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**The Long-Term Oxidation
of Selected Alloys in
Superheated Steam
at 482 and 538° C**

J. C. Griess
V. A. Maxwell

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THE LONG-TERM OXIDATION OF SELECTED ALLOYS
IN SUPERHEATED STEAM AT 482 AND 538°C

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THE LONG-TERM OXIDATION OF SELECTED ALLOYS
IN SUPERHEATED STEAM AT 482 AND 538°C

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

ABSTRACT

We studied the oxidation of several Cr-Mo steels and austenitic materials in superheated steam at 482 and 538°C (900 and 1000°F). The investigation was conducted in a once-through loop that received steam from the superheater circuit of the Bartow Power Plant of the Florida Power Corporation. This report presents the results from this investigation, which was terminated after 28,339 h when the mode of power plant operation was changed from baseload to peaking.

At both temperatures all materials examined exhibited parabolic oxidation kinetics during the first 5000-8000 h and subsequently oxidized at constant rates, which were lower than expected from extrapolation of the initial parabolic curves. The Cr-Mo steels containing 2 1/4 and 9% Cr showed little difference in oxidation rate, averaging 3.6 and 8.5 $\mu\text{m}/\text{year}$ (0.14 and 0.33 mils/year) at 482 and 538°C, respectively, after the first year. Sandvik HT9 (11.4% Cr) corroded at only slightly lower rates. Oxidation rates were nearly independent of surface conditions, but in two cases the presence of mill scale on the surface prior to steam exposure seemed to retard oxidation. All Cr-Mo steels developed two-layered scales in which the ratio of the thickness of the outer layer to the inner layer was 1.3 (independent of alloy composition, exposure time, and temperature). At 482°C only one specimen showed evidence of exfoliation, but at 538°C exfoliation occurred on some specimens of almost all of the Cr-Mo steels; the exceptions were the alloy with the highest chromium content (Sandvik HT9), one heat of 9 Cr-1 Mo steel with the highest silicon content, and Sumitomo 9 Cr-2 Mo, which was in test for only 19,345 h.

Cold-worked surfaces of alloy 800 corroded at lower rates than annealed and pickled ones, but in both cases the rates were very low. Alloy 800 specimens that had intergranular penetrations before exposure to steam corroded at much higher rates. Type 304 stainless steel oxidized nonuniformly, but the total extent of damage was low at both temperatures. Alloy 617 oxidized at the lowest rate of any material; even after 28,339 h surface films were thin enough to show interference colors.

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INTRODUCTION

For the past several years we have conducted a steam corrosion program at the Bartow Plant of the Florida Power Corporation in St. Petersburg, Florida, in which a variety of materials were exposed to superheated steam at 482 and 536°C (900 and 1000°F) in a once-through loop. Two reports concerning preliminary data from this program have been issued; one summarized data for the first 12,000 h¹ and the other for the first 25,000 h.² Shortly after 25,000 h of exposure, the Florida Power Corporation converted the Bartow Plant from baseload to peaking operation, and the periods of plant operation were sporadic and short. Therefore, we terminated the test at the Bartow Plant.

All test specimens and equipment have been returned to Oak Ridge, and we are trying to find a power plant where our loop can be located and the exposure continued. Although testing time has been extended only 3000 h since the last report was written, this report summarizes all of the data obtained during this run at the Bartow Plant and presents the results of a more thorough examination of the specimens than had previously been carried out.

EXPERIMENTAL PROCEDURES

Since earlier reports gave details of the experimental methods,¹⁻² only a summary of our testing procedure is given here.

All test specimens were mounted in a nonrecirculating loop made of Inconel alloy 617. The loop was located at the Bartow Plant and was operated for us by the NUS Corporation. The loop contained two autoclaves or test chambers, and the same materials were exposed in both. The temperature of the steam, which was taken from the superheater of the Bartow Plant, was adjusted to 482°C (900°F) before it entered the first autoclave. After leaving the first autoclave, the steam was heated to 538°C (1000°F) before it entered the second autoclave. On leaving the second autoclave, the steam was condensed and the condensate was discarded. The mass flow rate of steam through the loop was 45 kg/h (100 lb/h), which corresponded to a nominal velocity of 1.5 m/s (5 ft/s) past the test specimens. Steam pressure was 10.5 MPa (1525 psi).

Most of the specimens were flat rectangular strips, $73 \times 13 \times 1.6$ mm ($2\frac{7}{8} \times \frac{1}{2} \times \frac{1}{16}$ in.), that had 4.8-mm- ($\frac{3}{16}$ -in.-) diam holes near each end for mounting. Most of these specimens were ground on all surfaces using a 100-mesh belt grinder, but some were annealed and pickled. Other specimens were bent into U shapes for evaluating the effect of stress. The radius of curvature of the bends in these cases was 13 mm ($\frac{1}{2}$ in.), and the legs of the U's were held parallel by stainless steel bolts. Additional specimens that had slightly different dimensions were machined axially from heavy walled pipe so that one "flat" surface of the specimen was the inner wall of the pipe. This surface was covered with mill scale that was not disturbed during preparation.

Specimens containing both autogenous and filler metal welds were also tested. The former welds were made along the middle of 75-mm- (3 -in.-) wide strips of 1.6-mm- ($\frac{1}{16}$ -in.-) thick sheet in an inert atmosphere. The sheets had mill annealed and pickled surfaces, and except for the weld, the surfaces of the specimens were not altered. The filler metal welds were made from 15.9-mm- ($\frac{5}{8}$ -in.-) thick plate. The plates to be joined were machined to produce a 75° included angle with a 0.38-mm (0.015-in.) root face. For joining alloy 800 to itself or to 2 $\frac{1}{4}$ Cr-1 Mo steel, alloy 82 filler metal was used, and alloy 617 filler metal was used to weld alloy 617 plates together. Specimens were cut with a band saw across the thickness of the plate so that the weld was equidistant from the ends of the test specimen. The flat faces of these specimens were ground, but neither the face nor the root of the weld was disturbed. Some of the welded specimens were tested as U-bends, in which cases the weld was at the apex of the U, where the strain was greatest.

All specimens were periodically removed for examination, and the flat specimens were weighed at these times. Most specimens were returned for further exposure, but some were permanently removed for destructive examination. Those removed were usually replaced with new specimens of the same kind.

Until spalling or exfoliation occurred, the amount of metal oxidized was calculated from weight gain by assuming that the corrosion product

remained completely on the specimen and that the composition of the corrosion product was known. The corrosion products were assumed to be the following stoichiometric compounds: $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$, $\text{Fe}_2\text{O}_3 \cdot \text{NiO}$, $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$, and $\text{Mo}_2\text{O}_3 \cdot \text{FeO}$. In a few cases, steel specimens were chemically descaled in Clarke's Solution³ (concentrated HCl containing 20 grams Sb_2O_3 and 50 grams SnCl_2 per liter) to verify the validity of the weight-gain method of determining oxidation of the alloys.

Table 1 lists the composition of all alloys tested.

RESULTS

Test specimens of all materials showed weight gains that increased with time throughout the test period. For the first 5000-8000 h, log-log plots of weight gain vs time yielded straight lines with slopes of 0.4-0.5, indicating parabolic oxidation kinetics. However, after longer times the oxidation rates became constant and were lower than expected from extrapolation of the initial parabolic curves. In presenting the results, this point is illustrated for each alloy that corroded at a measurable rate by graphically presenting on linear coordinates weight-gain vs time curves for single specimens that had been in test for the longest times at 482 and 538°C (900 and 1000°F). To show the specimen-to-specimen variability, we made similar plots for eight specimens of each alloy (four at each temperature). The corrosion rates calculated from the slopes of the straight lines and the penetration obtained on extrapolation of the straight line to time zero are presented tabularly. Most of these specimens were installed in the loop at different times and were among those with the longest exposures. In the following sections, the oxidation behavior of the individual alloys is discussed.

