1500 F	1650 F	1800 F
Type 316 stainless	--(b)	0.5	1.6	--	0.2	1.0	0.05	--	2.0	0.1	0.15	--
Type 318 stainless	0.05	0.05	5.0	0.15	0.05	0.2	0.05	0.05	0.25	0.05	0.05	0.15
Type 347 stainless	--	0.05	5.0	--	0.6	0.4	0.05	--	0.3	0.05	0.2	--
Timken 16-15-6	0.3	0.1	1.3	0.5	0.15	0.9	0.1	0.3	1.0	0.2	0.6	0.9
Timken 16-25-6	0.3	0.3	0.6	0.3	0.3	0.5	0.15	0.3	0.5	0.1	0.4	0.6

(a) Specimen surface was ground to 240-grit finish.

(b) A dash indicates that the material was not tested.

TABLE 2. MAXIMUM DEPTH OF OXIDATION OF VARIOUS FERROUS ALLOYS EXPOSED TO OXIDIZING NITROGEN ATMOSPHERES FOR 500 HR AT 1650 F^(a)

Atmosphere Composition, volume per cent	Maximum Depth of Penetration in Alloy Shown, mils				
	Type 316	Type 318	Type 347	Timken 16-15-6	Timken 16-25-6
Nitrogen + 0.07 H ₂ O	1.3	0.6	1.5	0.6	0.7
Nitrogen + 0.1 oxygen	1.2	0.6	1.0	0.6	0.7

(a) Specimens were ground to 240-grit finish and annealed at 2150 F in hydrogen for 1-1/2 hr.

In Table 1, data for 100-hr exposures at 1500, 1650, and 1800 F are presented. These data are shown graphically in Figure 1. At the 1500 and 1650 F levels, Type 318 stainless was at least as good as, or superior to, the other four alloys in all environments. Again, at 1800 F it was oxidized to a lesser extent in each of the environments except for the one containing 0.07 volume per cent water vapor. In this case, both Types 318 and 347 stainless were oxidized to a depth of 5.0 mils. Generally Type 318 as well as Type 347 stainless showed less susceptibility to intergranular attack than the other alloys tested. Type 316 stainless and the two Timken alloys showed a stronger tendency toward intergranular oxidation, the tendency increasing with increasing test temperature.

The data obtained for 500 hr of exposure at 1650 F are listed in Table 2. In both test environments, the Type 318 and Timken 16-15-6 alloys were somewhat more resistant to oxidation than the other three tested.

The results of these tests led to the selection of Type 318 stainless as the standard material for further investigations in oxidizing nitrogen atmospheres which are discussed in the following sections. In some of the studies exposure periods as long as 3600 hr were used.

There are very few published data on the high-temperature properties of Type 318 stainless; however, the fact that the fuel-element cladding would be exposed for long periods of time in the sensitizing-temperature range made it desirable to select a stabilized grade. Both Types 318 and 347 stainless are stabilized alloys, but Type 318 has better high-temperature properties because it contains 2 to 3 w/o molybdenum.

Effect of Surface Condition on Oxidation Resistance

Although the condition of the surface of the fuel-element cladding alloy would tend to be fixed by the method of assembly, which would involve brazing under a hydrogen shield, a few tests to explore the effect of surface finish were run on Type 318 stainless. Two gas mixtures were employed, nitrogen plus 0.1 volume per cent oxygen, and nitrogen plus 1.0 volume per cent oxygen and 0.04 volume per cent water vapor. The specimens were tested at 1650 F for 100 hr. The various surface conditions used are shown in Table 3.

FIGURE 1. MAXIMUM DEPTH OF OXIDATION OF VARIOUS FERROUS ALLOYS EXPOSED FOR 100 HR IN NITROGEN CONTAINING SMALL AMOUNTS OF OXIDIZING GASES

TABLE 3. METHODS OF PREPARING TYPE 318 STRIP SPECIMENS
FOR STUDIES OF THE INFLUENCE OF SURFACE
CONDITION ON OXIDATION RESISTANCE

1. Ground - 240 grit	10. Cold rolled 20 per cent, annealed(a), pickled(b), and ground(c)
2. Ground - 600 grit	11. Cold rolled 30 per cent, annealed(a), pickled(b), and ground(c)
3. Metallographic polish	12. Ground(c) and pickled(b)
4. Electropolished	13. Ground(c) and annealed(d) in hydrogen
5. Sand blasted	14. Preoxidize 10 min at 800 F
6. Cold rolled 10 per cent	15. Preoxidized and pickled(b)
7. Cold rolled 20 per cent	
8. Cold rolled 30 per cent	
9. Cold rolled 10 per cent, annealed(a), pickled(b), and ground(c)	

(a) 2000 F, 15 min, water quench.

(b) 10 to 15 volume per cent HNO_3 -1 to 2 volume per cent HF.

(c) 240 grit.

(d) 2150 F, 1-1/2 hr, furnace cool.

The results of the study indicated that the surface finish of the cladding material did not affect the degree of attack to any great extent. The surface finish of the specimen annealed in hydrogen (No. 13 in Table 3) was closest to that expected in the fuel-element assemblage. It was attacked to no greater degree than were the other specimens.

Further Experiments With Type 318 Stainless Steel

To obtain additional information on the effect of oxygen concentration in the nitrogen environment and on the effect of water additions to oxygen-nitrogen mixtures, two further series of tests were made. The first involved short-term exposures of the material, up to 675 hr, at 1650 F to explore the question of the optimum concentration of oxygen. In the second series the material was given longer term exposures, up to 3650 hr, at various temperatures and at the optimum oxygen concentration found in the short-time series. This series of tests was run with and without water additions. The objectives here were to extend the study of the influence of time and to examine further the effect of water additions.

For these experiments, a single heat of Type 318 stainless steel was cold rolled 86 per cent (final thickness of 15 mils) and then annealed in hydrogen. For the short-term tests, the specimens were annealed at 2150 F for 2 hr and furnace cooled. For the long-term tests two different preanneals were used. These will be covered in detail in the next section. The chemical analysis of the heat used in both tests was as follows:

Composition (Balance Iron), w/o									
C	Mn	P	S	Si	Ni	Cr	Mo	Nb	Co
0.05	2.00	0.005	0.028	0.26	13.16	17.64	2.44	0.82	0.17

The analysis is typical for Type 318 stainless. The check for cobalt was included for interest, as it is closely associated with nickel and it could become activated in a radiation field.

Effect of Oxygen Concentration in the Atmosphere

Figure 2 shows graphically the oxidation obtained in nitrogen atmospheres at 1650 F to which additions of 0.05, 0.1, 0.5, and 5.0 volume per cent oxygen were made. The data are presented in Table 4. The points on Figure 2 show some scatter, but this might be expected from the nature of the experiment. The combination of several factors probably contributed to the deviations from the lines that were drawn to represent the data. First, the maximum depth of attack or oxidation was measured, rather than the average depth of attack. Identification of this dimension was limited because only one cross section perpendicular to the surface was examined. Second, each point on a curve represented a different specimen. Differences in behavior from specimen to specimen are not unlikely. Also, the precision of the measurements of the depth of attack was estimated to be no more than ± 0.1 mil. Finally, each time that a specimen was removed from a test for metallographic examination, the specimens still undergoing testing went through a cooling and reheating cycle. This means that contraction and

FIGURE 2. EFFECT OF OXYGEN IN NITROGEN ATMOSPHERES ON THE OXIDATION OF TYPE 318 STAINLESS STEEL AT 1650 F

TABLE 4. MAXIMUM DEPTH OF ATTACK OF TYPE 318 STAINLESS STEEL
EXPOSED AT 1650 F TO NITROGEN ATMOSPHERES
CONTAINING OXYGEN^(a)

Oxygen in Nitrogen, volume per cent	Exposure Time, hr	Depth of Attack, mils
0.05	124	0.6
	224	0.35
	400	0.85
	624	0.85
0.1	80	0.35
	84	0.25
	193	0.5
	470	0.8
	553	1.3
	830	2.9
	943	2.9
0.5	80	0.1
	176	0.15
	264	0.4
	357	0.25
	677	0.3
5.0	105	0.3
	114	0.2
	214	0.3
	223	0.4
	328	0.55

(a) Specimens preannealed in hydrogen at 2150 F for 2 hr.

expansion of both metal and scale occurred, a circumstance which would favor cracking and possible spalling of the scale.

On the basis of the results plotted in Figure 2, it appears that up to exposure periods of about 700 hr, the addition of 0.5 volume per cent oxygen to the nitrogen prevents nitriding with a minimum of oxidation. Three types of oxidation were observed in the specimens: scaling, intergranular attack, and, occasionally, subsurface-void formation. None of the specimens exhibited any evidence of a nitriding reaction. The slopes of the lines in Figure 2 suggest a parabolic rate law of oxidation. Thus, the oxidation is controlled by a diffusion process, and the rate decreases with time, at least for the time period included in these screening tests. On the basis of these results, 0.5 volume per cent oxygen was selected for further investigation as an additive to the nitrogen atmosphere.

