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ANL/MHD-93/02

**CHARACTERIZATION OF DEPOSITS AND EFFECT OF DEPOSITS ON
CORROSION OF MATERIALS FOR MHD
BALANCE-OF-PLANT APPLICATIONS**

by

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December 1993

Work supported by

THE U.S. DEPARTMENT OF ENERGY
Pittsburgh Energy Technology Center

MASTER

CONTENTS

ABSTRACT	1
INTRODUCTION.....	1
BACKGROUND	4
Low Mass Flow Train Tests in CFFF.....	4
Material Tests at ANL.....	9
RESULTS	11
Analyses of CFFF-Exposed Materials.....	11
Deposit Characterization.....	11
Analysis of Deposits on Specimen Tubes after 500-h Exposure.....	14
Thermal Characteristics of Deposits.....	18
Analysis of Tube Materials.....	21
Analysis of ANL-Tested Materials	41
SUMMARY.....	57
ACKNOWLEDGMENTS.....	58
REFERENCES.....	59

FIGURES

1. Schematic diagram of coal-fired MHD system.....	2
2. Gas, steam, and metal temperatures in a typical heat recovery/seed recovery system for retrofit and commercial plants.....	3
3. Schematic diagram of Low Mass Flow Train at DOE-CFFF.....	5
4. Steady-state temperature along axial direction in CFFF SHTM during fouling/corrosion test series LMF4-K through LMF4-N	6
5. Locations of CFFF-exposed ring specimens analyzed at Argonne National Laboratory	7
6. Average TS1 tube metal temperatures during 500 h of tests LMF4-K through LMF4-N.....	8
7. Schematic diagram of experimental setup used in laboratory test program.....	11
8. Macrophotographs of several tube specimens and deposits after exposure in test section TS1	15
9. Macrophotograph of deposits collected from tube- and gas-side surfaces and cross section of Type 304 stainless steel heat exchanger tube after exposure in LMF experiment.....	15
10. Macrophotographs of deposits collected from gas- and tube-side surfaces of tube in CS1 region and CS3 region.....	16

11.	Concentration-distance profiles for carbonate, bicarbonate, and soluble sulfate phases in deposits accumulated on tubes exposed in runs LMF4-N and LMF4-R.....	17
12.	X-ray analyses for Fe, Cr, Ni, Si, K, and S for composite specimen of Type 304H stainless steel with accumulated deposit on leading edge of specimen.....	17
13.	X-ray analyses for Fe, Cr, Ni, Si, K, and S for composite specimen of Type 304H stainless steel with accumulated deposit on trailing edge of specimen.....	18
14.	Tube/deposit assembly used for determination of thermal characteristics of deposit material.....	19
15.	Temperature distribution from tube wall into deposit material, obtained at different gas flow rates for gas temperature of 1000°C.....	20
16.	Influence of gas temperature on temperature distribution obtained at air flow rate of 800 cfm.....	20
17.	Thermal conductivity values as a function of temperature for composite deposit from CFFF.....	20
18.	SEM photomicrographs of leading and trailing edges of Type 304H stainless steel tube in Passes 1 and 2 after 500-h exposure in CFFF.....	22
19.	SEM photomicrographs of leading and trailing edges of Type 310 stainless steel tube in Passes 1 and 2 after 500-h exposure in CFFF.....	22
20.	SEM photomicrographs of leading and trailing edges of Alloy 253 MA tube in Passes 1 and 2 after 500-h exposure in CFFF.....	23
21.	Scale thickness/penetration data for several radial positions for tubes of Types 304H and 316H stainless steel after 500-h exposure in CFFF.....	23
22.	Scale thickness/penetration data for several radial positions for tubes of Type 310 stainless steel and Alloy 253 MA after 500-h exposure in CFFF.....	24
23.	Temperature distribution and corrosion thicknesses for Type 304H stainless steel after 1500-h exposure in test section 1 of CFFF.....	26
24.	Temperature distribution and corrosion thicknesses for Type 316H stainless steel after 1500-h exposure in test section 1 of CFFF.....	27
25.	Temperature distribution and corrosion thicknesses for Type 310 stainless steel after 1500-h exposure in test section 1 of CFFF.....	28
26.	Temperature distribution and corrosion thicknesses for 253 MA after 1500-h exposure in test section 1 of CFFF.....	29
27.	Temperature distribution and corrosion thicknesses for Type 304H stainless steel after 2000-h exposure in test section 1 of CFFF.....	30
28.	Temperature distribution and corrosion thicknesses for Type 316H stainless steel after 2000-h exposure in test section 1 of CFFF.....	31
29.	Temperature distribution and corrosion thicknesses for Type 310 stainless steel after 2000-h exposure in test section 1 of CFFF.....	32
30.	Temperature distribution and corrosion thicknesses for 253 MA after 2000-h exposure in test section 1 of CFFF.....	33
31.	SEM photomicrographs of Type 310 stainless steel after 2000-h exposure at metal temperatures of 522-669°C in CFFF.....	34

32. SEM photomicrographs of Type 310 stainless steel after 1500-h exposure at metal temperatures of 584-698°C in CFFF.....	34
33. SEM photomicrographs of Type 304H stainless steel after 1500-h exposure at metal temperatures of 516-576°C in CFFF.....	35
34. SEM photomicrographs of Type 316H stainless steel after 1500-h exposure at metal temperatures of 516-576°C in CFFF.....	36
35. SEM photomicrographs of Type 310 stainless steel after 1500-h exposure at metal temperatures of 577-599°C in CFFF.....	36
36. SEM photomicrographs of 253 MA after 1500-h exposure at metal temperatures of 574-597°C in CFFF	37
37. SEM photomicrographs of Type 316H stainless steel after 2000-h exposure at metal temperatures of 544-553°C in CFFF.....	38
38. SEM photomicrographs of Type 316H stainless steel after 2000-h exposure at metal temperatures of 438-524°C in CFFF.....	38
39. Schematic representation of reaction sequence for high-chromium alloys exposed to combustion environments.....	39
40. Corrosion loss data for Types 304H and 316H stainless steel as a function of exposure temperature.....	40
41. Corrosion loss data for Type 310 stainless steel and Alloy 253 MA as a function of exposure temperature.....	40
42. Macrophotographs of specimens tested for 2000-h at ANL.....	41
43. Cross sections of Type 310 stainless steel specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	43
44. Cross sections of RA 85H specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	43
45. Cross sections of Alloy 556 specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	44
46. Cross sections of 253 MA specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	44
47. Cross sections of CR35A specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	45
48. Cross sections of CR30A specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	45
49. Cross sections of HR-120 specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	46
50. Cross sections of HR-160 specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	46
51. Cross sections of Type 347 stainless steel and Alloy 8XX specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 982°C.....	47
52. Cross sections of chromized Type 304 stainless steel specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	47