Alloy 800

All unwelded alloy 800 weight-change specimens initially installed in the loop were prepared at the same time from mill annealed plate, and all were ground on a 100-mesh belt grinder. After grinding, half of the

Table 1. Composition of test materials

Alloy	Heat No.	Note	Composition (wt %)									
			C	Cr	Ni	Mo	Fe	Mn	Si	V	Other	
Alloy 800	HR7058 A	Weight change and welded specimens	0.08	19.77	33.90		43.46				0.44 Ti, 0.46 Al	
Alloy 800	HR5221 A	Mill annealed specimens	0.05	20.78	31.39		45.28		0.36		0.46 Ti, 0.38 Al	
Alloy 82	XX6537 D	Filler metal	0.02	20.01	72.50		1.16	3.07	0.09		0.39 Ti, 2.51 Nb	
Alloy 617	XX01A3US		0.07	20.10	57.35	8.58	1.01	0.05	0.16		11.72 Co, 0.76 Al	
304 stainless steel	8082800		0.06	18.04	8.90		Bal.	1.84	0.55			
Sandvik HT9	451718	Annealed and ground specimens	0.19	11.4	0.50	1.00	Bal.	0.50	0.26	0.27	0.49 W	
Sumitomo 9 Cr-2 No 9 Cr-1 No steel	451774	Specimens supplied by GA ¹	0.20	11.2	0.51	0.97	Bal.	0.50	0.32	0.29	0.51 W	
	454191	Specimens supplied by GA ¹	0.18	11.3	0.50	0.93	Bal.	0.52	0.35	0.29	0.51 W	
		Specimens supplied by GA ¹	0.04	8.80	0.11	2.06	Bal.	0.56	0.29			
	316381 A	Standard air melt	0.08	8.79	0.38	1.00	Bal.	0.34	0.46			
	XA-3177	ESR ² - supplied by GE ³	0.05	9.58	0.08	0.80	Bal.	0.44	0.17	0.15	0.46 W, 0.11 Nb	
	XA-3178	ESR ² - supplied by GE ³	0.10	9.52	0.16	1.55	Bal.	0.50	0.21	0.30	0.14 Nb	
	91147	ESR ² - supplied by GE ³	0.10	9.22	0.08	1.01	Bal.	0.38	0.08	0.22	0.15 Nb	
	31177	Argon - oxygen decarburized	0.05	10.43	0.44	1.02	Bal.	0.56	0.03	0.20		
	31378	Argon - oxygen decarburized	0.07	9.60	0.29	0.86	Bal.	0.44	0.01	0.16		
	31446	Argon - oxygen decarburized	0.06	10.21	0.17	0.96	Bal.	0.61	0.03	0.27		
	F-5349	Argon - oxygen decarburized	0.10	8.75	0.11	0.23	Bal.	0.42	0.37	0.21		
	30383	Argon - oxygen decarburized	0.09	8.29	0.09	1.00	Bal.	0.45	0.43	0.20	0.07 Nb	
	Lot 33	Air melt - supplied by GE ³	0.11	9.22	0.19	0.96	Bal.	0.51	0.71			
	15965	Air melt - supplied by GE ³	0.11	9.38	0.07	0.99	Bal.	0.59	0.63			
7 Cr-1 No steel	XA-3477	ESR ²	0.09	7.05	0.05	0.98	Bal.	0.34	0.17		0.14 Nb	
	XA-3478	ESR ²	0.09	7.00	0.05	1.02	Bal.	0.34	0.14		0.37 Nb	
5 Cr-1 No steel	XA-3475	ESR ²	0.10	5.18	0.16	1.02	Bal.	0.32	0.14			
	XA-3476	ESR ²	0.09	5.01	0.06	1.01	Bal.	0.34	0.11		0.38 Nb	
2 1/4 Cr-1 No steel	84042	Weight change and welded specimens	0.11	2.01		0.98	Bal.	0.54	0.22			
	86216	Autogenous weld specimens	0.17	2.19		1.00	Bal.	0.44	0.26			

¹General Atomic Company, San Diego, CA 92138.²Electroslag remelt.³Combustion Engineering, Inc., Chattanooga, TN 37402.

specimens were solution annealed at 1177°C (2150°F) for 30 min in argon and air cooled. This group was then pickled in a HNO_3 -HF solution to remove thin tarnish films produced by impurities in the argon. The other specimens were tested as ground. All of the welded and U-bend specimens were also placed in the loop at this same time. At a later time, specimens of as-received (mill annealed and pickled) strips were added to the specimen array.

Figure 1 shows weight gains for representative pickled specimens at 482 and 538°C and for a single ground specimen at 538°C. The linear behavior after an initial period is apparent for pickled specimens at both temperatures. For about the first 8000 h, the weight-gain curves were parabolic, after which a transition to linear kinetics occurred. Interestingly, the constant rates were significantly lower than expected from extrapolation of the parabolic part of the curves. Table 2 shows the initial penetrations calculated by extrapolation of the straight line parts of the curves to the origin and the penetration rates calculated from the slopes of the straight line parts of the curves for four specimens in test for the longest times at each temperature.

Fig. 1. Weight gains of alloy 800 in superheated steam.

Table 2. Calculated penetrations and corrosion rates for alloy 800 test specimens that were sensitized and pickled prior to steam exposure

Total time in test (h)	Initial penetration (μm)		Corrosion rate ($\mu\text{m}/\text{year}$)	
	482°C	538°C	482°C	538°C
28,339	6.1	14.2	2.1	2.7
27,835	3.3	12.6	1.8	2.9
26,719	2.9	9.7 ^a	1.8	3.9 ^a
25,288	2.6	12.6	2.1	4.1

^aActual test time - 23,267 h.

Specimens of ground alloy 800 corroded at very low rates, as indicated by the 538°C curve in Fig. 1. After 28,339 h, weight gains were 0.61 and 1.00 g/m², respectively, at 482 and 538°C. These small weight gains correspond to penetrations of only 0.21 and 0.33 μm (0.008 and 0.013 mils) during the entire 28,339-h test.

As noted in earlier reports,¹⁻² the annealed and pickled specimens had apparently been sensitized during cooling from the annealing temperature and were subsequently intergranularly corroded during pickling. Figure 2 shows transverse cross sections through annealed and subsequently pickled specimens exposed for 28,339 h and illustrates that the attack generally followed grain boundaries at both temperatures. The depth of grain boundary penetration produced by pickling was about 200 μm (8 mils), and this depth did not increase as a result of steam exposure. Also shown in Fig. 2 is a cross section of a ground specimen exposed for 28,339 h at 538°C. The very minor attack is evident.

Electron microprobe analysis of the oxide formed on pickled specimens showed that the outer oxide contained only iron and that the inner oxide contained chromium, nickel, and iron but was enriched in the former two elements. The metallic phase within the oxide is nickel. Microprobe measurements across the thickness of the oxide formed at 482°C (Fig. 2b) are shown in Fig. 3. Although microprobe measurements were taken at 1- μm intervals across the oxide, the diameter of the beam was approximately 10 μm , resulting in an appreciable overlap. However, the electrons

Fig. 2. Cross sections of alloy 800 specimens exposed to superheated steam for 28,339 h: (a) intergranularly corroded prior to steam exposure at 538°C; (b) intergranularly corroded at 482°C; (c) ground surface at 538°C.