Effect of Long-Term Operation and Water Additions to the Gas Atmosphere

Long-term tests were conducted in two atmospheres, nitrogen containing 0.5 volume per cent oxygen, with and without an addition of water vapor. It should be noted that the addition of water vapor was not made to inhibit nitriding primarily, but rather to examine the tolerance of the system for water vapor. Water vapor is a factor to contend with in reactor operation. When the reactor is shut down, it is flooded with water; it must then be dried before restarting. Questions then arise as to how dry the system must be, and as to what effect the residual water vapor will have on the fuel-element cladding. To gain information bearing on these questions, experiments were made in which specimens were exposed to atmospheres containing both 0.5 volume per cent oxygen and 0.6 volume per cent water vapor. The specimens used in the previous experiments had been preannealed at 2150 F, while the specimens in three of the series described in this section were preannealed at 2450 F. The reason for going to the higher annealing temperature was to allow for more freedom in the selection of fabrication methods.

The actual oxygen content of the gas used in these experiments varied between 0.4 and 0.5 volume per cent. It is listed as a nominal 0.5 volume per cent in the tables and figures in this section. Prepurified nitrogen was used in making up the nitrogen-oxygen mixtures, and the dew point of this mixture was approximately -90 F. For tests in atmospheres containing water vapor, the dew point was held between 31 and 33 F, which is equivalent to 0.58 and 0.63 volume per cent water vapor, respectively.

The results of the experiments are presented in Table 5 for dry atmospheres and in Table 6 for atmospheres containing water vapor. Figures 3, 4, and 5 were drawn from these data.

From Figure 3, the effect of temperature on the rate of oxidation of Type 318 stainless as measured by the maximum depth of penetration can be seen. The atmosphere was dry nitrogen containing 0.5 volume per cent oxygen. The data show that there was an increase in rate of attack with temperature.

An effect by annealing temperature is suggested in the plots of Tests 2 and 3 in Figure 3. The specimens annealed at the lower temperature were attacked to a slightly lesser extent than those annealed at the higher temperature. There was a marked

TABLE 5. MAXIMUM DEPTH OF ATTACK OF TYPE 318 STAINLESS STEEL
EXPOSED AT SEVERAL TEMPERATURES TO DRY NITROGEN
ATMOSPHERES CONTAINING 0.5 VOLUME PER CENT OXYGEN

Test	Specimen	Preanneal Temperature(a), F	Exposure Temperature, F	Exposure Time, hr	Depth of Attack, mils
1	5	2150	1750	215	0.45
	6	2150	1750	376	0.7
	44	2150	1750	479	0.7
	7	2150	1750	580	0.95
	41	2150	1750	683	1.1
	27	2150	1750	843	1.3
	8	2150	1750	1059	2.1
2	17	2150	1650	216	0.4
	18	2150	1650	478	0.5
	37	2150	1650	980	0.75
	76	2150	1650	1032	1.6
	58	2150	1650	2468	1.0
	20	2150	1650	2626	0.8
	40	2150	1650	3180	1.8
	19	2150	1650	3658	2.9
3	54	2450	1650	238	0.7
	77	2450	1650	417	0.5
	55	2450	1650	662	0.9
	73	2450	1650	1089	0.8
	56	2450	1650	1334	1.0
4	64	2450	1500	258	Nil
	80	2450	1500	417	0.25
	65	2450	1500	930	0.2
	72	2450	1500	1176	0.6
	66	2450	1500	1347	0.4
	67	2450	1500	1434	0.5

(a) All specimens were annealed in hydrogen. Those annealed at 2150 F were held for 2 hr and furnace cooled. Specimens annealed at 2450 F were held for 5 hr, cooled to 1850 F, and held for 2 hr, and then furnace cooled.

TABLE 6. MAXIMUM DEPTH OF ATTACK OF TYPE 318 STAINLESS STEEL EXPOSED AT SEVERAL TEMPERATURES TO NITROGEN ATMOSPHERES CONTAINING 0.5 VOLUME PER CENT OXYGEN PLUS 0.6 VOLUME PER CENT WATER VAPOR

Test	Specimen	Preanneal Temperature ^(a) , F	Exposure Temperature, F	Exposure Time, hr	Depth of Attack, mils
5	29	2150	1800	50	0.6
	30	2150	1800	210	2.8
	31	2150	1800	616	5.4
	32	2150	1800	808	5.6
6	33	2150	1650	50	0.15
	34	2150	1650	210	0.4
	79	2150	1650	417	0.9
	35	2150	1650	616	1.1
	74	2150	1650	1080	0.7
	36	2150	1650	1498	0.75
	52	2150	1650	1971	1.8
	50	2150	1650	2120	2.0
	43	2150	1650	2377	1.8
7	84	2450	1500	65	Nil
	68	2450	1500	210	Nil
	83	2450	1500	319	0.3

(a) All specimens were annealed in hydrogen. Those annealed at 2150 F were held for 2 hr and furnace cooled. Specimens annealed at 2450 F were held for 5 hr, cooled to 1850 F, and held for 2 hr, and then furnace cooled.

FIGURE 3. THE EFFECT OF TIME AND TEMPERATURE ON THE OXIDATION OF TYPE 318 STAINLESS STEEL IN DRY NITROGEN CONTAINING 0.5 VOLUME PER CENT OXYGEN

FIGURE 4. THE EFFECT OF TIME AND TEMPERATURE ON THE OXIDATION OF TYPE 318 STAINLESS STEEL IN NITROGEN CONTAINING 0.5 VOLUME PER CENT OXYGEN AND 0.6 VOLUME PER CENT H_2O

FIGURE 5. EFFECT OF WATER ADDITIONS TO A NITROGEN-OXYGEN ATMOSPHERE ON THE OXIDATION OF TYPE 318 STAINLESS STEEL AT 1650 F

difference in grain size between the material annealed at the two temperatures. The material annealed at 2450 F had large grains, corresponding to ASTM austenitic grain size Nos. 2 to 3; the grain size of the material annealed at 2150 F was much smaller, ASTM Nos. 6 to 7. There would appear to be merit in maintaining brazing temperatures as low as practical from the standpoint of minimizing oxidation attack. Figure 4 also shows the effect of test temperature, but with a wet rather than a dry atmosphere. Generally speaking, these curves bear out the trends shown with dry atmospheres in Figure 3.

The effect of temperature on the degree of attack is also illustrated by the photomicrographs in Figure 6. Results at about the same exposure time are shown for test temperatures of 1800, 1750, 1650, and 1500 F. There was a marked decrease in attack as the temperature was decreased.

Within the limitations imposed by the scatter of the data, it appears that oxidation rate decreased with time, as indicated in Figures 3, 4, and 5. The curves tend to be similar to those discussed earlier and shown in Figure 2. Straight lines on the logarithmic plots were drawn to represent the data, but it should be noted that the points for long periods of exposure, particularly for the 1650 F experiment, depart from the drawn line. This may indicate a change in the rate law of oxidation. It is conceivable that as the time of exposure is increased, the oxide film will develop cracks and possibly spall. This would tend to cause a change in diffusion and oxidation. A similar change in the rate of oxidation with time can be seen from the data in Table 4 for the experiment at 1650 F in a dry-nitrogen atmosphere containing 0.1 volume per cent oxygen and extending for a period of 943 hr. These data, and the data for Test 2 (Table 5) have been replotted in Figure 7 to indicate a change in rate of oxidation on long exposure periods. Under these circumstances, extrapolation of short-time tests to predict the life of the cladding would be misleading. The photomicrographs in Figure 8 show the difference in attack between 980 and 3658 hr of exposure at 1650 F.

Figure 5 indicates that up to 2400 hr of testing at 1650 F, a water addition of 0.6 volume per cent possibly caused a slight increase in the rate of attack. However, the water addition exerted a noticeable adverse effect upon the uniformity of attack. The degree of nonuniformity is illustrated in Figure 6a.

In none of the specimens in the seven oxidizing tests was there any visible evidence that nitriding had occurred. However, it could be expected that some nitrogen would diffuse into the specimens during testing. Therefore, nitrogen analyses were obtained for several tested and untested specimens. The results of this work, given in Table 7, show that appreciable amounts diffused into the alloy. Evidently the nitrogen present was in solution. The percentages of nitrogen noted in Table 7 would not be expected to have an adverse effect on the properties of Type 318 stainless.

250X

Glyceria Etch

N50708

- a. Exposed at 1800 F for 808 Hr in Nitrogen - 0.5 Volume
Per Cent Oxygen - 0.6 Volume Per Cent H_2O

Specimen was annealed at 2150 F.

250X

Glyceria Etch

N50711

- b. Exposed at 1750 F for 1059 Hr in Nitrogen - 0.5
Volume Per Cent Oxygen

Specimen was annealed at 2150 F.

250X

Glyceria Etch

N50709

- c. Exposed at 1650 F for 980 Hr in Nitrogen - 0.5 Volume
Per Cent Oxygen

Specimen was annealed at 2150 F.