53. Cross sections of chromized Alloy 800 specimens tested in presence of TS1 and TS1 plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	48
54. Cross sections of Type 310 stainless steel specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C	48
55. Cross sections of RA 85H specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	49
56. Cross sections of Alloy 556 specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	49
57. Cross sections of 253 MA specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	50
58. Cross sections of CR35A specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	50
59. Cross sections of CR30A specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	51
60. Cross sections of HR-120 specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	51
61. Cross sections of HR-160 specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C.....	52
62. Cross sections of chromized Type 304 stainless steel specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C	52
63. Cross sections of chromized Alloy 800 specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 762°C and 982°C	53
64. Cross sections of Type 347 stainless steel, Alloy 8XX, and Alloy 214 specimens tested in presence of K ₂ SO ₄ and K ₂ SO ₄ plus Fe ₂ O ₃ deposits at 982°C	54
65. Metal recession data for several advanced alloys and coatings in presence of TS1 deposit with and without iron oxide at 762°C.....	55
66. Metal recession data for several advanced alloys and coatings in presence of K ₂ SO ₄ deposit with and without iron oxide at 762°C	55
67. Metal recession data for several advanced alloys and coatings in presence of TS1 deposit with and without iron oxide at 982°C	56
68. Metal recession data for several advanced alloys and coatings in presence of K ₂ SO ₄ deposit with and without iron oxide at 982°C	56

TABLES

1. Composition of Illinois #6 coal used in CFFF tests.....	5
2. Inlet conditions for test section 1 for runs LMF4-K through LMF4-N in CFFF	5
3. Specimen exposure runs in CFFF.....	8
4. Compositions of alloys tested in CFFF	9

5. Nominal chemical composition of alloys used in ANL program.....	10
6. Chemical analysis of deposits collected at several locations in CFFF.....	13
7. X-ray diffraction analysis for deposits collected at several locations in CFFF.....	14

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ABSTRACT

Candidate heat exchanger materials tested in the Low Mass Flow Train at the Coal-Fired Flow Facility (CFFF) at Tullahoma, TN, were analyzed to evaluate their corrosion performances. Tube specimens obtained at each foot of the 14-ft-long U-bend tubes were analyzed for corrosion-scale morphologies, scale thicknesses, and internal penetration depths. Results developed on 1500- and 2000-h exposed specimens were correlated with exposure temperature. In addition, deposit materials collected at several locations in the CFFF were analyzed in detail to characterize the chemical and physical properties of the deposits and their influence on corrosion performance of tube materials.

INTRODUCTION

Magnetohydrodynamic (MHD) power generation is based on the direct conversion of fuel energy into electrical energy by flowing a heated, electrically conducting fluid through a magnetic field. In a coal-fired open-cycle MHD system, the working fluid is utilized on a once-through basis and consists of multiphase fossil-fuel combustion products. The overall plant (see Fig. 1) includes a topping cycle, where the electrical energy is directly produced by the MHD generator, and a steam bottoming plant, where additional heat energy and seed material used to increase electrical conductivity of the plasma are recovered.¹ The steam bottoming plant, in general, consists of a radiant boiler, high-temperature air heater, secondary combustor, superheater, reheater, intermediate-temperature air heater, and economizers. Metallic alloys are being considered for a variety of these components. The alloy materials selected being must be able to withstand the high operating temperatures and corrosive/erosive conditions encountered in MHD systems. In particular, the materials must be resistant to corrosion when exposed to high levels of alkalis (specifically, potassium compounds introduced into the system as seed materials) and various ash constituents released during the combustion process.

Two different concepts have been proposed for a steam bottoming plant, depending on whether an existing boiler system is retrofitted or a new commercial plant is built. In the retrofit system, oxygen-enriched air preheated to a moderate temperature is used in the combustion process. As a result, the intermediate-temperature air heater will be essentially an oxygen-enriched air heater constructed of metallic material. The temperature of the combustion gas entering the secondary superheater will be $\approx 1230^{\circ}\text{C}$ ($\approx 2250^{\circ}\text{F}$). On the other hand, in the commercial plant, air (without oxygen enrichment) will be preheated to a higher temperature for the combustion process. The high-temperature air heater will be made of ceramic materials, and the temperature of the

Fig. 2. Gas, steam, and metal temperatures in a typical heat recovery/seed recovery system for retrofit and commercial plants

However, the gas-to-air heat exchanger concept can result in metal temperatures of the ITAH as high as 816°C (1500°F). Even though the materials will not be subjected to pressures as high as those in the steam system, they must resist corrosion damage that arises from a combination of the elevated temperature and the seed/slag deposits.

Characterization of superheater and ITAH tube fouling and corrosion behavior resulting from deposits of coal ash and spent seed have been major research objectives in the U.S. MHD balance-of-plant programs. Ash/seed fouling experiments are being conducted in the Coal Fired Flow Facility (CFFF) at Tullahoma, TN.² At Argonne National Laboratory (ANL), a test program is being conducted to support the materials evaluation effort of the CFFF by performing long-term laboratory tests in simulated MHD environments.³ The significantly higher alkali content in the MHD environment

(deliberately added as seed in MHD units, in contrast to being an impurity in coal feedstock in conventional boilers) is of concern with regard to corrosion degradation of materials and seed/slag fouling of tube banks. The thermodynamic equilibria prevalent among the combustion environments from coal combustion with excess air, the seed components (e.g., K_2SO_4 , KOH, or K_2CO_3), and the slag components (such as Al_2O_3 , SiO_2 , CaO, or Fe_2O_3), enable one to establish the presence of potassium predominantly as K_2SO_4 . Under these conditions, because the vapor pressure of K_2SO_4 is significantly greater than the vapor pressures of the slag/ash components, K_2SO_4 is preferentially deposited on the tube bank material. This has been confirmed by the ≈ 83 wt.% K_2SO_4 content in actual deposits obtained from the Fossil Energy Users Laboratory test facility.^{4,5} Subsequently, the high K_2SO_4 content in the deposit was also confirmed in the Low Mass Flow (LMF) experiments in which superheater deposit materials from several locations were analyzed.⁶ Even though K_2SO_4 has been the dominant phase in the deposit material at K/S ratios of 1.1 or less, the deposit may contain free K_2CO_3 phase when K/S ratio exceeds 1.3. The presence of K_2CO_3 in the deposit can alter the stickiness of the deposit and can lead to low-melting eutectics in the deposit, the implications of which on corrosion of tube bank materials and fouling behavior are not known. As a first step in the development of a data base on characteristics of deposits and their influence on the corrosion of tube bank alloys, extensive physical, chemical, and microstructural analyses were performed on samples of materials tested in the LMF facility. Results from such an evaluation are presented in the present report. In addition, ANL-developed 2000-h data on the corrosion performance of a number of advanced materials are presented. Data developed to evaluate the effect of iron oxide in deposit on the corrosion performance of materials are also presented. The latter tests were conducted to examine the differences in deposit chemistry that arise in combustion of eastern versus western U.S. coals.