Fig. 3. Electron microprobe analysis across a transverse section of oxide formed on alloy 800 in superheated steam at 482°C.

were not uniformly distributed in the beam but were more concentrated in the center than the edges so that the overlap was not as great as implied. Nevertheless, the lack of sharpness in the curves at the phase boundaries is due to this fact.

It has been established that ground (cold-worked) surfaces of alloy 800 corrode less in steam than annealed ones.⁴ The mill annealed and pickled specimens tested in our loop also illustrate this point. Seven annealed specimens with unground surfaces were exposed at each temperature for 15,890 h. The average weight gains at several intermediate times during the test are shown in Table 3. Why the specimens at the lower temperature showed greater weight gains after 5551 h than those at 538°C is not known. The likelihood that these specimens were inserted into the incorrect autoclave after 5551 h is extremely remote. Regardless of this discrepancy, the weight gains on the annealed surfaces were substantially greater than those on ground surfaces.

Further evidence of the effect of grinding can be seen by comparing the weight gains of the welded specimens prepared with filler metal which had ground surfaces with those of the autogenous welds which were on mill annealed and pickled surfaces. Four of each type were exposed at both temperatures for the entire 28,339 h. Average weight gains, as functions of time, are shown in Fig 4. Those specimens with the ground

Table 3. Average weight gains of alloy 800 specimens with mill annealed and pickled surfaces in superheated steam

Time at weighing (h)	Weight gain (g/m^2)	
	482°C	538°C
2,615	1.7	2.1
5,551	2.4	2.5
8,837	3.1	2.5
12,718	3.7	2.7
15,890	4.0	2.8

Fig. 4. Weight gains of welded alloy 800 specimens.

surfaces gained considerably less weight than those with the annealed surfaces. The reason for the increased weight gains for the last two points on all curves is not apparent. It should be noted, however, that weight gains were low in all cases. A weight gain of $1 \text{ g}/\text{m}^2$ corresponds to a penetration of only $0.33 \text{ }\mu\text{m}$.

The U-bend specimens were weighed only at the beginning and the end of test. The weight changes were essentially the same as those shown by

the last points for the ground specimens on the curves in Fig. 4. Furthermore, the oxides that formed on the most highly strained parts of these specimens had the same appearance as those on the flat specimens.

Alloy 617

The alloy 617 specimens, including welded and U-bend types, had ground surfaces and showed very little corrosion during test. Weight gains for the entire specimens (0.0024 m^2) averaged only 0.7 and 1.0 mg at 482 and 538°C, respectively, for the unwelded specimens during 28,339 h. These weight gains correspond to penetrations of 0.03 and 0.05 $\mu\text{m}/\text{year}$. The specimens that contained filler metal welds showed weight gains 2.5-3.0 times greater than those of the unwelded specimens, but the reason is not obvious. The cast structure of the filler metal experienced no obvious preferential attack. The appearance and weight gains of the U-bends were the same as those for the flat specimens. In all cases, metallographically polished cross sections showed no localized attack, and the oxide was so thin that it could not be detected at a magnification of 500x.

Type 304 Stainless Steel

All specimens of type 304 stainless steel were made from mill annealed and pickled plate, and all surfaces were ground before the test. Weight gains experienced by specimens exposed for 28,339 h are shown in Fig. 5. The consistency of the data is illustrated in Table 4 where data are shown for the specimens in test for the longest times. Although the specimen-to-specimen variation was relatively large, both the penetrations and corrosion rates were small compared with those for the ferritic steels (see later sections). At the end of the test the specimens exposed at 538°C were covered with a very adherent black oxide, but at 482°C the surfaces of the specimens had thin irregular oxides with interference colors visible in localized areas.

Though weight gains increased at a constant rate after an initial period, attack was not uniform. Figures 6a and 6b show polished cross sections through specimens exposed for 28,339 h at 482 and 538°C, respectively. Figure 7 shows the cation content of the oxide across one

Fig. 5. Weight gains of type 304 stainless steel.

Table 4. Calculated penetrations and corrosion rates for type 304 stainless steel test specimens exposed to superheated steam

Total time in test (h)	Initial penetration (μm)		Corrosion rate ($\mu\text{m}/\text{year}$)	
	482°C	538°C	482°C	538°C
28,339	0.20	8.9	1.20	3.1
27,835	0.20	4.8	0.21	2.5
26,546	0.07	5.9	0.56	3.3
23,267	0.00	5.9	0.31	2.9

section of the scale formed at 482°C (Fig. 6b) as determined by electron microprobe analysis. The outer oxide layer contained only iron, whereas the inner layer contained chromium and nickel in addition to iron. The metallic inclusions in the oxide are presumably nickel, as was observed with alloy 800.

Fig. 6. Cross sections of type 304 stainless steel exposed to superheated steam for 28,339 h at (a) 538°C and (b) 482°C.

Fig. 7. Electron microprobe analysis across a transverse section of oxide formed on type 304 stainless steel in superheated steam at 482°C.

Sandvik HT9

The Sandvik HT9 test specimens were made from 31.8-mm (1 1/4-in.-) OD pipe with a 3.6-mm (1/7-in.) wall (heat no. 451738, Table 1). The pipe was quartered axially, and the pieces were rolled to a thickness of 1.6 mm (1/16 in.). The flats were solution annealed at 1050°C (1922°F) for 30 min in argon, furnace cooled, tempered at 760°C (1400°F) for 30 min in argon, and, again, furnace cooled. Specimens were then machined from the flat strips. Those specimens initially installed were ground on a 100-mesh belt grinder. Later, another set of specimens from the same material was placed in test, but the surfaces were not disturbed. Still later, specimens machined from the walls of two pipes (heat Nos. 451774 and 454191) were included in the test array. In the latter two cases, the inner wall of the pipes, which was covered with mill scale, formed one of the "flat" surfaces of the specimen, and all other surfaces were ground. Specimens machined from the interior of the wall of one of the pipes (heat No. 454191) were also tested. All of these specimens were ground on all surfaces, and some were heavily pickled before testing.

All specimens completely retained their scales under all conditions. Figure 8 shows weight-gain vs time plots for ground specimens at 482 and 538°C that were tested for 28,339 h; Table 5 shows corrosion rates and

Fig. 8. Weight gain of Sandvik HT9 in superheated steam.

Table 5. Calculated penetrations and corrosion rates for Sandvik HT9 specimens exposed to superheated steam

Total time in test (h)	Initial penetration (μm)		Corrosion rate ($\mu\text{m}/\text{year}$)	
	482°C	538°C	482°C	538°C
28,339 ^a	10.6	14.3	2.7	3.7
27,835 ^a	11.0	15.3	3.0	4.1
26,719 ^a	10.3	12.6	3.0	4.2
23,267 ^a	9.0	14.9	3.2	4.5
20,334 ^b	6.8	12.3	3.1	4.6
19,345 ^c	7.1	10.5	3.6	7.0

^aGround surfaces, heat No. 451738.

^bAnnealed surfaces, heat No. 451738.

^cGround surfaces, heat No. 454191.

intercepts for other ground specimens placed in test at different times. The annealed specimens of the same heat were in test for a shorter time but showed the same behavior as those with ground surfaces. Since all annealed specimens were placed in test at the same time and since the agreement among specimens was very good, only the average corrosion rate and intercept are shown in Table 5.