250X

Glyceria Etch

N50710

- d. Exposed at 1500 F for 930 Hr in Nitrogen - 0.5
Volume Per Cent Oxygen

Specimen was annealed at 2450 F.

FIGURE 6. EFFECT OF TEMPERATURE ON THE RATE OF ATTACK OF TYPE 318
STAINLESS STEELS IN NITROGENOUS ATMOSPHERES

Note marked decrease in attack as exposure temperature is decreased.

FIGURE 7. PLOT SHOWING POSSIBLE CHANGE IN RATE OF OXIDATION OF TYPE 318 STAINLESS STEEL ON LONG PERIODS OF EXPOSURE AT 1650 F

FIGURE 8. EFFECT OF EXPOSURE TIME ON THE OXIDATION ATTACK OF
TYPE 318 STAINLESS STEEL IN A 1050 F NITROGEN - 0.5
VOLUME PER CENT OXYGEN ATMOSPHERE

Specimen was annealed at 2150 F.

TABLE 7. KJELDAHL NITROGEN ANALYSIS OF SEVERAL TESTED AND UNTESTED SPECIMENS OF TYPE 318 STAINLESS STEEL

Specimen History	Nitrogen, w/o
Precannealed at 2150 F, untested	0.033
Precannealed at 2450 F, untested	0.006
Precannealed at 2450 F, untested	0.013
Precannealed at 2150 F, exposed at 1650 F for 1143 hr in 0.5 volume per cent oxygen, specimen not stressed	0.23
Precannealed at 2150 F, exposed at 1650 F for 1000 hr in 0.5 volume per cent oxygen, 1000-psi stress applied to specimen	0.073

Effect of Carbon Monoxide Additions to the Dry Nitrogen Environment

Nitriding occurring in an atmosphere of molecular nitrogen proceeds by catalytic dissociation of the molecular nitrogen. Therefore, an analogy may be drawn between this phenomenon and ammonia-synthesis processes. It is known that carbon monoxide poisons the catalysts used in such synthesis processes. Hence, there is reason to postulate that the presence of carbon monoxide in the nitrogen coolant might retard or prevent nitriding. This fact is supported by a recent observation that the addition of 0.08 volume per cent carbon monoxide to a 90 volume per cent nitrogen-10 volume per cent hydrogen atmosphere prevents nitriding of chromium steels at 1750 to 1850 F.⁽²⁾

To check these ideas, two tests were conducted at 1650 F in dry nitrogen atmospheres containing small amounts of carbon monoxide (0.1 and 0.5 volume per cent). These were run in the same manner as were the tests with the oxygen additions. Specimens were preannealed at the lower temperature, namely 2150 F. The results are summarized in Table 8. A comparison of the effect of carbon monoxide additions versus oxygen additions in dry nitrogen atmospheres is shown in Figure 9. Up to 400 to 500 hr, the attack when the 0.1 volume per cent CO was present was substantially less than when 0.1 volume per cent oxygen was present in the environment. At the 0.5 volume per cent concentration, little difference between the effects of oxygen and carbon monoxide could be detected.

FIGURE 9. EFFECT OF OXYGEN AND CARBON MONOXIDE ADDITIONS ON THE DEPTH OF ATTACK OF TYPE 318 STAINLESS STEEL IN DRY NITROGEN ATMOSPHERES AT 1650 F

TABLE 8. MAXIMUM DEPTH OF ATTACK OF TYPE 318 STAINLESS STEEL EXPOSED AT 1650 F TO NITROGEN ATMOSPHERES CONTAINING CARBON MONOXIDE^(a)

CO Addition to Nitrogen, volume per cent	Exposure Time, hr	Depth of Attack, mil
0.1	48	0.15
	144	0.2
	538	0.3
	682	0.25
0.5	162	0.15
	261	0.2
	423	0.4
	423	0.25

(a) Specimens preannealed in hydrogen at 2150 F for 2 hr.

The attack in both carbon monoxide-containing environments was rather shallow. Little difference was noted between the specimens removed from either environment. The attack consisted of both scaling and intergranular corrosion; no nitriding was observed. The scale appeared to be quite thin, although increasing slightly in thickness as the time of exposure increased. The scale was completely adherent in all of the specimens. The specimens exhibited a sparse intergranular attack, which in most cases was deeper than the thin scale.

Though carbon monoxide is frequently thought of as a reducing agent, it is not necessarily reducing to stainless steels. Thus, the fact that oxidation occurred when carbon monoxide was added to the atmosphere is not inconsistent with expectations.

Description of Attack Generally Observed

In the initial stages, the attack took the form of a thin surface scale beneath which intergranular penetration occurred. As time increased, scaling tended to predominate. Increased temperature tended to favor scaling. The scale began to spall when it reached a thickness of 0.5 to 0.9 mil. Instances of subsurface voids were noted occasionally on specimens after exposure at temperatures of 1650 F and above. There was not enough of this type of attack to show any trends, however.

Generally speaking, high test temperatures and water additions tended to promote nonuniformity of attack (see Figures 7a and 7b). However, this is not reflected in the data from which the curves in Figures 3, 4, and 5 were drawn because the maximum depth of attack was the criterion used in these curves. The extremes in the spread between the maximum depth of attack and the mean depth of attack are noted in the following tabulation:

Test	Conditions	Specimen	Preannealing Temperature, F	Exposure Time, hr	Depth of Attack, mils		
					Maximum	Mean	Difference
1	1750 F, dry atmosphere	27	2150	843	1.3	1.1	0.2
		8	2150	1059	2.1	1.4	0.7
6	1650 F, wet atmosphere	35	2150	616	1.1	0.6	0.5
		52	2150	1917	1.8	0.7	1.1
		50	2150	2120	2.0	0.8	1.2
		43	2150	2377	1.8	0.8	1.0
5	1800 F, wet atmosphere	31	2150	616	5.4	1.8	3.6
		32	2150	808	5.6	2.5	3.1

Structural Studies of the Oxidation Products of Type 318 Stainless Steel

Most of the work on the structural examination of the oxidation products was limited to specimens which had been exposed less than 1000 hr.

A complete report of the investigation of the composition and structure of the oxidation products of Type 318 stainless steel by means of X-ray diffraction and fluorescence analyses is given in the Appendix. Briefly summarizing these results, indications are that chromium and manganese diffused from the base metal at a greater rate than did iron and nickel. At 1650 F, the composition of the oxide layer reached a maximum in chromium and manganese and a minimum in iron and nickel after 500 to 600 hr of exposure. This corresponds roughly to the period during the tests when spalling of the scale began.

The amount of preferential diffusion of chromium and manganese when the specimens were exposed to atmospheres containing water vapor was significantly less than occurred when the atmospheres were dry.

Presence of Sigma Phase in Type 318 Stainless and the Relative Importance of Its Embrittling Effect

The presence of sigma phase in stainless steels is likely to cause embrittlement. However, it is felt that any embrittlement of the fuel-element cladding material caused by the presence of sigma would be overshadowed by irradiation hardening and loss of ductility by irradiation when the material is in actual service in the reactor.

In any case, a metallographic examination of several specimens was made to investigate the presence or absence of sigma. Examination of an untested specimen which had been annealed at 2150 F did not reveal any sigma. However, two specimens which were untested but annealed at 2450 F did contain traces of sigma. Evidently it precipitated upon cooling from the annealing temperature. Two specimens which were annealed at 2450 F and tested at 1500 F, both with approximately 900 hr in test, showed small amounts of sigma. Examination of three specimens which were annealed at 2150 F and tested at 1650 F for 2626, 1498, and 662 hr showed varying amounts of this phase. The specimen in test for 2626 hr showed a considerable amount of sigma, while

the specimen in test for 1498 hr showed less and that tested for 662 hr showed still less. The amount of sigma present in the specimens appeared to be time dependent which, of course, is entirely the behavior expected.