BACKGROUND

Low Mass Flow Train Tests in CFFF

Figure 3 is a schematic diagram of the LMF Train used in the CFFF tests. The Superheater Test Module (SHTM) consists of pendant tube bundles contained in a horizontal 1.2 by 2.3 m (4 by 7.5 ft) duct connected to the exit of the radiant furnace. Three steam-cooled tube bundles (identified as test sections TS1, TS2, and TS3) simulate superheaters, reheaters, and ITAHs and are used for fouling and corrosion studies.² Water-cooled tube bundles (identified as CS1, CS2, and CS3) are used to cool the gas between test sections. The SHTM also contained a tube bank for heating secondary combustion air. Table 1 lists the composition of Illinois #6 coal used in CFFF tests. Details on the combustion gas exiting the radiant furnace and entering the SHTM are given in Table 2. It was reported that particulate loading (both solid and liquid materials) in the SHTM was ≈ 0.1 kg of ash/kg of coal, corresponding to ≈ 1.5 times that of a conventional pulverized-coal-fired boiler and ≈ 5 times that of a cyclone furnace.² The increased particulate loading of the combustion gas was attributed to seed addition to the coal.

Fig. 3. Schematic diagram of Low Mass Flow Train at DOE-CFFF

Table 1. Composition of Illinois #6 coal used in CFFF tests

Coal Constituents		Ash Constituents	
Species	wt. %	Species	wt. %
Carbon	68.0	SiO ₂	55.8
Hydrogen	4.82	Al ₂ O ₃	22.9
Nitrogen	1.54	Fe ₂ O ₃	16.5
Sulfur	3.15	TiO ₂	1.12
Oxygen	13.1	CaO	0.78
		MgO	0.93
		Na ₂ O	0.42
		K ₂ O	2.38
		SO ₃	1.22

Table 2. Inlet conditions for test section 1 (TS1) for runs LMF4-K through LMF4-N in CFFF

Gas temperature (°C)	1238
Gas flow rate (kg/h)	17754
Gas particulate loading	
kg/h	239
kg/kg of coal	0.157
kg/kg of gas	0.0135
kg/million dry SCF	7.98
Gas composition (mol%)	
N ₂	58.43
CO ₂	23.85
H ₂ O	14.98
O ₂	2.74
Excess air (mol%)	13
Particulate composition (wt. %)	
K ₂ SO ₄	75
Fly ash	20
Ca, Fe, Na sulfates and excess SO ₃	5

The significantly higher alkali content in the MHD environment (deliberately added as seed in MHD units, in contrast to occurring as an impurity in coal feedstock in conventional boilers) is of concern with regard to corrosion degradation of materials and seed/slag fouling of tube banks. The thermodynamic equilibria prevalent among the combustion environments from coal combustion with excess air, the seed components (e.g., K₂SO₄, KOH, or K₂CO₃), and the slag components (such as Al₂O₃, SiO₂, CaO, or Fe₂O₃), enable one to establish the presence of potassium predominantly as K₂SO₄.

Under these conditions, because the vapor pressure of K_2SO_4 is significantly higher than the vapor pressures of the slag/ash components, K_2SO_4 is preferentially deposited on the tube bank material. This has been confirmed by the ≈ 83 wt.% K_2SO_4 content in actual deposits obtained from the Fossil Energy Users Laboratory test facility.^{3,4} Subsequently, the high K_2SO_4 content in the deposit was also confirmed in the LMF experiments in which the SSH deposit materials from several locations were analyzed.⁵ Even though K_2SO_4 has been the dominant phase in the deposit material at K/S ratios of 1.1 or less, the deposit may contain free K_2CO_3 phase when the K_2/S ratio exceeds 1.3.

Figure 4 shows the axial temperature profile for the gas in the SHTM observed during the LMF4-K fouling/corrosion test. Figure 5 is a schematic diagram of the pendant tubes in the three test sections. Test sections TS1 and TS2 had two passes, while TS3 had four. Gas flow was from left to right, as shown in Fig. 5. Sheathed thermocouples were mounted to tube surfaces by weld pads at locations indicated by the capital letters. In TS1 and TS2, tubes 1 and 4 had surface thermocouples on their leading edges at positions A through E, shown in Fig. 5. Tubes 5 and 8 had a thermocouple at position D only, at the leading edge. In TS3, tube 4 had surface thermocouples on the leading edge at positions A through J, shown in Fig. 5. In TS1 and TS2, 0.50-in.-long ring-sections of different alloy tubes were cut at every foot along the axial direction (both Pass 1 and 2) and the rings were marked to indicate the leading edge. These specimens, identified by numbers 1 through 14, were obtained for detailed analysis at Argonne National Laboratory.

Fig. 4. Steady-state temperature along axial direction in CFFF SHTM during fouling/corrosion test series LMF4-K through LMF4-N

Fig. 5. Locations of CFFF-exposed ring specimens analyzed at Argonne National Laboratory

It was reported that the TS1 deposits at a gas temperature of 1125°C (2060°F) were up to 200 mm long during tests with low soot-blowing pressure.² TS2 deposits with gas at 770°C (1420°F) and TS3 deposits at 650°C (1200°F) gas were 6.35 mm or less and 19.1 mm or less in thickness, respectively. TS2 and TS3 deposits were reported as friable and readily removable, in comparison to the very hard deposits at TS1. Average pass 1 frontal metal surface temperature for all tubes at TS1 location was 712°C (1314°F), with maximum brief excursions to 898°C (1648°F). On the back of Pass 1 at TS1, average and maximum metal temperatures were 606 and 813°C (1123 and 1495°F), respectively. Pass 2 average and maximum temperatures were 500 and 838°C (932 and 1540°F) at the front ("leading edge") and 490 and 780°C (915 and 1435°F) at the back ("trailing edge"). Troublesome deposits occurred only at TS1 and CS1 locations where gas temperature always exceeded 1069°C (1956°F), i.e., the melting temperature of K₂SO₄. However, when the K₂/S ratio exceeded ≈1.1, the deposit contained K₂CO₃, which accelerated the deposit growth and led to plugging. Tube metal temperatures at TS1 are shown in Fig. 6.

Superheater deposits were obtained from two different test periods. The first deposit was collected after ≈496 h (comprising Runs LMF4-K through LMF4-N, conducted during August 1987 to May 1988) of coal combustion, while the second deposit was collected after 263 h (Run LMF4-R conducted during July-August 1989) of coal combustion. In the first test period, the system was run with a K₂/S ratio of 1.0 to 1.1, whereas in the second test, ≈210 h were run with K₂/S ratio of 1.0-1.1 and the last ≈50 h were under a K₂/S ratio of 1.3. Heat exchanger tube materials exposed for periods of ≈500, 1500, and 2000 h (see Table 3 for list of runs) were also obtained from the CFFF for detailed metallurgical and morphological analysis.