An inner third oxide layer in addition to the two-layered oxide typical of this type of material existed on specimens exposed at 482°C, but at 538°C only an occasional hint of such an inner layer was found (Fig. 9). At 538°C, however, the interface between the oxide and metal

Fig. 9. Cross sections of Sandvik HT9 exposed to superheated steam at (a) 538°C and (b) 482°C.

was much more irregular than at 482°C. The third layer has been observed before and has been referred to as an inner oxidation zone.⁵ Ion microprobe analysis showed that the metal concentration of the inner oxidation zone was the same as the middle layer. Both contained chromium and molybdenum at the same volume concentration as the substrate metal, whereas the outermost layer contained only iron.

Specimens from heat no. 454191 with mill scale on one face had distinctly lower weight gains after 19,345 h (total test time) than those with all ground surfaces: 34.2 vs 44.1 g/m² at 482°C and 58.0 vs 78.0 g/m² at 538°C. The values for the "all ground" specimens were in good agreement with the data shown in Fig. 8. The average values of the initial penetrations and corrosion rates for the all ground specimens are included in Table 5. Assuming that the ground surfaces on those specimens with mill scale initially on one face developed oxide to the same extent as on those specimens with all surfaces ground, the surfaces with mill scale gained only 19.6 and 28.5 g/m² at 482 and 538°C, respectively. Those specimens with mill scale from heat no. 451774 showed weight gains almost identical to similar specimens with mill scale from heat No. 454191, and cross sections through the oxides showed similar thicknesses. The scales formed on surfaces that initially had mill scale on them did not have a sharp interface between the outer and inner oxide layers (Fig. 10).

Fig. 10. Cross section of a Sandvik HT9 specimen that had mill scale on its surface prior to 19,345 h exposure to superheated steam at 482°C. Note lack of sharp interface between outer and inner oxide layers.

Sumitomo 9 Cr-2 Mo

Two groups of specimens were machined from the wall of a heavy-walled pipe. One of the "flat" surfaces of one group of specimens was the concave interior surface of the pipe with mill scale on it. All other surfaces were ground. Five specimens of this type were tested at each temperature. A second group of specimens was machined from the interior wall of the pipe, and all of their surfaces were initially ground. Four specimens with the ground surfaces and three additional ones that had been heavily pickled after grinding were tested at each temperature.

All specimens were placed in test at the same time and were weighed at five intermediate times and at the end of the 19,345-h test period. For any group of specimens, the reproducibility of weight gains at each weighing was good (standard deviations between 0.8 and 5.5%), and average values of weight gains are shown in Fig. 11. The data show that

Fig. 11. Weight gain of Sumitomo 9 Cr-1 Mo steel in superheated steam.

weight gains were independent of surface treatment, and only one curve has been drawn at each temperature. In contrast to the results obtained with Sandvik HT9, the presence of mill scale seemed to have no consistent effect on weight gains. At 482°C the specimens with scale appeared to gain slightly less weight than the others, but at 538°C there was no difference among the specimens. The curves as drawn in Fig. 11 correspond to corrosion rates of 4.0 and 8.9 $\mu\text{m}/\text{year}$ and intercepts of 7.6 and 18.9 μm at 482 and 538°C, respectively. These values are in good agreement with those for other 9 Cr and 2 1/4 Cr alloys (see later sections).

The oxides formed on the ground and pickled specimens were identical to those formed on all 9 Cr alloys (see later section). As with Sandvik HT9, the interface between the inner and outer oxide layers was much less distinct on those specimens that had mill scale on them than on those that were ground or pickled.

9 Cr-1 Mo Steels

Four different heats of 9 Cr-1 Mo steel were exposed for long periods in this testing program: one air-melted heat (no. 316381A) and three experimental electroslog remelted (FSR) heats (nos. XA-3177, XA-3178, and 91887). In addition, other heats of 9 Cr-1 Mo steels and a few heats with lower chromium contents were exposed for shorter times, and the results from these are presented in a later section. All of these specimens were tested with ground surfaces. At 482°C all specimens retained their oxides, but at 538°C only the oxide on the air-melted material completely resisted exfoliation. Some specimens of all heats of the ESR materials began to lose oxide after 12,000 h, but heat No. 91887 showed less tendency to spall than the others. A few specimens of all ESR heats, however, completely retained their oxides throughout the 24,965 h, the total of the test times for the ESR materials. Figure 12 shows representative specimens of the ESR materials and illustrates the type of blistering and exfoliation noted on all Cr-Mo alloys that lost oxide.

Figure 13 shows weight-gain vs time curves for single specimens of each heat at both temperatures, and Table 6 gives calculated corrosion

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Fig. 12. Photograph of representative ESR 9 Cr-1 Mo alloys that had blistered or lost oxide during 24,965 h exposure to steam at 538°C. Specimen length is 73 mm (2 7/8 in.).

rates and initial penetrations for several specimens of each heat that were in test for the longest times. These data indicate that the corrosion rates of the ESR alloys tended to be slightly higher than those of the air-melted material, but the difference was not great. One difference between the air-melted and ESR materials was the higher silicon content of the air-melted alloy (Table 1).

Figure 14 shows cross sections of scales through typical specimens. In all cases, the oxide formed at 538°C consisted of two layers plus an inner oxidation zone; at 482°C, however, there was no trace of an inner oxidation zone. This same behavior was noted with the Sumitomo 9 Cr-2 Mo, but with Sandvik HT9 an inner oxidation zone was noted only at 482°C.

Fig. 13. Weight gains of different heats of 9 Cr-1 Mo steel in superheated steam.

As in the other cases, the outer layer was pure magnetite, whereas both the inner layer and the inner oxidation zone contained chromium and molybdenum in about the same volume concentration as the metal substrate. In cases where spalling did not occur, no difference in the character of the oxide between the air-melted and ESR heats could be detected. In those cases where spalling occurred, the detached oxide always contained an outer light colored phase (Fig. 14). Examination of the lighter phase with a normal x-ray diffractometer using copper radiation and a graphite crystal diffracted beam monochrometer showed that the light phase in the oxide was hematite.

The exposure of one specimen of heat No. XA-3177 at 538°C for 24,965 h produced a blister that contained a few cracks but was basically intact. This specimen was placed in a mold that was evacuated before the epoxy resin was added so that the epoxy filled the void between the adherent and detached oxide. Figure 15 shows a cross section through the blister, and Fig. 16 shows two enlarged views of the cross section.

Table 6. Calculated penetrations and corrosion rates for specimens of 9 Cr-1 Mo steels exposed to superheated steam

Total time in test (h)	Initial penetration (μm)		Corrosion rate ($\mu\text{m}/\text{year}$)	
	482°C	538°C	482°C	538°C
Heat No. 316381A				
28,339	11.9	18.2	3.2	5.1
27,835	11.3	19.6	2.9	5.0
26,719	10.6	18.2	3.3	5.1
23,267	9.0	16.6	3.5	6.5
Heat No. XA-3177				
24,965	13.9	19.8	3.9	8.3
23,267	9.4	17.2	4.1	9.2
23,267	9.1	19.2	4.1	9.0
Heat No. XA-3178				
24,965	12.7	19.5	4.1	9.4
23,267	10.0	19.7	4.1	9.0
23,267	10.0	22.4	4.1	7.0
Heat No. 91887				
24,965	10.6	20.3	4.0	7.5
23,267	8.2	20.7	4.1	8.5
23,267	8.2	21.3	4.3	8.3

Although both scales consist of two layers, the outer layer of the detached oxide contained a light phase that was not present in the corresponding layer of the attached oxide. X-ray analysis showed the light phase to be hematite. It is interesting to note that conversion of magnetite to hematite seems to have stopped at the inner chromium- and molybdenum-containing layer. Furthermore, in the region where the detached oxide joined the attached oxide, the latter became thinner and thinner until it merged into a single two-layer attached oxide. Judging by the thickness of the attached oxide under the blister, the outer

Fig. 14. Cross sections of 9 Cr-1 Mo specimens exposed to superheated steam: (a) heat No. 316381A - 28,339 h at 538°C; (b) ESR heat No. XA-3178 - 24,965 h at 538°C; (c) ESR heat No. XA-3177 - 24,965 h at 482°C.