Conclusions

- (1) Type 318 stainless steel has better resistance to oxidizing attack in wet and dry oxygen-containing nitrogen atmospheres than do Type 347, Type 316, Timken 16-15-6, and Timken 16-25-6 alloys. Type 347 stainless was nearly as satisfactory as Type 318.
- (2) The relationship between depth of attack and time of exposure seems to be diffusion controlled, indicating that the rate of attack decreases with time. This relationship may be disturbed adversely by spalling, the occurrence of which would cause the rate to increase.
- (3) Within wide limits the surface finish does not affect the rate of oxidation of Type 318 stainless in wet or dry oxygen-containing nitrogen atmospheres.
- (4) Nitriding reaction is inhibited when small amounts of oxygen are present in a nitrogen atmosphere. Some nitrogen diffuses into the metal, but nitrides do not appear to form. The resulting oxidation attack is much less severe than the nitriding attack.
- (5) The concentration of oxygen in nitrogen which was found to be optimum from the standpoint of minimum oxidation attack and inhibition of nitriding was 0.5 volume per cent. The concentration of oxygen found to be next most effective was 5 volume per cent, followed by 0.1 and 0.05 volume per cent. The results obtained when 5 volume per cent oxygen was added to the atmosphere would warrant trying out dry and moist air atmospheres in the future.
- (6) The addition of 0.6 volume per cent water vapor to a dry nitrogen atmosphere does not affect to any great extent the rate of attack of Type 318 stainless as measured by the maximum depth of penetration, but it does result in a more nonuniform attack.
- (7) On the basis of limited work, it can be said that nitrogen atmospheres with addition of small amounts of carbon monoxide cause shallower oxidation attack than do nitrogen atmospheres containing small amounts of oxygen.
- (8) Several conclusions concerning the mechanism of attack can be drawn from the X-ray diffraction and fluorescence analyses of the oxidation products. These are:

- (a) The initial oxidation of the alloy produces an oxide film in which the major phase is of the R_2O_3 type. An oxide of the R_2O_3 spinel type is a minor component in the initial film. The metal constituents of the initial film are presumed to be essentially those of the alloy.
 - (b) Preferential diffusion of chromium and manganese from the base metal into the oxide layer during the next step results in the formation of increasing amounts of the R_3O_4 -type oxide.
 - (c) The amount of preferential diffusion is reduced significantly by the addition of water vapor to the oxidizing gas mixture. Diffusion is only slightly decreased by increasing the oxygen content of the gas over the range 0.05 to 5.0 volume per cent.
 - (d) At 1650 F, the composition of the oxide layer reaches a maximum in chromium and manganese and a minimum in iron and nickel after 500 to 600 hr of oxidation.
 - (e) The composition of the adherent oxide, after 500 to 600 hr of oxidation, varies considerably due to spalling of parts of the oxide layer.
 - (f) Oxidation of the thicker noncoherent oxide layer results in the formation of a chromium-rich R_2O_3 oxide.
- (9) Specimens that were preannealed at 2150 F in hydrogen appeared to be slightly more resistant to attack than specimens preannealed in hydrogen at 2450 F.

STRESS-CORROSION STUDIES AT ATMOSPHERIC PRESSURE

Leonard P. Rice and John A. VanECHO

This phase of the report contains the results of a study of certain stress-corrosion properties of AISI Type 318 stainless steel sheet material exposed in a special atmosphere at elevated temperatures.

Although Type 318 steel is noted for its corrosion-resistance and elevated-temperature properties, certain information was needed for the specific applications considered. Tests were made at temperatures of 1500 and 1650 F at various stresses in an atmosphere of nitrogen plus 0.5 volume per cent oxygen and containing 0.02 to 0.6 volume per cent of water vapor. In some cases the stress or temperature was cycled periodically throughout the test.

Experimental Techniques

The Type 318 stainless steel used for this work came from the same sheet stock as did the specimens which were used in the other phases of the program. The specimens which were to be subjected to stress-corrosion tests were given the following pretreatments:

Specimen Series	Prior Heat Treatment	ASTM Grain Size
A	Annealed in purified hydrogen at 2150 F for 2 hr and cooled in furnace	6-8
A-S	Same heat treatment as above and then clamped and reheated to 1500 F in hydrogen for straightening	6-8
C	Annealed in purified hydrogen at 2450 F for 5 hr, cooled in furnace and clamped and reheated in hydrogen to 1500 F for 2 hr for straightening	1-3

The test specimens used were typical sheet-type tensile coupons with a gage width of 0.500 in. and gage length of 2.5 in. The nominal thickness was 0.015 in. For most of the tests, two specimens were used, one of which was stressed while the other was placed alongside it with no stress imposed.

A vacuum-creep furnace was employed for all tests. The test chamber of the furnace was constructed of Inconel tubing, which was externally heated by means of a Chromel A heating element wound on a ceramic sleeve. The chamber was gastight, and brass bellows at the top and bottom of the Inconel tube allowed the specimen to elongate. Each stressed specimen was provided with an optical extensometer system with which deformation was measured to a sensitivity of 0.00005 in. The minimum or second-stage creep rate was obtained from creep curves of time versus total deformation.

The basic gas atmosphere consisting of nitrogen plus 0.4 to 0.5 volume per cent oxygen was purchased by the cylinder as a special mixture. Varying amounts of water vapor were added to the gas before it was fed into the furnace. The amount of water vapor added to the gas mixture was kept under control with periodic checks of dew point as the gas emerged from the test furnace. The water-vapor content was maintained at various levels ranging from 0.02 to 0.6 volume per cent, as shown in Table 9.

Each of the test specimens, whether stressed or unstressed, was subjected to a maximum temperature of either 1500 or 1650 F in the special gas atmosphere. In some cases the temperature was cycled once daily from 1650 F to 900 F or the stress was cycled once daily from 1000 psi to 375 psi for the entire time of the test. The test duration varied from 434 to 1249 hr.

Following the stress-corrosion exposure, the test specimens were measured and examined visually for general appearance. They were then sectioned in the gage length for metallographic determination of general structure and depth of corrosive attack. Since, under actual conditions of use, only one face or side of the material will be exposed to the corrosive atmosphere, the maximum depth of corrosive attack was

TABLE 9. DATA ON THE STRESS-CORROSION CREEP PROPERTIES OF TYPE 318 STAINLESS STEEL SHEET TESTED IN NITROGEN + 0.5 VOLUME PER CENT OXYGEN ATMOSPHERE CONTAINING VARIOUS AMOUNTS OF WATER VAPOR

Test	Specimen ^(a)	Temperature, F	Stress, psi	Water Vapor, volume per cent	Total Time, hr	Minimum Creep Rate, per cent per hr	Total Strain, per cent	Maximum Depth of Corrosive Attack for 0.015-In. - Thick Specimens	
								In.	Per Cent of Thickness
1	A-1	1650	1000	0.02	580	0.0022	2.4	0.0005	3.3
	A-1A	1650	None	0.02	580	--	--	0.0004	2.7
2	A-S-1	1650-900 ^(b)	1000	0.02	527	0.0019	0.8	0.0007	4.6
	A-S-2	1650-900	None	0.02	527	--	--	0.0008	5.3
3	A-S-3	1650	1000	0.02	1000	0.0011	2.4	0.0008	5.3
4	A-S-4	1650	1500	0.02	1000	0.0048	7.8	0.0009	6.0
	A-S-5	1650	None	0.02	1000	--	--	0.0013	8.6
5	A-2	1650	1000-375 ^(c)	0.02	1034	0.0052	8.6	0.0010	6.7
	A-3	1650	None	0.02	1034	--	--	0.0007	4.6
6	A-6	1650	1000	0.15	1122	0.0023	3.9	0.0009	6.0
	A-7	1650	None	0.15	1122	--	--	0.0008	5.3
7	A-S-6	1500	1800	0.02	643	0.00023	0.4	0.00025	1.7
	A-S-7	1500	None	0.02	643	--	--	0.00020	1.3
8	A-4	1500	1800	0.15	593	0.00063	0.6	0.00020	1.3
	A-5	1500	None	0.15	593	--	--	0.00015	1.0
9	A-8	1650-900 ^(b)	1000	0.6	1249	0.0027	5.4	0.0012	8.0
	A-9	1650-900	None	0.6	1249	--	--	0.0010	7.3
10	A-S-8	1650	1000	0.6	1148	0.0040	14.5	0.0022	14.7
	A-S-9	1650	None	0.6	1148	--	--	0.0024	16.0
11	C-1	1650	1000	0.6	665	0.00015	0.8	0.0029	19.3
	C-2	1650	None	0.6	665	--	--	0.0030	20.0
12	C-3	1650-900 ^(b)	1000	0.6	628	0.0048	4.0	0.0037	24.6
	C-4	1650-900	None	0.6	628	--	--	0.0046	30.6
13	C-5	1650	1000-375 ^(c)	0.6	1030	0.00023	1.17	0.0050	33.3
	C-6	1650	None	0.6	1030	--	--	0.0038	25.4
14	C-7	1650-900 ^(b)	1000	0.2	435	0.00031	1.2	0.0013	8.6
15	C-8	1650	1000	0.2	434	0.00013	0.78	0.0016	10.7

(a) The A series specimens were hydrogen annealed at 2150 F and are nominally fine grained. The C series specimens were hydrogen annealed at 2450 F and are grain coarsened.

(b) The temperature was cycled from 1650 F to 900 F once every 24 hr (3/4 hr to drop to 900 F and 1-3/4 hr to return to 1650 F).

(c) The stress was cycled once every 24 hr, being at 1000 psi for 22 hr and at 375 psi for 2 hr.

measured from the surface inward across the specimen thickness. Areas immediately adjacent to the edges were avoided in this measurement.

Table 9 contains a summary of the test data together with the conditions for each of the tests.