Fig. 6. Average TS1 tube metal temperatures during 500 h of tests LMF4-K through N

Table 3. Specimen exposure runs in CFFF

Specimen exposure period (h)	Run number	Run time (h)
500	LMF4-K	198.0
	LMF4-L	63.3
	LMF4-M	56.9
	LMF4-N	179.0
1500	LMF4-O	252.3
	LMF4-P	101.2
	LMF4-Q	40.9
	LMF4-R	265.4
	LMF4-S	134.6
	LMF4-T	216.9
	LMF4-U	252.0
	LMF4-V	240.5
	LMF4-K through LMF4-V	

Four different structural alloys were used in high-temperature test sections 1 and 2. Table 4 lists the compositions of the alloys. All four alloys are chromia formers when exposed to an oxidizing environment. Type 304 and 316 stainless steels contain 18.3 and 17.3 wt.% Cr, respectively, while Type 310 stainless steel contains 25 wt.%Cr. Alloy 253 MA contains 20.7 wt.% Cr and 1.8 wt.% Si, which can impart additional resistance to oxidation/sulfidation attack in combustion atmospheres. The materials were exposed as U-bend tubes with lengths of 7 ft each in passes 1 and 2 and an overall length of 14 ft. Average metal temperatures along the tube lengths were obtained from the CFFF for correlation of corrosion data with exposure temperature. This report discusses the physical and chemical characteristics of the deposit materials and the corrosion behavior of metallic alloys exposed to such deposits.

Table 4. Compositions (wt.%) of alloys tested in CFFF

Alloy	Cr	Ni	Fe	Other
304	18.3	8.1	Bal*	Mn 1.5, Si 0.4
316	17.3	13.8	Bal	Mo 2.2, Mn 1.6
310	25.0	18.7	Bal	Mn 1.2, Si 0.6
253 MA	20.7	10.9	Bal	Si 1.8, Ce 0.03

*Bal = balance.

Materials Tests at ANL

Earlier corrosion tests at ANL showed that austenitic alloys exposed to ITAH conditions will develop predominantly oxide scales, with substantial internal penetration of sulfur and oxygen and precipitation of sulfides and oxides in the grain boundaries of alloy substrates. On the basis of linear kinetics, the scale thickness and metal recession data showed that the corrosion rates of the austenitic steels (except Type 310 stainless steel) exceeded the limit of 0.5 mm/yr. Even though the corrosion rates of these alloys for parabolic kinetics may be acceptable, the corrosion scale/penetration morphologies indicated that the steels are susceptible to accelerated/breakaway corrosion in oxygen/sulfur coal-combustion environments. Further, another aspect to materials selection for ITAH tubes is the adequacy of mechanical properties of materials at elevated temperatures. At the high temperatures of interest in ITAH (750-850°C), time-dependent properties such as creep rate and creep rupture life will determine the adequacy of the material. Even though corrosion resistance of Type 310 stainless steel is good under ITAH conditions, the creep rupture strength of the material is low at temperatures above $\approx 600^\circ\text{C}$, and thus this alloy is not recommended as a monolithic material for long-term service at these temperatures.

The materials selected for corrosion evaluation in the ANL program included Fe-Cr-Ni, Fe-Cr-Ni-Co, Ni-Cr-Co alloys, and Fe-Cr-Ni alloys with chromized coatings. A list of the compositions of different materials is given in Table 5. The specimens were 12.7 mm in diameter by ≈ 16 mm long and were micromachined to obtain a smooth surface finish. A gas mixture that simulated a combustion gas with an air/coal stoichiometric ratio (SR) of 1.05 was used for the test. The oxygen and sulfur partial pressures calculated for an SR of 1.05 were $\approx 6.9 \times 10^{-3}$ and 2.0×10^{-24} atm, respectively, at a gas temperature of 982°C (1800°F). The partial pressures of SO_2 and SO_3 were 1.7×10^{-3} and 2.4×10^{-5} atm, respectively. Experiments were conducted with four different deposit materials: K_2SO_4 , K_2SO_4 -25 wt.% Fe_2O_3 , TS1 deposit from CFFF, and TS1 deposit-25 wt.% Fe_2O_3 . The TS1 deposit material was of composition (in wt.%): 9.1 SiO_2 , 3.2 Al_2O_3 , 4.2 Fe_2O_3 , 0.5 CaSO_4 , 81.0 K_2SO_4 , and 2.0 others. The deposit materials were made into a water-base paste and applied to the alloy specimens. Thickness of the deposit layer was 0.5-1.5 mm. The specimens with the deposit layer were dried overnight at room temperature and visually examined to ensure adherence of the deposit to the substrate prior to exposure in the simulated combustion gas at elevated temperatures.

Table 5. Nominal chemical composition (wt.%) of alloys used in ANL program

Material	C	Cr	Ni	Mn	Si	S	Mo	Al	Fe	Other
310	0.07	25.0	18.7	1.2	0.64	0.006	-	-	Bal. ^a	-
347	0.06	18.9	10.8	1.5	0.58	0.014	-	-	Bal.	Nb+Ta 0.57
RA 85H	0.20	18.5	14.5	0.8	3.50	-	-	1.0	Bal.	-
556	0.10	22.0	20.0	1.5	0.40	-	3.0	-	Bal.	Co 20, W 2.5
253 MA	0.10	20.7	10.9	0.3	1.80	-	-	-	Bal.	Ce 0.03
8XX	-	20.2	32.5	-	-	-	-	3.0	Bal.	-
CR35A	0.05	36.6	45.0	-	0.04	-	-	0.1	Bal.	Nb 0.5
CR30A	0.06	30.5	51.0	0.2	0.27	-	2.1	0.1	Bal.	Ti 0.18
HR-120	0.05	25.0	37.0	0.7	0.60	-	-	0.1	Bal.	Nb 0.7, N 0.2
HR-160	0.05	28.0	Bal.	0.5	2.75	-	-	-	4.0	Co 27
214	0.04	16.0	Bal.	-	-	-	0.5	4.5	4.0	-
800 ^b	0.08	20.1	31.7	1.0	0.24	-	0.3	0.4	Bal.	Ti 0.31
304 ^b	0.08	18.3	8.1	1.5	0.27	-	-	-	Bal.	-

^aBal. = balance. ^bSurface of alloy chromized.