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Fig. 15. Cross section of a blister formed on a 9 Cr-1 Mo steel (heat No. XA-3177) during a 24,965-h exposure to superheated steam at 538°C.

Fig. 16. Enlarged cross sections of the blister shown in Fig. 15. (a) Region where dual oxide layers merge into a single two-layered section. (b) Region where oxides are separated showing difference between attached and detached oxides.

oxide must have become detached about 5000 h before this specimen was removed from test. Examination of the specimen 3000 h before the end of the test, however, did not show the blister, which indicates that even though the oxide was detached and a new oxide was forming under it, most of the blistering occurred later.

2 1/4 Cr-1 Mo Steel

These specimens were machined from mill annealed plate, and all surfaces were ground. Subsequently, some specimens were annealed (732°C for 2 h, furnace cooled) and some were pickled. All three surface conditions were tested simultaneously. Within the reproducibility of the data, there were no significant differences in weight gains experienced by the specimens with the different surface treatments or in the tendency of the scale to exfoliate. Only one specimen lost oxide at 482°C. The oxide on this specimen had developed a few blisters by 12,000 h, and appreciable spalling had occurred by 16,000 h. At 538°C a few specimens exhibited exfoliation by 12,000 h, and with increasing exposure both the number of specimens showing loss of oxide and the area on the specimen undergoing exfoliation increased. However, the amount of oxide lost on all exfoliated specimens, except two, was small. Weight gains continued to increase with exposure time. It should be noted that some specimens of each surface treatment retained their oxides for the entire 28,339 h.

Figure 17 shows representative weight-gain vs time curves for specimens with different surface treatments. Although there is a slight variation in the data among individual specimens, only a single curve has been drawn for each temperature. Table 7 shows corrosion rates and penetrations for four specimens with each surface treatment at both temperatures and illustrates the agreement among specimens regardless of surface treatment.

Figure 18a shows a cross section through an intact oxide and illustrates the two-layered scale normally found. Figure 18b shows a similar cross section through a scale that had undergone spalling. It is interesting to note that the outer layer of the detached oxide

Fig. 17. Weight gains of 2 1/4 Cr-1 Mo steel exposed to superheated steam.

Table 7. Calculated penetrations and corrosion rates for 2 1/4 Cr-1 Mo steel test specimens exposed to superheated steam

Total time in test (h)	Initial penetration (μm)		Corrosion rate ($\mu\text{m}/\text{year}$)	
	482°C	538°C	482°C	538°C
Ground surfaces				
28,339	13.9	18.3	3.0	9.8
27,835	13.6	21.4 ^a	3.3	11.0 ^a
26,711	13.6	21.0	3.6	9.3
25,288	11.9	15.6 ^b	3.8	11.3 ^b
Annealed surfaces				
28,339	14.2	19.3	3.2	8.8
27,835	13.9	20.7 ^a	3.4	9.1 ^a
25,288	12.2	21.7	3.0	9.5
23,267	8.5	23.7	3.8	5.9
Pickled surfaces				
28,339	16.3	21.0	3.0	7.8
27,835	15.9	14.9 ^c	3.8	11.4 ^c
26,719	13.5	24.1	2.9	8.6
25,288	11.5	18.3	3.2	10.0

^a18,235 h.

^b20,334 h.

^c26,719 h.

^d23,267 h.

(a)

40 μm

(b)

Fig. 18. Cross sections of oxide on 2 1/4 Cr-1 Mo steel specimens exposed to superheated steam for 28,339 h at (a) 482°C and (b) 538°C.

contains hematite (light phase) as was observed with the 9 Cr steels. It is also apparent from Fig. 18b that more than two layers exist in part of the oxide; this suggests that at some time the initial two-layered scale became detached from the metal, a new two-layered scale formed, and the layers subsequently joined.

The autogenously welded specimens, including the U-bend specimens, behaved in the same manner as the wrought specimens. Weight-change data were in good agreement with those shown in Fig. 17 and Table 7, and there was no difference in the extent of exfoliation. The 2 1/4 Cr-1 Mo steel welded to alloy 800 with alloy 82 filler metal also showed the same behavior. There were a few small regions in some of the latter specimens where there was a lack of fusion, which became apparent during formation of U-bend specimens. These small cracklike regions showed no unusual corrosion as a result of 28,339 h in steam.

Short-Term Tests With Cr-Mo Steels

Specimens made from different alloys containing 5-9% Cr and 1% Mo were placed in the loop late in the test and received an exposure of only 5729 h before the operation of the loop in Florida was terminated. Duplicate specimens of each alloy with ground surfaces were exposed at the two temperatures. Because the data obtained with the 9 Cr alloys (earlier section) and other data reported by Hurst and Cowen⁶ suggested that silicon may be important in the oxidation process, alloys with a range of silicon concentrations were included in this group of materials.

Table 8 shows the alloys tested, their silicon contents, and the average weight gains for duplicate specimens after 997, 2556, and 5729 h. In all cases except two the duplicates agreed within 5%; in the other two cases the agreement was within 8%. Although the exposure time was too short to attach much significance to the results, it was interesting to note that the weight gains were generally lower the higher the silicon content.

In addition to the above alloys, three other heats of 9 Cr-1 Mo steel with relatively high silicon concentrations were installed in the loop very near the end of the test. Either 10 or 12 ground specimens of

Table 8. Average weight gains of duplicate Cr-Mo steel specimens in superheated steam

Steel designation	Heat No.	Silicon content (wt %)	Temperature (°C)	Average weight gain (g/m ²)		
				997 h	2556 h	5729 h
5 Cr-1 Mo	3476	0.11	482	19.1	23.3	36.4
			538	35.2	47.8	75.1
5 Cr-1 Mo	3475	0.14	482	18.1	22.6	35.4
			538	34.7	46.4	73.1
7 Cr-1 Mo	3478	0.14	482	18.9	23.0	35.4
			538	34.2	45.2	70.0
7 Cr-1 Mo	3477	0.17	482	17.7	21.5	32.9
			538	33.3	44.0	70.1
9 Cr-1 Mo	31378	0.01	482	19.0	24.4	43.0
			538	45.6	68.1	121.1
9 Cr-1 Mo	31446	0.02	482	18.6	23.5	39.3
			538	40.4	53.2	92.1
9 Cr-1 Mo	31577	0.04	482	17.9	23.1	39.8
			538	41.8	61.8	103.3
9 Cr-1 Mo	F-5349	0.36	482	15.5	18.8	29.3
			538	25.7	34.4	58.4

each heat were tested at each temperature, and the results are presented in Table 9. The agreement among replicate specimens was excellent. These results are presented only for the sake of completeness. If our test facility can be relocated at another power plant, all of the specimens discussed in this section will be returned to test for additional exposure.