Discussion of Results

Creep and Deformation

Table 9 shows that for a temperature of 1650 F and a constant stress of 1000 psi, the fine-grained specimens (A and A-S series) displayed creep rates increasing from 0.0011 to 0.0040 per cent per hr as the water vapor in the gas mixture was increased from 0.02 to 0.6 volume per cent. This increase in creep rate is not large enough to be especially significant, however. When the temperature was cycled from 1650 F to 900 F once daily (Tests 2 and 9) the creep rate remained about the same as it was with a constant temperature of 1650 F. That is, the two tests made in the gas mixture containing 0.02 and 0.6 per cent water vapor showed creep rates of 0.0019 and 0.0027 per cent per hr, respectively. Cycling the stress once daily from 1000 psi to 375 psi (Test 5) resulted in a slight increase in creep rate to 0.0052 per cent per hr.

Total strain or deformation of the fine-grained specimens tested at 1650 F, under maximum loads of 1000 psi, varied from 0.8 to 14.5 per cent. The highest deformation values occurred when the load was cycled from 1000 to 375 psi (Test 5 at 8.6 per cent) and when the water-vapor content was at 0.6 volume per cent (Test 10 at 14.5 per cent). In both of these cases, it appeared that the test conditions hastened the start of third-stage creep and thereby increased the total deformation. One test made at 1650 F and 1500 psi is not included in the above comparisons since the higher load would be expected to increase the creep rate and total deformation. It should be pointed out that the tests were made for various lengths of time and total-deformation values should be compared only for equivalent exposure times.

Fine-grained specimens tested at 1500 F (Tests 7 and 8) had markedly lower creep rates and total deformation than those tested at 1650 F, even though the stress was 1800 instead of 1000 psi.

With one exception, coarse-grained specimens (Tests 11 through 15) had, on the average, much lower creep rates than did the fine-grained specimens tested under similar conditions. The creep rates ranged from 0.00013 to 0.00031 per cent per hr or about one-tenth that of the fine-grained material. The one exception (Test 12) in which the temperature was cycled from 1650 F to 900 F showed a creep rate of 0.0048 per cent per hr. The reason for the much higher creep rate observed in this one test is not known, but it may be the result of a combination of high vapor content in the atmosphere and the cycling of the temperature.

Corrosive Attack

The data contained in Table 9 show that within the range of stresses which were imposed during the stress-corrosion tests, no effect of stress on the depth of corrosive attack was noted. In each case where the pairs of specimens were tested at the same time, the corrosive attack on the stressed and unstressed specimens was of the same order of magnitude. The amount of water vapor in the atmosphere, the temperature of the test, and the grain size (or grain-coarsening treatment) had a considerable effect on susceptibility to corrosive attack at 1650 F.

All fine-grained (A and A-S series) specimens exposed to the basic atmosphere of nitrogen plus 0.5 volume per cent oxygen and containing 0.02 to 0.15 volume per cent of water vapor had about the same degree of corrosive attack, if the difference in time of exposure is taken into account. Cycling the temperature or stress, or increasing the stress to 1500 psi seemed to have no significant influence on depth of corrosive attack. Lowering the temperature from 1650 F to 1500 F (Tests 7 and 8) resulted in an appreciable decrease in corrosive attack.

Increasing the water-vapor content of the gas mixture from 0.02 to 0.6 volume per cent resulted in a greater depth of corrosion of the fine-grained material, as shown in Test 10. Cycling the temperature of the specimen (Test 9) tested in 0.6 volume per cent vapor seemed to be less corrosive than maintaining a constant temperature. This may be largely due to the fact that the specimen was at a lower temperature part of the time.

Specimens which had been given the grain-coarsening treatment (C-series specimens) suffered a definite loss of corrosion resistance, especially when exposed to atmospheres containing 0.6 volume per cent water vapor. Tests 11 through 13 revealed heavy corrosive attack in grain-coarsened specimens in less time than their fine-grained counterparts in Tests 9 and 10. For example, in Test 11, the coarse-grained specimens showed greater corrosive attack than the fine-grained specimens in Test 10, even though the exposure time was about half that of the fine-grained specimens. Cycling the temperature of the coarse-grained specimens appeared to be detrimental to their corrosion resistance in 0.6 volume per cent water vapor, as can be seen by comparing Tests 11 and 12. Grain-coarsened specimens exposed to a drier atmosphere (Tests 14 and 15 at 0.2 volume per cent water vapor) showed less corrosive attack than similar specimens exposed at a level of 0.6 volume per cent water vapor. This was also true for the fine-grained specimens as shown earlier.

The type of corrosive attack differed among the various specimens. Both coarse- and fine-grained specimens exposed to atmospheres containing from 0.02 to 0.2 volume per cent water vapor showed a rather uniform scale formation. On the other hand, the specimens exposed to 0.6 volume per cent water vapor showed a spotty attack - heavy in some areas and light in others.

In general, the data show that the grain-coarsening treatment increased the susceptibility to corrosive attack of specimens tested at 1650 F in the nitrogen plus 0.5 volume per cent oxygen atmosphere containing 0.2 to 0.6 volume per cent water vapor. The greatest attack occurred when the factors of grain coarsening and high (0.6 per cent) water vapor were combined.

It is not entirely clear that a coarse grain size, per se, is responsible for poor corrosion resistance. Microstructural changes in the steel resulting from the high

temperature of the grain-coarsening heat treatment, as well as changes occurring over long periods of time during testing, are undoubtedly related to corrosion behavior. A metallographic study of a number of representative specimens which had been subjected to stress corrosion has shown the presence of various amounts of sigma phase as well as carbides precipitated in the grain boundaries and within the grains. The metallographic structure found in pairs of specimens which had presumably the same history was not uniform. This was especially true in the grain-coarsened material and may be related to the spotty corrosive attack noted in those specimens.

Although there was heavy precipitation of sigma phase and probably carbide in the grain boundaries, there was no tendency for heavy intergranular corrosion to occur. There was some grain-boundary attack in some of the specimens but it was relatively shallow. The heaviest corrosive attack did not favor grain boundaries.

Conclusions

This study of the stress corrosion of Type 318 stainless steel sheet material in an atmosphere of nitrogen plus 0.5 volume per cent oxygen containing from 0.02 to 0.6 volume per cent of water vapor led to the following conclusions:

- (1) There was only a negligible effect of water vapor (0.02 to 0.6 volume per cent in the testing atmosphere) on creep rate.
- (2) Periodic cycling of the stress between 1000 psi and 375 psi tended to increase the total deformation of the specimens tested at 1650 F, probably by hastening third-stage creep.
- (3) Fine-grained specimens tested at 1500 F and at 1800 psi had much lower creep rates than those tested at 1650 F and 1000 psi.
- (4) Coarse-grained specimens averaged much lower minimum creep rates than did fine-grained specimens tested under the same conditions of stress and temperature.
- (5) Unstressed specimens were corroded about the same as stressed specimens regardless of whether they were fine grained or coarse grained.
- (6) Susceptibility to corrosive attack increased with increase in grain size and increase in water-vapor content. The worst attack occurred in coarse-grained specimens exposed to 0.6 volume per cent water vapor.
- (7) Cycling the temperature from 1650 F to 900 F during the test seemed to aggravate the corrosive attack of grain-coarsened specimens tested in gas containing 0.6 per cent water vapor.

STUDIES AT HIGH PRESSURES

John F. Kircher, Ward S. Diethorn, and Paul Schall, Jr.

This phase of the program was concerned with the effect of time and temperature on the oxidation resistance of candidate fuel-element cladding materials in nitrogen environments at a pressure of 200 psi.

Experimental Techniques

Flow Apparatus

All tests were conducted in a flow apparatus at 200 psi. Specimens were exposed to the flowing gas in a vertical, electrically heated, Inconel furnace (496 cm³). The gas flow rate was 74 cm³ per min at 200 psi in all the tests. The furnace heater was designed to maintain a large temperature gradient along the axis of the furnace for large heat inputs. In the tests described below, this temperature gradient was about 800 F. In any one test, a maximum of six specimens could be heated at each of three temperatures within this large temperature gradient. During a test, the furnace temperature was regulated by a Foxboro controller.

Nominal 15- or 62-mil-thick specimens were used in all tests. These specimens were about 7/16 in. wide and 9/16 in. long. A hole was drilled near one edge of each specimen for suspension in the apparatus. The specimens were hung in the gas stream from Inconel hooks attached to three collars which in turn were mounted on an Inconel rod running the entire length of the furnace axis. Each collar had six hooks and, therefore, six specimens. The collar position along the rod and, therefore, the temperature of each series of six specimens was adjustable. With this arrangement both sides of each specimen were exposed to flowing gas at one of three temperatures.

The gas entered the vertical furnace at the bottom and contacted the lowest, medium, and highest temperature specimens in that order. A thermocouple in the gas stream adjacent to each series of six specimens measured the temperature. Temperatures were recorded continuously during the tests. Thermocouple readings during the tests did not vary more than 15 F.

All nitrogen-oxygen mixtures used in the tests were the purest grade of dry pre-mixed gas supplied by Matheson. Mass spectrometric determinations of the oxygen content of the entrance and exit furnace gas during the tests with nitrogen-oxygen mixtures showed that oxygen consumption during the tests with this gas was negligible at a flow rate of 74 cm³ per min. Earlier oxygen determinations during tests at much smaller flow rates showed that oxygen depletion was serious.