To simulate the air tubes in an MHD steam-bottoming plant, the ring specimens of the selected alloys and coatings were assembled in a corrosion probe and internally cooled with air. A schematic diagram of the experimental setup is shown in Fig. 7. The corrosion probe was ≈ 0.4 m long, with a specially designed head that incorporated the cooling fluid path and thermocouples. The entire specimen probe was inserted into a reaction chamber constructed of alumina. The specimens and gases were heated by resistance-wound heating elements surrounding the reaction chamber. Chromel/Alumel thermocouples, located at the outer surface of the reaction chamber, were used to monitor the temperature of the simulated combustion gas. The gas temperature was measured with a thermocouple inserted in the thermowell from the top flange of the reaction chamber. The temperature of the metal was monitored with three Chromel/Alumel thermocouples spot welded onto the inside surfaces of the specimens at the top, center, and bottom levels of the assembly. The output of all thermocouples was either recorded on a strip-chart recorder or monitored in a Data-Pro digital display unit for the entire course of the run. Flow rates of air, 1.0 vol.% SO₂ in N₂, and N₂ were adjusted by on-line flowmeters to achieve a gas composition that yielded an air/coal combustion SR of 1.05. Each of the gases flowed through low-pressure regulators and flowmeters before they mixed and entered the reaction chamber. The final gas mixture flowed through a 4-mm-OD quartz tube located inside the reaction chamber and was preheated before passing over the specimens. The flow rates of all the inlet gases were periodically monitored to ensure that the desired inlet gas mixture was present at all times during the tests. Each run was conducted for a period of 2000 h.

Upon completion of the exposures, both macroscopic and microscopic examinations of various specimens were conducted. Cross sections of the ring specimens were examined with a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyzer (EDX). An electron microprobe was used to identify the morphological features of the corrosion products and the phases in the scale layers, and to establish the thickness of scales and the depth of intergranular penetration, if any, of the substrate material.

Fig. 7. Schematic diagram of experimental setup used in laboratory test program

RESULTS

Analysis of CFFF-Exposed Materials

Analysis of CFFF-exposed materials at Argonne National Laboratory involved (a) characterization of deposits via wet chemical analysis and X-ray diffraction, (b) microstructural characterization of deposit materials collected from several locations in the LMF Train, (c) measurement and calculation of heat transfer in the presence of deposit, and (d) metallurgical analysis of heat exchanger tube materials from CFFF after three different exposure periods.

Deposit Characterization

The deposit samples, collected after a 500-h accumulation of run time at several locations in the LMF experiments, were characterized by X-ray diffraction and wet chemical analysis.

The deposits are generally expected to contain alkaline species such as KOH, K_2CO_3 , and $KHCO_3$ and K_2SO_4 . The hydroxide, carbonate, and bicarbonate species were determined by a classical titrimetric procedure in which an aqueous solution of the sample components was titrated with a standard acid, first to a pH of 8.3 and then to a pH of 4.5. The total and relative amounts of acid required to reach each end point permits determination of the quantities of hydroxyl, carbonate, and/or bicarbonate ions present in the solution. Approximately 1 g of each sample was weighed and added to 30 mL of deionized water in a beaker and stirred for 5 to 10 min to dissolve alkaline salts that might be present in the deposit sample. Typically, insoluble material remained after mixing; this was expected because of the silica and other slag components present in these samples but these constituents did not interfere with the titration. Each sample was titrated with 0.1 N HCl, with the aid of automatic titrator (Brinkman Model 670 Titroprocessor), which was programmed to monitor the volume of titrant as a function of pH (read from a calibrated glass electrode) and to output values for hydroxyl, carbonate, and bicarbonate ions determined from the analysis.

A potential drawback of this approach is that some interaction of species can occur when the sample is dissolved, which may obscure the composition of the solid material. For example, it is possible to have a mixture of solids containing KOH, $KHCO_3$, and K_2CO_3 . When this mixture is dissolved, the hydroxyl and bicarbonate ions will react to give carbonate ions and water. Thus, titration of the solution will show the presence only of the more abundant of the hydroxyl and bicarbonate species, and may be enriched in carbonate relative to the solid. With the CFFF deposit samples, only carbonate and bicarbonate ions were detected, with bicarbonate being more abundant. From these data, the possibility of some hydroxide present in the solid cannot be discounted. However, because of the predominance of bicarbonate in these samples, it seems unlikely that the conditions under which they were formed would be sufficiently basic for a hydroxide component to exist.

To determine the sulfate in each sample, ≈ 0.05 g of sample was weighed into a clean, dry, screw-cap, scintillation vial, and 20 mL of 0.003 M $NaHCO_3$ –0.002 M Na_2CO_3 solution was added. The sample and liquid were thoroughly mixed and allowed to stand overnight. A portion of the resulting leach solution was then passed through a syringe-mounted, 0.22 μm filter and injected into a Dionex Model 4340i Ion Chromatograph fitted with a HPIC-AG4A Guard Column, HP1C-AS4A Separator Column, Anion Micromembrane Suppressor, and a conductivity detector. The chromatographic eluant had the same composition as the buffer employed in leaching the deposit material. Sulfate concentration in each solution was determined by comparing the sulfate peak response of the sample to the response of the standard solutions of known sulfate concentration. The concentration of soluble sulfate in each solid sample was calculated as the product of the leachate volume (20.00 mL) and the sulfate concentration ($\mu g SO_4/mL$) divided by the weight of sample (g) that was leached.

Table 6 lists the analytical results for deposits collected at several locations in CFFF. In Run LMF4–N with a K_2/S ratio of 1.0–1.1, deposits were collected from the front and

back sides of TS1 and water-cooled section CS-3. Also nodular deposits were collected from a location downstream of the secondary air inlet but ahead of test section TS1. During the deposition process, average values for gas and metal temperatures in TS1 were ≈ 1288 and 760°C (≈ 2350 and 1400°F), respectively, and the corresponding temperatures in the CS-3 section were 954 and 120°C (1750 and 250°F), respectively. The initial pH of deposits collected in the high-temperature regions was 9.0 – 10.2 , while that collected from CS-3 region was 3.1 . Chemical analysis showed that the deposits in all locations were predominantly soluble sulfate of potassium, while carbonate and bicarbonate contents were negligible. Table 5 also shows the analytical results for deposits collected after run LMF4-R. During this run, the K_2/S ratio was maintained in a range of 1.0 – 1.1 for the first ≈ 200 h and was increased to ≈ 1.3 for the last ≈ 50 h. Deposit samples were collected from the TS1 hopper, leading and trailing edges of tube 4/pass 2, tube 6/pass 1, and leading and trailing edges of TS2/pass 1 and pass 2. The pH of all the deposits obtained after this run was 9.6 – 10.4 . The higher K_2/S ratio for the last 50 h in run LMF4-R seems to slightly increase the carbonate content of the deposit when compared with that for the deposit from run LMF4-N, but the soluble sulfate content was almost the same after both runs. The data show that the chemistry of the deposit does not change significantly with the variations in K_2/S ratio anticipated in the MHD downstream system.