Table 9. Average weight gains of 9 Cr-1 Mo steels
in superheated steam

Heat No.	Silicon content (wt %)	Temperature (°C)	Average weight gain (g/m ²)	
			458 h	667 h
30383	0.43	482	9.5	11.2
		538	24.7	30.9
15965	0.63	482	6.8	8.8
		538	23.3	28.5
Lot 35 ^a	0.71	482	8.5	10.5
		538	22.3	28.7

^aBritish material supplied by Combustion Engineering, Chattanooga, Tennessee.

Measurements of Steel Corrosion Product Scales

Cross sections of representative specimens of all the Cr-Mo alloys were polished and examined. In all cases the characteristic two-layered oxide was found, and as indicated earlier, an internal oxidation zone was also present in some cases. Electron microprobe analysis across the oxides showed that the internal oxidation zone and the inner layer contained chromium and molybdenum in approximately the same volume concentration as the alloy whereas the outer layer contained neither and was essentially pure magnetite. These observations are in agreement with those of others who have investigated the composition of steam-formed scales on Cr-Mo alloys.⁷⁻¹⁰

We also measured the thicknesses of the inner and outer oxide layers on the polished cross sections. For a given alloy there was no significant difference in the ratio of outer to inner oxide thickness as a result of either temperature or exposure time. This latter point is especially significant because if the outer layer were preferentially dissolved or eroded away the ratio would have decreased with time. The ratios noted for the different alloys are shown in Table 10. Within the standard deviations there were no significant differences in the ratios

Table 10. Ratio of outer and inner oxide thicknesses
on Cr-Mo alloys

Alloy	Number of measurements	Average ratio (outer oxide) (inner oxide)	Standard deviation
2 1/4 Cr-1 Mo steel	20	1.40	0.16
9 Cr-1 Mo steel ^a	18	1.27	0.08
9 Cr-1 Mo steel ^b	15	1.31	0.08
Sandvik HT9	24	1.37	0.22

^a Air-melted heat No. 316381A.

^b ESR heat Nos. XA-3177, XA-3178, and 91887.

among the alloys with respect to either exposure time or chemical composition. The internal oxidation zone that existed in some cases (482°C for Sandvik HT9 and 538°C for 9 Cr-1 Mo steels) was not included in the inner oxide thickness measurement. Had it been included, the ratio would have been near unity in those cases. Effertz and Meisel⁷ noted that the demarcation line between the outer and inner layers on Cr-Mo steels occurs at a position corresponding to 40-60% of the total scale thickness, and our values are within this range.

Although we noted previously that the oxidation rates for these Cr-Mo steels changed from apparent parabolic to linear kinetics between 5000 and 8000 h, there appears to have been no change in the ratio of the inner to the outer oxide layer thickness before or after 8000 h. As will be discussed, this behavior is inexplicable by an oxidation model based on a simple cation or anion solid-state diffusion process.

We have assumed that weight gain is a reliable measure of the amount of metal oxidated so long as exfoliation of the oxide has not occurred. An indication that such is the case is shown in Fig. 19, where total oxide thickness (excluding the inner oxidation zone) is plotted vs weight gain. Since each oxide thickness was measured from a photomicrograph (as, for example, in Figs. 9, 14, and 18) that surveyed only one field of view along the long axis of the specimen, the fit of the data points to the line as drawn is satisfactory. Furthermore,

Fig. 19. Comparison of oxide thickness with weight gain. Dashed line assumes Fe_3O_4 of theoretical density (5.2 Mg/m^3).

there appears to be no major difference in the thickness to weight-gain ratio among the alloys. The dashed line in Fig. 19 represents oxide thickness as a function of weight gain if the corrosion product were stoichiometric Fe_3O_4 of theoretical density (5.2 Mg/m^3). The experimental points as an average lie about 10% above this line; this results primarily from obvious porosity in the scale, which increased as the scale thickened.

Further confirmation of the validity of weight gain as a measure of corrosion was obtained by defilming several specimens in Clarke's³ solution and determining the weight of oxide and the amount of metal oxidized on each specimen. The weight of oxide actually formed was compared with the amount expected assuming that the metal oxidized to stoichiometric $(\text{FeCr})_3\text{O}_4$. The average amounts of oxide found were 93% of that expected for 2 1/4 Cr-1 Mo steel, 94% for Sandvik HT9, and 91% for the ESR 9 Cr alloys. On one 2 1/4 Cr-1 Mo steel specimen that had lost some oxide, only 89% of the oxide expected was present. Attempts to descale air melted 9 Cr-1 Mo steel specimens resulted in a heavy attack of the base metal while appreciable amounts of scale remained on the

specimen. All the descaled weight losses included some base metal loss; however, by removing the specimens from the descaling solution at the first exposure of bare metal (as evinced by formation of hydrogen bubbles), loss of the base metal was held to a minimum. Because the oxide scales were quite uniform in thickness (except where exfoliation had occurred), exposure of bare metal began only at the end of the descaling process (except for the air-melted 9 Cr-1 Mo alloy). Although slight, the attack on the base metal was sufficient to account for the indicated less than 100% oxide retention. Nevertheless, the data clearly indicate that Cr-Mo steels exposed to steam form magnetite $[(\text{FeCr})_3\text{O}_4]$ scales that are retained on the surface until exfoliation occurs.

DISCUSSION

The nature of the kinetic processes was perhaps the most striking feature of the results obtained in this investigation. All materials that oxidized at measurable rates (including Cr-Mo alloys, type 304 stainless steel, and alloy 800) gained weight at decreasing rates [weight gain proportional to $(\text{time})^{1/2}$] for about the first year, after which the rates became constant. For almost all materials a minimum of seven specimens was exposed, and in all cases this type of behavior was observed. The constant rates following the transition fell below extrapolation of the initial parabolic curves; that is, the behavior was opposite to the breakaway phenomenon sometimes observed in other systems where loss of a protective oxide results in a change from a low decreasing rate to a constant higher rate. The transition from parabolic to linear kinetics did not occur at a given oxide thickness. The time of transition was approximately independent of temperature and alloy composition although the oxide thickness varied with both. Thus, at both temperatures the transition to linear kinetics occurred after 5000-8000 h for the Cr-Mo steels that oxidized uniformly, for type 304 stainless steel that corroded less and irregularly, and for alloy 800 that had been intergranularly corroded before steam exposure. Furthermore,

we detected no changes in the character of the oxide before and after transition; that is, the composition and apparent compactness of the oxide layers remained unchanged despite the transition in oxide growth kinetics.

Other features of our results were the long test time and the relatively low steam temperature. Most other quantitative oxidation studies that we are aware of have used higher temperatures and shorter times. The few long-term studies with Cr-Mo steels conducted in the same temperature range that we used usually relied on the measurement of scale thickness on the steam side of superheater tubes or on corrosion specimens exposed in steam lines at power plants. Each data point represented a separate specimen that was destructively examined. Inherent in this approach are the assumptions that specimen-to-specimen variation is small, that the operating conditions (steam purity and temperature) remain constant, and that oxide is not lost from the specimen throughout the test period. It is questionable whether these assumptions are justified during long-term testing in operating power plants. The fact that conflicting statements about the oxidation kinetics of Cr-Mo steels in steam are found in the literature may indicate that the above assumptions were not achieved in all cases. For example, Effertz and Meisel⁷ and Manning and Metcalfe⁵ concluded that the growth in oxide thickness is adequately described by the parabolic oxidation law even for long times, whereas Grobner⁸ and Eberle and Kitterman⁹ indicated a shift from parabolic to linear kinetics after some time. In the latter cases it was not possible to tell whether the linear rate was above or below that indicated by extrapolation of the parabolic curve. On the other hand, we had controlled conditions with frequent examinations of any given specimen. So far as we know our results represent the longest controlled steam exposures of these materials reported to this time.