In the test with a nitrogen-water vapor mixture the best grade of Matheson pre-purified tank nitrogen was passed (74 cm³ per min) through chips of copper sulfate pentahydrate at 200 psi to introduce water vapor. At room temperature the vapor pressure of water over this hydrate is 7 mm. At a total gas pressure of 200 psi this corresponds to about 0.07 volume per cent. The calculated water content was verified before the test by passing nitrogen at a flow rate of 74 cm³ per min and a pressure of 200 psi through the hydrated copper sulfate and into a desiccant, and weighing the

amount of water absorbed from a known volume of gas flow. This same method was used to show that for all practical purposes depletion of water vapor in the test gas during a 100-hr test was negligible.

Specimen Preparation and Examination

The test specimens were cut from the same sheet stock as the specimens which were used in the studies at atmospheric pressure. For a few of the tests, the specimens were rough ground on one side and polished to a mirror finish on the other side. Most of the specimens were heat treated prior to exposure. Surface preparation and heat treatments are described below.

In the 1000-hr run, specimens were weighed before and after exposure. Following exposure, the specimens were cut along their 7/16-in. dimension and one-half of the specimen was examined metallographically for the extent of corrosion. Maximum depth of attack was measured by the method described previously in the section on the studies at atmospheric pressure.

Screening Tests on Candidate Cladding Materials

Water Vapor-Nitrogen Atmosphere

In the early phases of the study, Type 347, Type 316, and Timken 16-25-6 alloys were exposed to a 0.07 volume per cent water vapor-99.93 volume per cent nitrogen mixture at 200 psi for 100 hr. The nominal thickness of the specimens in this screening test was 62 mils. These specimens were cut from as-received sheet stock and were not pickled or heat treated prior to exposure. However, one face of each specimen was ground with 600-grit emery paper, while the other side was polished to a mirror finish. The purpose of this surface treatment was to cast light on whether surface condition had any large effect on the depth of attack. The results are reported in Table 10.

TABLE 10. RESULTS OF 100-HR EXPOSURE IN 0.07 VOLUME PER CENT WATER VAPOR-99.93 VOLUME PER CENT NITROGEN MIXTURE AT 200 PSI

Specimen	Surface	Maximum Depth of Oxide Penetration After 100 Hr at Temperature Shown, mils		
		1700 F	1650 F	1420 F
Type 347 stainless	Polished	0.5	Nil	1.0
	Ground	0.8	0.3-1.0	0.7
Type 316 stainless	Polished	0.7	0.7(a)	0.2
	Ground	0.3-1.5	Nil(a)	Nil
Timken 16-25-6 alloy	Polished	0.3(a)	0.3	0.03
	Ground	0.3(a)	0.15	Nil

(a) Specimen holder failed during test. Specimen temperature was less than 800 F for part of the test period.

Most of the specimens exhibited intergranular attack which penetrated below a continuous or spotty film of oxide on the surface. There was no visible evidence of nitride formation. Any difference in the results for the rough and polished surfaces was not considered significant, since the corresponding penetrations were within or approached the limits of precision of the method of measurement.

Following this screening test, the emphasis in the high-pressure studies was shifted to oxygen additions. No further tests were conducted with water vapor-nitrogen atmospheres.

Oxygen-Nitrogen Atmosphere

A 100-hr screening test was conducted in 0.1 volume per cent oxygen-99.9 volume per cent nitrogen gas mixture at 200 psi. Specimen dimensions and preparation were identical to those described for the specimens used in the water vapor-nitrogen study. The results are summarized in Table 11.

TABLE 11. RESULTS OF 100-HR EXPOSURE IN 0.1 VOLUME PER CENT OXYGEN-99.9 VOLUME PER CENT NITROGEN GAS MIXTURE AT 200 PSI

Specimen	Surface	Maximum Depth of Oxide and Nitride Penetration After 100 Hr at Temperature Shown, mils					
		1810 F		1620 F		1460 F	
		Oxide	Nitride	Oxide	Nitride	Oxide	Nitride
Type 316 stainless	Polished	4.0	15.0	0.6	18.0	0.05	Nil
	Ground	4.0	15.0	1.8	10.2	0.05	Nil
Type 347 stainless	Polished	2.0	0.30	0.6	Nil	Nil	Nil
	Ground	2.0	Nil	0.30	Nil	Nil	Nil
Timken 16-25-6 alloy	Polished	1.5	3.0(a)	0.30	1.0(a)	0.1	Nil
	Ground	1.5	3.0(a)	0.3	Nil	0.1	Nil
Type 318 stainless	Polished	1.5	Nil	0.3	Nil	0.05	Nil
	Ground	2.5	Nil	0.1	Nil	0.05	Nil

(a) Nitriding observed at specimen corners only.

It is to be noted that both oxidation and nitriding occurred in numerous cases. In all nitrified specimens, nitride formation occurred below surface oxide layers. Most of the specimens exposed at the low and medium temperatures exhibited a rather uniform oxide layer on the specimen surface. At the highest temperature, the oxide layers were not uniform and intergranular penetration of the oxide occurred.

In earlier work, studies at both 200 psi and 15 psi showed that nitriding was severe in pure nitrogen at the higher temperatures listed in Table 11. The amount of nitriding observed in Type 347 stainless with the oxygen additive was considerably lower than with pure nitrogen in the same range of temperature. When oxygen was added, no visible nitrides formed in Type 318 stainless at any exposure temperature. Accordingly, oxide formation reduces nitriding of these two materials and exhibits a protective action.

Based on the promising results with Type 318 stainless at 200 psi, and the work at atmospheric pressure, this material was selected for further study. Since oxide formation occurred in short exposures, it was important to determine whether oxide attack is intolerable during long exposures or levels off to some value compatible with the reference thickness of the GCRE cladding.

Experiments With Type 318 Stainless Steel in Nitrogen
Atmospheres Containing 0.1 Volume
Per Cent Oxygen

A long-time test of Type 318 stainless was conducted in a 0.1 volume per cent nitrogen mixture at 200 psi. The purpose of this test was to investigate the influence of time on the attack of this material. Specimens were removed from the furnace for metallographic examination and determinations of weight change at various time intervals up to 1000 hr.

As-received 100-mil thick Type 318 sheet was cold rolled to a thickness of 15 mils. Specimens were cut from the rolled sheet and hydrogen annealed at 2150 F for 2 hr and furnace cooled. Test results are reported in Table 12.

In a 1000-hr test a large amount of test gas is used. During this period the flow apparatus was shut down about every 150 hr to change supply tanks on the gas manifold. Thermal cycling of the specimens occurred during these shutdowns and during the scheduled removal of specimens.

Carbide precipitation occurred in all the specimens. In some specimens the precipitation was general and not interconnected while in other specimens the precipitation was intergranular. However, the type of precipitation observed in the early history at any temperature did not necessarily appear during the later history at this temperature. The relationship between carbide formation and oxide penetration is, therefore, not readily defined.

There was no evidence of nitrides in any of the specimens. The relationship between oxide penetration and time at a given temperature is not certain because of the scatter in the data. The weight changes show that spalling of the oxide film occurred, particularly at 1425 F. The data in Table 12 also indicate that there was no strong temperature effect on oxide penetration over the range investigated.

Experiments With Type 318 Stainless Steel in Nitrogen
Atmospheres Containing 1.0 Volume Per Cent Oxygen

Additional experiments were conducted with a higher concentration of oxygen in the nitrogen atmosphere to cast light on the influence of oxygen concentration on the rate of oxidation at high pressure. It was also hoped that information could be gained on the upper and lower limits of oxygen content which would be most effective in inhibiting nitriding and, at the same time, not produce severe oxidation. Three gas pressures were employed in the study: 200 psi, 100 psi, and 1 atm. The results are summarized in Table 13. In addition to the data for 1.0 volume per cent oxygen-99 volume per cent

TABLE 12. RESULTS OF EXPOSURE OF TYPE 318 STAINLESS STEEL TO 99.9 VOLUME PER CENT NITROGEN-0.1 VOLUME PER CENT OXYGEN MIXTURE AT 200 PSI

Exposure Temperature, F	Exposure Time, hr	Cumulative Weight Increase, mg per cm ²	Maximum Depth of Oxide Penetration, mil	Carbide Formation	
				General	Intergranular
1650	44	0.40	0.25	--	--
	155	0.31	0.30	--	--
	310	0.60	0.40	--	--
	585	0.90	0.10	Yes	--
	700	0.47	0.55	--	Yes
	1010	1.2	0.55	Yes	--
1425	44	0.62	0.25	--	--
	155	0.42	0.35	--	--
	310	0.28	0.35	--	--
	430	0.15	Nil	--	Yes
	700	0.37	Nil	Yes	--
	966	0.093	Nil	Yes	--
1290	44	0.25	0.07	--	--
	155	0.37	0.30	--	--
	310	0.43	0.35	--	--
	585	0.31	1.0	--	Yes
	700	0.094	Nil	Yes	--
	1010	0.50	0.30	Yes	--