Table 6. Chemical analysis of deposits collected at several locations in CFFF

Sample location	Initial pH	Carbonate (wt.%)	Bicarbonate (wt.%)	Soluble sulfate (wt.%)
Run: LMF4-N (K_2/S ratio 1.0 – 1.1)				
TS1-front	8.9	0.01	0.30	16.7
TS1-back 1	9.2	0.03	0.20	34.7
TS1-back 2	9.0	0.02	0.21	34.0
CS-3	3.1	–	–	35.8
Nodules	10.4	0.09	0.22	2.02
Run: LMF4-R (K_2/S ratio 1.0 – 1.1 for ≈ 210 h and 1.3 for ≈ 50 h)				
TS1-hopper	9.6	0.09	1.76	45.1
TS1-4-P2 front	10.3	0.16	0.38	30.0
TS1-4-P2 back	10.3	0.13	0.25	36.8
TS1-6-P1 front	10.4	0.24	0.53	27.7
TS1-6-P1 back	10.3	0.17	0.36	35.1
TS2-P1 front	10.3	0.14	0.26	36.2
TS2-P1 back	10.1	0.08	0.15	43.0
TS2-P2 front	10.4	0.12	0.11	36.9
TS2-P2 back	10.2	0.11	0.15	41.0

Table 7 lists the X-ray diffraction analysis of deposits collected at different locations in CFFF after both runs LMF4-N and LMF4-R. The nodular material collected downstream from the secondary air inlet, but before the TS1 region, was predominantly KAlSiO_4 . This indicates that the metal temperature in the ducted region is not low enough to condense K_2SO_4 vapors. In the regions of TS1 and TS2 where metal temperatures were low, the predominant material in the deposit was K_2SO_4 , with minor amounts of KAlSiO_4 . The only difference in the chemistry of the deposits from the two runs is the presence of minor amounts of KAlSi_2O_6 and KFeSi_2O_6 in the back side of TS1 region after run LMF4-N, while the deposit in run LMF4-R exhibited only KAlSiO_4 as a minor phase.

Table 7. X-ray diffraction analysis for deposits collected at several locations in CFFF

Sample location	Major	Minor	Trace
Run: LMF4-N (K_2/S ratio 1.0-1.1)			
TS1-front	K_2SO_4	KAlSiO_4	KFeSi_2O_6
TS1-back 1	K_2SO_4	—	—
TS1-back 2	K_2SO_4	$\text{KAlSi}_2\text{O}_6/\text{KFeSi}_2\text{O}_6$	—
CS1-front	K_2SO_4	—	—
CS3-front	K_2SO_4	KFeSi_2O_6	$\text{K}_3\text{Al}(\text{SO}_4)_3$
Nodules	KAlSiO_4	—	—
Run: LMF4-R (K_2/S ratio 1.0-1.1 for ≈ 210 h and 1.3 for ≈ 50 h)			
TS1-hopper	K_2SO_4	—	—
TS1-4-P2 front	K_2SO_4	KAlSiO_4	—
TS1-4-P2 back	K_2SO_4	KAlSiO_4	—
TS1-6-P1 front	K_2SO_4	KAlSiO_4	—
TS1-6-P1 back	K_2SO_4	KAlSiO_4	—
TS2-P1 front	K_2SO_4	KAlSiO_4	—
TS2-P1 back	K_2SO_4	KAlSiO_4	—
TS2-P2 front	K_2SO_4	KAlSiO_4	—
TS2-P2 back	K_2SO_4	KAlSiO_4	—

Analysis of Deposits on Specimen Tubes after 500-h Exposure

In addition to deposits from several locations from the LMF Train at CFFF, tube specimens with deposits intact were obtained after several experimental runs. These specimens had a cumulative exposure time of ≈ 500 h. Figure 8 shows macrophotographs of leading and trailing edge regions of tube specimens of Types 316, 310, and 304 stainless steel (TS1-2A-P1, TS1-6A-P1, and TS1-7A-P1, respectively) from pass 1 after exposure in the LMF experiment. The tubes exhibit significant accumulation of deposit material on their leading edges. The deposits were peeled from the tube samples for detailed analysis by SEM and EDX. Figure 9 shows the tube- and gas-side deposit materials and cross section of the deposit with the tube removed for TS1-7A-P1 (typical of all specimens). Figure 10 shows macrophotographs of deposits collected the water-cooled sections CS1 and CS3 in the LMF Train.

Fig. 8. Macrophotographs of several tube specimens and deposits after exposure in test section TS1

Fig. 9. Macrophotograph of deposits collected from tube- and gas-side surfaces, and cross section of Type 304 stainless steel heat exchanger tube after exposure in LMF experiment

Fig. 10. Macrophotographs of deposits collected from gas- and tube-side surfaces of tube in CS1 region and CS3 region

Several sections of deposit material were cut at different distances from the tube surface and analyzed for carbonate, bicarbonate, and soluble sulfate by the wet chemical methods described earlier. Figure 11 shows the concentration profiles for these chemical compounds as a function of distance from the tube surface for deposits collected after runs LMF4-N and LMF4-R. It is evident that the deposit contained predominantly soluble sulfate of potassium on the tube surface and that the carbonate and bicarbonate phases were virtually absent at 55 and 97 mm into the deposit in the two runs. The thickness of the deposit in the latter run was much greater than in the former, possibly due to the stickiness of the deposit with higher K_2/S ratio, but no significant difference is noted in the concentration of carbonate/bicarbonate in the two deposits.

Specimens were also cut from the TS1-7A-P1 tube, with the metal tube and its deposit intact for analysis by SEM and EDX. The composite specimens were mounted and polished and their cross sections were analyzed. Figure 12 shows the leading-edge elemental analysis for Fe, Cr, Ni, Si, K, and S from the tube wall to a depth of 48 mm into the deposit. The tube wall contained predominantly Fe, Cr, and Ni, the major constituents of Type 304 stainless steel. For a region of 1 mm into the deposit from the tube wall, the deposit contained primarily K and S, but virtually no steel constituents. Even though the oxygen content of the deposit was not analyzed, the composition of this layer can be deduced primarily as K_2SO_4 on the basis of the K-to-S ratio of the layer adjacent to the tube wall and the X-ray analysis of the deposit reported above. Further, significant concentrations of K and S (and Si from slag) were observed in the entire thickness of the deposit layer. Figure 13 shows the EDX profiles for Fe, Cr, Ni, Si, K, and S for the deposit

Fig. 11. Concentration-distance profiles for carbonate, bicarbonate, and soluble sulfate phases in deposits accumulated on tubes exposed in runs LMF4-N and LMF4-R

Fig. 12. X-ray analyses for Fe, Cr, Ni, Si, K, and S for composite specimen of Type 304H stainless steel with accumulated deposit on leading edge of specimen

Fig. 13. X-ray analyses for Fe, Cr, Ni, Si, K, and S for composite specimen of Type 304H stainless steel with accumulated deposit on trailing edge of specimen

on the trailing edge of the tube wall. The deposit thickness was only ≈ 3.5 mm on the trailing edge, in contrast with ≈ 48 mm on the leading edge. EDX analysis conclusively indicates a layer of K- and S-rich phase adjacent to the tube wall, even on the trailing edge.