Except for the change in kinetics after about the first year, our results for type 304 stainless steel and annealed and cold-worked alloy 800 are in general agreement with those reported in the literature. Thus, the irregular nature of attack on type 304 stainless steel¹⁰

(Fig. 6) and the beneficial effect of cold-working alloy 800⁴ have been noted before. The corrosion observed with intergranularly corroded alloy 800 was much greater than on annealed or cold-worked material, but no similar data were found with which to compare our results. Generally, these austenitic materials and alloy 617 are capable of withstanding higher steam temperatures than those used in this investigation. Certainly, as a class, these materials are significantly more resistant to either steam or air than the Cr-Mo alloys that we investigated.

The growth of oxides on Cr-Mo steels (and the austenitic stainless alloys) in steam is generally believed to result from both the outward migration of iron ions to the surface, where they react with water molecules, and the inward diffusion of oxygen ions to the metal-oxide interface, where they react with the metal.⁷ Since the solid-state diffusion rates of chromium and molybdenum ions in the oxides are much lower than that of iron ions, they are oxidized in place. Consequently, the interface between the two layers marks the original surface of the steel. However, unless accompanied by some morphological change in the oxide (porosity, cracking, roughness, etc.), such oxides should grow in accordance with parabolic kinetics, and a transition to a lower constant corrosion rate is unexpected. Since our examination of the oxide films has revealed no apparent changes in chemical compositions or morphology (including the inner to outer oxide thickness ratio) accompanying the transition, the reason for the change to linear kinetics remains obscure.

Some of the specimens of 2 1/4 Cr-1 Mo steel and ESR 9 Cr-1 Mo steels underwent exfoliation at 538°C, but no specimen of the air-melted 9 Cr-1 Mo steel or Sandvik HT9 showed any signs of exfoliation or spalling. The chromium content of the latter alloy was 11.4%, a value approaching that necessary to give it a stainless character. However, its corrosion rate was only slightly less than the lower Cr ferritic alloys. Corrosion rates experienced by the air-melted 9 Cr-1 Mo, the 9 Cr-2 Mo, the ESR 9 Cr alloys, and the 2 1/4 Cr-1 Mo steel were similar; yet, only the air-melted 9 Cr-1 Mo and the 9 Cr-2 Mo steels remained free of exfoliation. (The latter alloy was only in test for 19,345 h.) The fact that Cr-Mo alloys with chromium contents between 2 and 9%

behave about the same in steam has been noted by several investigators,^{5-7,10} some of whom have concluded that within this range silicon is more important than chromium in determining corrosion behavior. Although we did not specifically investigate the effect of silicon content in our long-term exposures, it is interesting to note that of the alloys tested, the air-melted 9 Cr-1 Mo steel had the highest silicon concentration (0.46%), followed by the Sumitomo 9 Cr-2 Mo (0.29%), the 2 1/4 Cr-1 Mo steel (0.22%), and the ESR 9 Cr alloys (0.08-0.21%). Thus, based on results from those specimens exposed for the longest times, our data suggest that the higher silicon level retarded the onset of exfoliation but, within the range examined, had only a small effect on the corrosion rate prior to exfoliation. On the other hand, our short-term tests indicate some effect of silicon during the early stages of oxidation. Rahmel¹¹ notes that silicon dioxide accumulates at the metal-oxide phase boundary during oxidation; this fact may inhibit the diffusion of iron ions to the oxide-steam interface, thereby reducing the oxidation rate, and improve the interlocking of the scale and metal, thereby reducing the tendency to exfoliate.

Usually as the oxide thickened on Cr-Mo steels beyond some level, voids in the scale increased in number and size and frequently concentrated at the metal-oxide interface or between the two oxide layers. Even at 538°C this behavior was not evident until after many thousands of hours, and at 482°C it was not observed even after 28,000 h except for the one specimen of 2 1/4 Cr-1 Mo steel referred to earlier. Our data, as well as those of McNary,¹² generally indicate that when spalling occurred the separation was at the oxide-metal interface followed by the formation of a new two-layered oxide. The cause of the separation is not altogether clear although differential expansion between the metal and oxide during cooling is suggested as one reason.¹² It has been stated that the formation of a hematite layer on the outer oxide surface enhances spalling because the mismatch between the expansion coefficients of oxide and metal is greater with hematite than with magnetite.¹⁰ In our tests the only times we saw significant amounts of hematite on top of magnetite were after separation of the oxide from the metal had occurred, indicating that the hematite was a result of the separation

rather than a cause of it. This observation suggests that with adherent oxides the flux of ferrous ions at the steel-oxide interface preserves the magnetite structure, but once the oxide becomes detached from the steel the magnetite can be oxidized to hematite. It was previously noted that regions of faster duplex oxide growth often contained less Fe_2O_3 than slower growth regions,¹⁰ and the above explanation is consistent with this observation.

Examination of the blistered specimen in Fig. 15, both before and after the blister became apparent, indicated that the outer oxide scale was detached from the substrate and a new layer was forming under it before the outer oxide had raised up to a perceptible level. That this was apparently happening in other cases was indicated by the fact that at 538°C occasional weight gains greater than expected were observed in the linear region and this always occurred shortly before exfoliation began. It seems reasonable to assume that parts of the original scale had been detached and a new oxide was growing at a greater rate than the old. Why blistering apparently takes place only some time after detachment has occurred is probably related to the fact that the outer layer of the attached layer is slowly oxidized to hematite. Although the hematite has a greater density than the magnetite, there is a net 2.2% volume increase in going from magnetite to hematite due to the oxygen uptake.¹³ Thus, as the hematite forms, the oxide buckles and, because of its lack of ductility, cracks form in the raised oxide.

Armstrong et al.,¹⁰ in a review of the corrosion of steels in power plants and in experimental programs in the United Kingdom, noted that oxides on ferritic steels often show degradation by "through scale" cracking and by accelerated oxidation associated with multiple laminations in the inner layer. We also noted multiple laminations, usually when spalling had either occurred or was imminent, but only rarely were cracks found perpendicular to the surface. Our data indicate that at random locations the oxide, which was under compression as a result of cooling, cracked at the metal oxide interface and in some cases formed a blister; a new oxide then formed on the metal; and, at least at the edge of the blister, these oxides grew together. In this regard our data are

consistent with McNary's explanation of the formation of multiple laminations.¹²

Armitt et al.¹⁰ further noted that voids are frequently found in scales formed in power plants but that scales grown in the laboratory contain few voids. The oxides that formed isothermally on our specimens contained few voids until after many thousands of hours and usually not until spalling was about to begin, at which time numerous voids were apparent. On the other hand, experiments conducted with 2 1/4 Cr-1 Mo steel in which a high heat flux existed across the corroding surfaces showed numerous voids even in the early stages of oxidation.¹⁴⁻¹⁵ Furthermore, oxides formed under these conditions appeared to be much less firmly anchored to the substrate than those in our isothermal tests. Comparison of isothermal results with those obtained with a high heat flux across the corroding surface suggests that under otherwise similar conditions a high heat flux produces in a short time the same type of oxide degradation that only occurs after much longer times without heat flux.