TABLE 13. SUMMARY OF DATA ON THE INFLUENCE OF PRESSURE ON THE OXIDATION OF TYPE 318 STAINLESS STEEL IN A NITROGEN ATMOSPHERE CONTAINING A SMALL AMOUNT OF OXYGEN (a)

Series	Gas Composition, volume per cent	Absolute Pressure	Exposure Temperature, F	Time, hr	Maximum Depth of Oxide Penetration, mils
1	0.1 oxygen 99.9 nitrogen	200 psi	1650	310	0.40
			1650	1010	0.55
			1425	310	Nil
			1425	966	0.35
2	1 oxygen 99 nitrogen	200 psi	1750	196	1-2
			1625	196	0.25-1
			1410	196	0.25
3	1 oxygen 99 nitrogen	200 psi	1750	334	0.5
			1425	334	2.0
4	1 oxygen 99 nitrogen	1 atm	1750	197	0.6-1.6
			1580	197	Nil
			1380	197	Nil
5	1 oxygen 99 nitrogen	1 atm	1750	1000	1.2-1.4
			1580	1000	0.1-0.4
			1380	1000	0.1-0.4
6	1 oxygen 99 nitrogen	100 psi	1750	210	1.3
			1580	210	Nil
			1400	210	Nil
7	1 oxygen 99 nitrogen	100 psi	1750	922	1.2
			1580	922	0.3
			1400	922	Nil

(a) Specimens were annealed in hydrogen for 2 hr and furnace cooled before exposure.

nitrogen, data for 0.1 volume per cent oxygen-99.9 volume per cent nitrogen are summarized and included in the table.

In Series 2, in addition to oxidation, evidence of nitriding was observed in the specimens exposed at 1625 F. At 1750 F in Series 5 and 7, no effect of pressure on oxide penetration was noted for ~1000-hr tests in 1 volume per cent oxygen-99 volume per cent nitrogen. No large pressure effect was apparent at the lower temperatures in these two series either, but this is less defined. Results from Series 2, 4, and 6 supported these same two conclusions for ~200-hr tests in the same gas mixture. When the long tests (~1000 hr, Series 5) are compared with the short tests (~200 hr) it is apparent that the rate of attack decreased after 200 hr.

Conclusions

Because of the limited amount of data and the scatter in the data, only a few general conclusions concerning the behavior of Type 318 stainless steel at high gas pressures should be drawn from this work. In both nitrogenous environments (0.1 volume per cent and 1.0 volume per cent oxygen) the corrosive attack was oxidizing rather than nitriding. However, a precipitated phase was observed in one specimen which was exposed at 1625 F in the 1.0 volume per cent oxygen-nitrogen atmosphere. This phase resembled a nitride structure. The rate of oxidation seemed to be about the same for specimens tested in either the 0.1 volume per cent oxygen-nitrogen or 1.0 volume per cent oxygen-nitrogen atmospheres. The effect of temperature on the rate of oxidation was not particularly evident at test temperatures below 1650 F. However, just as was the case in the work at atmospheric pressure, the rate of oxidation at temperatures above 1650 F (1750 F in this case) was much greater than at 1650 F.

The important conclusion which can be stated as a result of this work is that, on a qualitative basis, there does not appear to be a great effect of pressure on the rate of oxidation in nitrogenous environments containing 1.0 volume per cent oxygen. However, at lower concentrations (0.1 volume per cent oxygen) the corrosive attack was less at 200 psi than at a 1-atm pressure.

REFERENCES

- (1) Engineer Research and Development Laboratories, unpublished data (1957).
- (2) Hollingsworth, T. E., Matter, R. C., and Smith, O. H., "Nitriding of Chromium Steel", U. S. Patent 2,786,003 (March 19, 1957).

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APPENDIX

STRUCTURAL STUDIES ON THE OXIDATION
PRODUCTS OF TYPE 318 STAINLESS STEEL

APPENDIX

STRUCTURAL STUDIES ON THE OXIDATION
PRODUCTS OF TYPE 318 STAINLESS STEEL

D. A. Vaughan

Introduction

An investigation of the composition and structure of the oxidation products which formed on Type 318 stainless steel during exposure at 1500 to 1800 F in various nitrogen-plus-oxygen, nitrogen-plus-water vapor, or nitrogen-plus-carbon monoxide mixtures was made to aid in understanding the mechanism of oxidation. The effect of the oxygen content of the gas on the diffusion-oxidation process was evaluated to help in the selection of the coolant gas of a reactor in which the fuel elements would be clad with Type 318 stainless steel.

X-ray diffraction and fluorescence analyses were employed to study the phase composition and metal-ion concentration of the adherent oxidation products on Type 318 stainless steel specimens which were supplied from the study of oxidation rates as a function of gas compositions and temperature. The specimens were approximately 1/2 in. by 3/16 in. by 15 mils, with the oxide layer varying in thickness from interference color films to as much as 1 or 2 mils. All of the X-ray data were obtained with the oxide film in situ, and thus only a limited amount of information could be obtained from the very thin films. However, in most cases, the oxidation times were over 100 hr and the films were thick enough to provide adequate sampling of the oxide with only a small contribution of the base metal to the diffraction and fluorescence analyses.

Results of X-Ray Analyses

The results of X-ray diffraction and X-ray fluorescence analyses of the oxidation products on Type 318 stainless steel after exposure to nitrogen containing various amounts of oxygen, water vapor, or carbon monoxide at temperatures ranging from 1500 to 1800 F are given in Tables A-1 through A-6. In these tables, the diffraction data are presented in terms of the relative phase composition of the oxide layers. The oxide film was made up of two oxides of the R_2O_3 and the R_3O_4 types. The amounts shown in the tables are only relative because they are based only upon the diffraction-pattern intensity of each phase and are uncorrected for structure or density. The actual metal composition of the oxide phases cannot be ascertained from the diffraction data because of the mutual solubility of chromium, iron, manganese, and nickel in the oxides and because of the opposing effects of these elements upon the cell dimensions of the oxides. In special cases, it was evident that the distinct compounds Cr_2O_3 or Fe_2O_3 were present. In the R_3O_4 oxide the high-lattice-parameter phase (8.50 Å), as indicated in the tables by the numbers in parentheses, was most likely a manganese-rich oxide while the low-lattice-parameter R_3O_4 phase (8.35 Å) was probably high in chromium.

The R_2O_3 oxide phase appeared to be the major oxide phase during the first 100 hr of oxidation at 1650 F in all gases except for samples that were oxidized in the nitrogen plus carbon monoxide (Table A-6). The amounts of the R_3O_4 oxide phase or phases increased with time of oxidation. At higher temperatures, however, where diffusion is more rapid, the amount of R_3O_4 oxide was somewhat greater in short oxidation periods. In a number of cases, after 600 to 1000 hr of oxidation at 1650 F, it appeared that the oxide reverted to the R_2O_3 type. This would indicate a change in the diffusion process which is probably due to loss of coherency with the base metal, or due to cracks in the oxide layer (i. e., spalling).

The diffusion of the metal ions into the oxidation products is shown by the results of X-ray fluorescence analyses. These results are given in Tables A-1 through A-6, for the elements chromium, manganese, iron, and nickel. The relative amounts which are given in the tables for these elements were multiplied by a constant so that a direct comparison could be made with the actual analysis of the base metals before oxidation. By wet analysis the base metal contained 17.6 w/o chromium, 2.0 w/o manganese, 63.4 w/o iron, and 13.2 w/o nickel plus a total of approximately 4 w/o of the elements cobalt, molybdenum, niobium, phosphorus, silicon, and sulfur. The X-ray analysis for the cobalt, molybdenum, and niobium in the oxidation products was not sufficiently sensitive to indicate changes and was therefore omitted from this report. It is seen from Tables A-1 through A-6 that the relative contents of the metal ions in the oxides differed appreciably from the base metal for all oxidizing conditions. The chromium and manganese concentrations increased, while the iron and nickel concentrations decreased as the oxidation time or temperature increased.

Three specimens, 60A, 61A, and 62A in Table A-2 which were oxidized in nitrogen plus 0.1 volume per cent oxygen at 200 psi did not exhibit the above diffusion behavior in that the relative concentration of nickel in the oxide layer also increased and only the iron content of the oxide decreased from that of the base metal. This difference may be due to the higher oxidizing potential at the higher gas pressure. Further study of the effect of high pressure on the oxidation of this steel is needed to understand this change in the diffusion process and its effect on the life of Type 318 stainless steel as a fuel-element cladding for a gas-cooled reactor.

In the case of samples oxidized at 1650 F in nitrogen-plus-oxygen mixtures (Tables A-1 through A-4) the amount of diffusion in 400 hr appeared to decrease slightly with increasing oxygen content of the gas. The significance of this is not understood. Also, the diffusion in the oxide of samples which were oxidized in gas containing the higher oxygen content appeared to stop in shorter oxidation periods. This would suggest a partial loss of coherency with the base metal due to more rapid growth of the oxide film induced by the higher oxygen content of the gas. A loss of coherency would be expected to decrease the rate of diffusion. However, the effect of higher oxygen content of the gas on the diffusion rate is too small to be of great importance in the life of this material.