Thermal Characteristics of Deposits

To examine the thermal properties of the deposit material, deposits were removed from tube specimens (supplied by the University of Tennessee Space Institute) and fastened onto a new tube of Type 304 stainless steel with alumina cement and stainless steel wire. Figure 14 shows a schematic drawing and a photograph of the new assembly. The new tube had ≈ 10 -mm inlet and outlet tubes welded onto it for air flow through the tube. A thermocouple (identified as A in Fig. 14) was inserted in a thermowell to measure the air temperature inside the tube. Thermocouples B and C were fastened to the tube wall at the top and bottom regions of the tube, away from the deposit material. Thermocouple D was fastened to the outside surface of the tube prior to cementing the deposit onto the tube. Small holes (identified as 1 through 7 in Fig. 14) were drilled at several locations in the deposit material for insertion of Chromel-Alumel thermocouples.

Fig. 14. Tube/deposit assembly used for determination of thermal characteristics of deposit material

Heat transfer experiments were conducted at gas temperatures of 1000 and 1100°C. The air flow rate through the tube was varied in a range 200-800 cubic feet per hour (cfh). Temperature distributions in the tube wall and in the deposit were determined by measuring the output of different thermocouples. Figure 15 shows the temperature distribution in the deposit at several flow rates of air, for a fixed gas temperature of 1000°C. At an air flow rate of 200 cfh, the tube wall temperature was 818°C and the temperature in the deposit showed a steep increase to 906°C at 1 mm into the deposit. The steepness of this increase was more pronounced as the air flow rate increased. For example, at a flow rate of 800 cfh, the tube wall temperature was 626°C while the temperature at 1 mm into the deposit was 808°C. In general, the temperature profile in the deposit showed that $\approx 98\%$ of the gas temperature is attained at a deposit thickness range of 15-20 mm. Figure 16 shows the influence of gas temperature on the temperature distribution in the deposit at an air flow rate of 800 cfh. Thermal conductivity values for the composite deposit were calculated as a function of deposit thickness using the measured temperature distribution data and heat flux data. Figure 17 shows that the conductivity value adjacent to the tube surface was ≈ 0.02 W/m K, while the value at the gas combustion-gas side of the was ≈ 3.7 W/m K. The value adjacent to the tube surface corresponds to the value for almost pure K_2SO_4 , while that in the gas side of the deposit is predominantly that for the ash constituents.

Fig. 15. Temperature distribution from tube wall into deposit material, obtained at different gas flow rates for gas temperature of 1000°C

Fig. 16. Influence of gas temperature on temperature distribution obtained at air flow rate of 800 CFH

Fig. 17. Thermal conductivity values as a function of temperature for composite deposit from CFFF

Analyses of Tube Materials

The tube specimens obtained from the CFFF after 500, 1500, and 2000 h of exposure in the LMF train were analyzed to evaluate the corrosion-product scale layer chemistries and thicknesses. Specimen cross sections were examined by SEM to evaluate scale thickness and internal penetration of the underlying substrate alloy. In addition, EDX analysis was used to establish the chemical compositions of the corrosion-product scales and the phases in the grain-boundary regions of the substrate alloy.

500-h Exposure

During the first 500 h of exposure of the tube specimens, the average and maximum temperatures for the combustion gas were 1126 and 1242°C (2059 and 2267°F), respectively. Average and maximum temperatures of the tubes in Pass 1 at the leading edges were 712 and 898°C (1314 and 1648°F), respectively. The corresponding temperatures at the trailing edges of tubes in Pass 1 were 606 and 813°C (1123 and 1495°F), respectively. Average and maximum temperatures at the leading edges of tubes in Pass 2 were 500 and 838°C (932 and 1540°F), respectively. The corresponding temperatures at the trailing edges of tubes in Pass 2 were 490 and 780°C (915 and 1435°F), respectively.

A limited number of specimens after 500 h of exposure were obtained for analysis at ANL; these specimens were from tubes exposed to the highest temperatures in test section 1 of passes 1 and 2. Figures 18-20 show SEM photographs of cross sections of Types 304 and 316 stainless steel and 253 MA alloy at the leading and trailing edges of tube specimens after exposure. The figures show scaling in Type 304 stainless steel at both the leading and trailing edges, even though there is ~100°C difference in temperature between these specimen locations in pass 1. Scaling was minimal in pass 2 specimens, and the light phase seen on the leading edge is primarily a deposit material. The scaling behavior of Type 316 stainless steel was similar to that of 304 steel. Specimens of Type 316 stainless steel exhibited the least attack in Passes 1 and 2 at both leading and trailing edges. Alloy 253 MA exhibited much less scaling than did Type 304 stainless steel. In all the specimens examined, the scale consisted primarily of a Fe-rich or Cr-rich mixed oxide and internal penetration consisted of oxide and some sulfide particles. No sodium or potassium was noted in either the scale or the substrate alloy after 500 h of exposure.

Ring specimens of different materials were analyzed along their radial positions to evaluate corrosion scaling and substrate alloy penetration at different locations. Figures 21 and 22 show corrosion data for the four materials exposed in Passes 1 and 2 in test section 1. Type 304 stainless steel exposed in Pass 1 exhibited the most scaling/penetration, followed by Type 316 stainless steel. Type 316 stainless steel and 253 MA alloy exhibited less corrosion in Pass 1. In Pass 2, the temperatures were ~100°C lower than in Pass 1 and corrosive attack was less in the three stainless steels. 253 MA alloy

contains 1.8 wt.% silicon. The presence of 1.8 wt.% Si in alloy 253 MA has a corrosion-retarding effect at the higher temperature of Pass 1 by forming silica phase at the scale/metal interface and in the grain boundaries of the substrate alloy, thereby minimizing outward transport of Fe and Cr to enable further scaling. At the lower temperature of Pass 2, silica phase was virtually absent and corrosion scaling/penetration was similar to that of the lower chromium stainless steels.