Although we do not have a rational kinetic model to explain our results either for the austenitic stainless steels or for the Cr-Mo ferritic steels, our data show all materials which corroded at measurable rates had long-term steam oxidation rates at 482 and 538°C that were significantly lower than predicted on the basis of short-term data. In the case of the Cr-Mo steels that are frequently used in parts of liquid-metal- and inert-gas-cooled nuclear reactors, this fact (combined with the lack of exfoliation at 482°C) is particularly significant since recent trends have been toward operating temperatures in the range of these experiments. Furthermore, from purely a steam oxidation standpoint there is no reason to choose a Cr-Mo alloy with greater than 2 1/4% Cr or to be concerned about surface treatment; between 2 1/4 and 9% Cr there were no significant differences in corrosion rates regardless of the surface treatment. Sandvik HT9 (11.4% Cr) exhibited slightly lower corrosion rates at 538°C than the other Cr-Mo alloys, but even in this case surface treatment had no major effect.

SUMMARY

This report presents data obtained during exposure of several alloys to superheated steam at 482 and 538°C for periods of time up to 28,339 h. The principal results are summarized below.

(1) Alloy 617 and alloy 800 specimens with both mill annealed and cold-worked surfaces corroded at very low rates at both temperatures. Alloy 800 specimens that had been intergranularly corroded prior to steam exposure corroded much more extensively than other specimens, but intergranular penetration did not progress during the test.

(2) Type 304 stainless steel oxidized nonuniformly, but attack was relatively light. At both temperatures oxidation followed parabolic kinetics for about the first year, after which there was a transition to linear kinetics. There was no loss of oxide during the test.

(3) The greatest effort in this investigation was devoted to a study of the steam oxidation behavior of Cr-Mo steels. All of these materials showed the same type of kinetics as type 304 stainless steel regardless of temperature, that is, parabolic kinetics for the first 5000-8000 h followed by a constant rate. The constant rate was lower than expected from extrapolation of the initial parabolic curve, and the oxidation rates were independent of surface treatment.

(4) Except for one specimen, 2 1/4 Cr-1 Mo steel retained its scale during the 28,339-h test at 482°C. However, at 538°C, specimens began to experience exfoliation after about 12,000 h, and by 25,000 h most had lost some oxide. After the first year average corrosion rates were 3.7 and 8.5 $\mu\text{m}/\text{year}$ (0.15 and 0.33 mils/year) at 482 and 538°C, respectively.

(5) Test specimens of an air melted heat of 9 Cr-1 Mo steel (0.46% Si) completely retained their oxides at both temperatures and showed essentially the same corrosion rates as 2 1/4 Cr-1 Mo steel. On the other hand, three ESR heats of 9 Cr steel with low silicon contents underwent appreciable exfoliation at 538°C although none did so at 482°C. The corrosion rates of those materials with low silicon contents appeared to be slightly higher than for the air melted alloy. Short tests with a group of alloys containing 5-9% Cr and 1% Mo with variable

silicon contents also seemed to indicate that initial weight gains were less as the silicon content became higher.

(6) Sumitomo 9 Cr-2 Mo steel behaved in approximately the same manner as the other 9 Cr alloys. During the 19,345 h that this material was in test, there was no exfoliation. The presence of mill scale on the surface before steam exposure had no significant effect.

(7) The corrosion of Sandvik HT9 (11.4% Cr) was slightly less than 2 1/4 or 9 Cr steels, but the general behavior — constantly decreasing rate for first year followed by a low constant rate — was the same. There was no evidence of exfoliation during the entire 28,339-h test, and there was no difference between annealed and cold-worked surfaces. In contrast to 9 Cr-2 Mo steel, mill scale on the surface tended to reduce corrosion.

(8) No unusual corrosion of welds and no signs of localized attack in U-bends were noted.

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REFERENCES

1. J. C. Grass and W. A. Maxwell, *The Corrosion of Several Alloys in Superheated Steam at 482 and 538°C*, ORNL/TM-6465 (November 1978).

2. J. C. Griess and W. A. Maxwell, *The Oxidation of Selected Alloys During 25,000 h in Superheated Steam at 482 and 538°C*, ORNL/TM-7114 (March 1980).
3. S. M. Clarke, "The Use of Inhibitors (with Special Reference to Antimony) in the Selective Removal of Metallic Coatings and Rust," *Trans. Electrochem. Soc.* 69: 131-42 (1936).
4. S. Leistikow, "Isothermal Steam Corrosion of Commercial Grade Austenitic Stainless Steels and Nickel Base Alloys in Two Technical Surface Conditions," pp. 278-90 in *Proc. 4th Int. Cong. Metallic Corrosion*, ed. by N. E. Hammer, National Association of Corrosion Engineers, Houston, Texas, 1972.
5. M. I. Manning and E. Metcalfe, "Oxidation of Ferritic Steels in Steam," paper 63 in *Proc. Int. Conf. on Ferritic Steels for Fast Reactor Steam Generators*, British Nuclear Energy Society, London, 1977.
6. P. Hurst and H. C. Cowen, "The Oxidation of 9 Cr-Mo and Other Steels in 6.9 MN/m² Steam at 748 and 823°K," paper 62 in *Proc. Int. Conf. on Ferritic Steels for Fast Reactor Steam Generators*, British Nuclear Energy Society, London, 1977.
7. P. H. Effertz and H. Meisel, "Scaling of High Temperature Steels in High Pressure Steam after Long Service," *Maschinenschaden* 44(1): 14-20 (1971) (C.E.G.B. Translation 5799).
8. P. J. Grobner et al., "Steam-Side Oxidation and Exfoliation of Cr-Mo Superheater and Reheater Steels," paper 172, NACE Corrosion/80, Chicago, Illinois, March 5, 1980.
9. F. Eberle and J. H. Kitterman, *Behavior of Superheater Alloys in High Temperature, High Pressure Steam*, p. 67, American Society of Mechanical Engineers, New York, 1968.
10. J. Armitt et al., *The Spalling of Steam-Grown Oxide from Superheater and Reheater Tube Steels*, EPRI FP-686, Electric Power Research Institute, Palo Alto, California (February 1978).
11. A. Rahmel, "Fundamental Processes of Metal Oxidation at High Temperature and Their Significance in the Oxidation of Iron, Iron Alloys, and Steel," in *Chemical Metallurgy of Iron and Steel*, pp. 395-406, The Iron and Steel Institute, London, 1973.

12. T. A. McNary, *The Exfoliation of Steam-Side Scale in Reheater Tubing of Cr Alloys 2 1/4, 5, and 9*, Babcock and Wilcox Research Report 7724, Alliance, Ohio (July 1966).
13. D. Caplan, M. J. Graham, and M. Cohen, "Effect of Oxygen Pressure and Experimental Method on the High Temperature Oxidation of Pure Iron," *Corros. Sci.* 10: 1-8 (1970).
14. J. C. Griess, J. H. DeVan, and W. A. Maxwell, "Effect of a High Heat Flux on the Corrosion of 2 1/4 Cr-1 Mo Steel in Superheated Steam," *Mater. Perform.* 17: 9-15 (1978).
15. J. C. Griess, J. H. DeVan, and W. A. Maxwell, "The Effect of a High Heat Flux on the Oxidation of 2 1/4 Cr-1 Mo Steel Tubing in Superheated Steam," *Mater. Perform.* 19: 46-52 (1980).