The effect of the addition of water vapor or carbon monoxide to the gas mixtures (Tables A-5 and A-6) on diffusion was more pronounced than that of an increase in the oxygen content. These two gases probably affect the diffusion process differently.

TABLE A-1. STRUCTURAL-COMPOSITIONAL VARIATIONS OF THE
OXIDATION PRODUCTS ON TYPE 318 STAINLESS
STEEL OXIDIZED IN NITROGEN PLUS
0.05 VOLUME PER CENT OXYGEN

Specimen	Exposure Time, hr	Relative Composition of Oxide				Relative Phase Composition	
		Cr	Mn	Fe	Ni	R ₂ O ₃	R ₃ O ₄ ^(a)
<u>At 1650 F</u>							
43D	100	19.1	1.4	63.6	13.1	100	--
67A	124	28.3	6.4	53.0	8.8	10	58(8.50) + 32(8.35)
69A	124	30.2	5.0	53.7	11.1	15	55(8.48) + 30(8.35)
68A	224	36.5	7.7	45.1	7.1	18	82(8.50)
70A	400	49.5	13.7	27.8	5.6	12	74(8.50) + 14(8.35)
71A ^(b)	675	30.4	5.8	51.3	9.0	--	86(8.50) + 14(8.35)
<u>At 1800 F</u>							
50D	100	28.0	8.3	48.0	12.2	--	100(8.40)

(a) The numbers in the parentheses indicate the lattice parameter of the R₃O₄ phase or phases, while the numbers preceding the parentheses indicate the relative amount of that phase in the oxide layer.

(b) The outer oxide on this sample flaked off during oxidation or subsequent handling.

TABLE A-2. STRUCTURAL-COMPOSITIONAL VARIATIONS OF THE
OXIDATION PRODUCTS ON TYPE 318 STAINLESS
STEEL OXIDIZED IN NITROGEN PLUS
0.1 VOLUME PER CENT OXYGEN

Specimen	Exposure Time, hr	Relative Composition of Oxide				Relative Phase Composition	
		Cr	Mn	Fe	Ni	R ₂ O ₃	R ₃ O ₄ (a)
<u>At 1460 F</u>							
62A ^(b)	100	18.3	2.1	62.0	14.3		Not measurable
<u>At 1500 F</u>							
50A	100	18.5	3.1	65.0	10.1	97	3 (-)
<u>At 1620 F</u>							
61A ^(b)	100	25.3	3.4	49.5	18.5	57	43(8.48)
<u>At 1650 F</u>							
53A	80	27.2	5.8	56.2	7.1	63	37(8.48)
72A	84	23.6	2.4	60.7	11.0	72	28(8.48)
53B	193	30.0	8.8	51.0	7.2	36	64(8.48)
53C	553	43.9	16.2	31.6	4.0	4	84(8.48) + 12(8.35)
<u>At 1800 F</u>							
60A ^(b)	100	37.5	5.6	28.5	25.5	6	94(8.35)
<u>At 1800 F</u>							
43C	100	26.1	4.6	54.2	12.3	45	55(8.46)

(a) Numbers in parentheses indicate the lattice parameter of the R₃O₄ phase or phases.

(b) This specimen was oxidized under a 200-psi gas pressure; except where noted all other specimens were oxidized at atmospheric pressure.

TABLE A-3. STRUCTURAL-COMPOSITIONAL VARIATION OF THE OXIDATION PRODUCTS ON TYPE 318 STAINLESS STEEL OXIDIZED IN NITROGEN PLUS 0.5 VOLUME PER CENT OXYGEN

Specimen	Exposure Time, hr	Relative Composition of Oxide				Relative Phase Composition	
		Cr	Mn	Fe	Ni	R ₂ O ₃	R ₃ O ₄ ^(a)
<u>At 1500 F</u>							
43B	100	19.1	1.4	63.6	13.1	Not measurable	
<u>At 1650 F</u>							
50C	100	20.1	2.6	65.6	9.5	97	3 (-)
63A	264	32.1	5.6	48.1	10.9	29	57(8.48) + 14(8.55)
64A	357	36.2	8.1	43.3	9.2	29	67(8.48) 4(8.55)
86A	478	31.8	6.3	45.0	9.1	--	100(8.45)
103A	662	57.3	5.4	27.7	5.8	--	100(8.40)
76A ^(b)	1034	34.4	11.9	41.7	11.8	9	91(8.48)
87A ^(b)	1196	37.8	12.3	39.2	7.7	40(Cr ₂ O ₃)	60(8.40)
<u>At 1750 F</u>							
88A	216	38.2	8.2	41.3	8.5	10	90(8.45)
89A	376	23.3	4.9	57.8	8.2	12	60(8.38) + 28(8.45)
90A	1059	29.4	4.3	54.0	8.6	42	58(8.38)

(a) Numbers in parentheses indicate the lattice parameter of the R₃O₄ phase or phases.

(b) This specimen was oxidized under a 200-psi gas pressure; except where noted all other specimens were oxidized at atmospheric pressure.

TABLE A-4. STRUCTURAL-COMPOSITIONAL VARIATIONS OF THE OXIDATION PRODUCTS ON TYPE 318 STAINLESS STEEL OXIDIZED IN NITROGEN PLUS 5.0 VOLUME PER CENT OXYGEN

Specimen	Exposure Time, hr	Relative Composition of Oxide				Relative Phase Composition	
		Cr	Mn	Fe	Ni	R ₂ O ₃	R ₃ O ₄ ^(a)
54A	105	23.8	3.1	57.8	11.0	28	20(8.48) + 25(8.44) + 27(8.35)
54D	114	23.6	2.2	57.4	12.9	100	--
54B	214	27.8	5.1	54.8	9.0	18	33(8.48) + 18(8.44) + 30(8.35)
54C	328	35.9	7.3	45.5	7.0	29	35(8.48) + 10(8.44) + 26(8.35)

(a) Numbers in parentheses indicate the lattice parameter of the R₃O₄ phase or phases.

TABLE A-5. STRUCTURAL-COMPOSITIONAL VARIATIONS OF THE OXIDATION PRODUCTS ON AISI TYPE 318 STAINLESS STEEL OXIDIZED IN NITROGEN-OXYGEN-WATER VAPOR MIXTURES

Specimen	Exposure Time, hr	Relative Composition of Oxide				Relative Phase Composition	
		Cr	Mn	Fe	Ni	R ₂ O ₃	R ₃ O ₄ (a)
Nitrogen + 0.1 Volume Per Cent Oxygen + 0.2 Volume Per Cent H ₂ O at 1650 F							
65A	124	24.9	6.3	51.0	9.5	36	61 (8.48) + 3 (8.35)
66A	224	26.4	6.7	54.2	9.2	33	64 (8.48) + 3 (8.35)
Nitrogen + 0.5 Volume Per Cent Oxygen + 0.6 Volume Per Cent H ₂ O at 1650 F							
91A	50	21.1	3.5	61.4	10.2	37	63 (8.38)
92A	210	26.6	5.5	56.6	8.1	12	40 (8.48) + 48 (8.36)
93A	616	34.6	8.1	46.8	6.7	11	59 (8.48) + 30 (8.36)
105A	1498	38.5	13.9	37.9	6.0	10	90 (8.48)
Nitrogen + 0.5 Volume Per Cent Oxygen + 0.6 Volume Per Cent H ₂ O at 1800 F							
94A	50	34.1	9.6	46.3	6.3	64	36 (8.48)
95A	210	41.8	18.6	30.8	5.0	36	64 (8.48)
96A (b)	616	2.8	6.5	79.8	7.0	75 (Fe ₂ O ₃)	25 (8.48)

(a) Numbers in parentheses indicate the lattice parameter of the R₃O₄ phase or phases.

(b) This specimen was oxidized under a 200-psi gas pressure; all other specimens were oxidized at atmospheric pressure.

TABLE A-6. STRUCTURAL-COMPOSITIONAL VARIATIONS OF THE
OXIDATION PRODUCTS ON TYPE 318 STAINLESS
STEEL OXIDIZED AT 1650 F IN NITROGEN PLUS
0.1 VOLUME PER CENT CARBON MONOXIDE

Specimen	Exposure Time, hr	Relative Composition of Oxide				Relative Phase Composition	
		Cr	Mn	Fe	Ni	R_2O_3	$R_3O_4^{(a)}$
81A	48	22.2	3.1	58.9	11.9	--	83(8.38) + 17(8.45)
82A	144	25.7	4.0	57.8	10.9	--	100(8.45)
83A	538	23.6	5.3	56.9	10.3	--	100(8.44)
84A	682	24.8	6.3	55.5	9.7	4	96(8.44)

(a) Numbers in parentheses indicate the lattice parameter of the R_3O_4 phase or phases.