Fig. 18
SEM photomicrographs of leading and trailing edges of Type 304H stainless steel tube in Passes 1 and 2 after 500-h exposure in CFFF

Fig. 19
SEM photomicrographs of leading and trailing edges of Type 310 stainless steel tube in Passes 1 and 2 after 500-h exposure in CFFF

Fig. 20
SEM photomicrographs of leading and trailing edges of Alloy 253 MA tube in Passes 1 and 2 after 500-h exposure in CFFF

Fig. 21
Scale thickness/penetration data for several radial positions for tubes of Types 304H and 316H stainless steel after 500-h exposure in CFFF

Type 304H ss

Type 316H

Type 310 ss

Alloy 253 MA

Fig. 22

Scale thickness/penetration data for several radial positions for tubes of Type 310 stainless steel and alloy 253 MA after 500-h exposure in CFFF

1500-and 2000-h Exposures

Samples from the SHTM test section tubes removed from the CFFF after LMF4-V consisted of rings with 2000 h of exposure (runs LMF4-K through LMF4-V) and rings with 1500 h of exposure (runs LMF4-O through LMF4-V). After the LMF4-V run, the tubes were cleaned of loosely adherent deposits and cut with a bandsaw, with no coolant, into 1-ft lengths, the cuts being at multiples of 1 ft from the tubesheet. For TS1 and TS2 tubes, three 0.5-in.-long rings were cut by bandsaw from the top of each 1-ft length of tube, one for each for UTSI, B&W, and ANL. A mark was placed with a chisel on the top side of each sample at approximately the center of the leading side. The ring specimens of the tube material were examined at each foot of Passes 1 and 2. Each ring specimen was analyzed at four locations, i.e., leading edge (facing the oncoming combustion gas), trailing edge (180 degrees from the leading edge), and the two sides (at 90 degrees on either side of the leading edge).

Figure 23 shows corrosion thickness in terms of scale thickness and internal penetration for Type 304H stainless steel (tube 7) along the 14-ft length of the tube after 1500 h of exposure in the LMF Train. Also shown in the figure are the temperature variations in the leading and trailing edge locations along the 14-ft length of the tube. The results showed a lack of scales (probably spalled on cooling of the tubes) in a number of locations, and only thin scales, if present, in a range of 10-60 μm . Substrate alloy penetration was significant at a number of locations, especially in the U-bend section of the

tube (i.e., locations 6-9 ft along the tube). Alloy penetration was observed even in the trailing edge at 8-9 ft along the tube. The 8-ft location corresponds to the bottom of the U-bend on Pass 2 of the tube. The penetration depths varied in a range of 10-210 μm . Figure 24 shows data for Type 316H stainless steel (tube 2) after 1500 h of exposure in the LMF Train, and corrosion performance is similar to that of Type 304H stainless steel.

Figure 25 shows data for Type 310 stainless steel (tube 6) after 1500 h of exposure in the LMF Train. Scales were fairly thin and in a range of 5-10 μm at all locations, even though the temperature range was 405-695°C (760-1280°F). Further, the penetration depths for this material at all locations were also low (0-80 μm). Figure 26 shows corrosion data for Alloy 253 MA (tube 3) after 1500 h of exposure in the LMF Train. The tube had no discernible scale on the leading edge at any location along the axial direction. The internal penetration of the tube in the leading edge was high and comparable to those for Types 304H and 316H stainless steels. Somewhat lower corrosion penetrations were observed at the trailing edge and sides 1 and 2 of the tubes. Figures 27-30 show the temperature distribution and corrosion scale thicknesses for the Types 304H, 316H, and 310 stainless steel, and Alloy 253 MA after 2000 h of exposure in the LMF train. A comparison of corrosion thickness data for all four alloys indicated that the alloy with the highest chromium content (Type 310 stainless steel with 25 wt.%Cr) exhibited the best performance. Types 304H and 316H stainless steel exhibited similar behavior and were the worst from the corrosion standpoint. Performance of Alloy 253 MA was intermediate.

Microstructural Analysis

Figure 31 shows SEM photomicrographs of cross sections of Type 310 stainless steel after 2000 h of exposure in the LMF Train at metal temperatures of 522-669°C (972-1237°F) at a distance of 1 ft from the tubesheet in Pass 1. Almost no scale was detected on the leading edge, and the extent of scales at the trailing edge and sides of the tube was low. The specimen surfaces were wavy and exhibited some corrosion, but the extent of intergranular penetration was small. The scale was predominantly (Cr,Fe) oxide, and internal penetration consisted of both (Cr,Fe) oxide and Cr-rich sulfide. Figure 32 shows SEM photomicrographs of Type 310 stainless steel after 1500 h of exposure in the LMF train at metal temperatures of 584-698°C (1084-1288°F) at a distance of 1 ft from the tubesheet in Pass 1. The tubes in this exposure developed scales 10-25 μm in thickness and exhibited penetration depths of 25-60 μm . The grain-boundary phase was predominantly oxide, but discrete particles of sulfides were seen ahead of the oxide stringers.

Fig. 23. Temperature distribution and corrosion thicknesses for Type 304H stainless steel (tube 7) after 1500-h exposure in test section 1 of CFFF

Fig. 24. Temperature distribution and corrosion thicknesses for Type 316H stainless steel (tube 2) after 1500-h exposure in test section 1 of CFFF

Fig. 25. Temperature distribution and corrosion thicknesses for Type 310 stainless steel (tube 6) after 1500-h exposure in test section 1 of CFFF

Fig. 26. Temperature distribution and corrosion thicknesses for 253 MA (tube 3) after 1500-h exposure in test section 1 of CFFF

Fig. 27. Temperature distribution and corrosion thicknesses for Type 304H stainless steel (tube 4) after 2000-h exposure in test section 1 of CFFF

Fig. 28. Temperature distribution and corrosion thicknesses for Type 316H stainless steel (tube 5) after 2000-h exposure in test section 1 of CFFF

Fig. 29. Temperature distribution and corrosion thicknesses for Type 310 stainless steel (tube 1) after 2000-h exposure in test section 1 of CFFF

Fig. 30. Temperature distribution and corrosion thicknesses for 253 MA (tube 8) after 2000-h exposure in test section 1 of CFFF

Fig. 31. SEM photomicrographs of Type 310 stainless steel (1 ft from tubesheet, Pass 1) after 2000-h exposure at metal temperatures of 522-669°C (972-1237°F) in CFFF

Fig. 32. SEM photomicrographs of Type 310 stainless steel (1 ft from tubesheet, Pass 1) after 1500-h exposure at metal temperatures of 584-698°C (1084-1288°F) in CFFF

Figures 33-36 show SEM photomicrographs of cross sections of Types 304H, 316H, and 310 stainless steel, and Alloy 253 MA after 1500 h of exposure in the LMF Train at a distance of 7 ft from the tubesheet in Pass 1 (near the U-bend of the tubes). The tubes at these locations were exposed at temperatures of 516-599°C (961-1110°F). Magnification in the photographs for Type 310 stainless steel (Fig. 35) is 10 times larger than that in photographs of other specimens. The morphologies show that all four alloys exhibit intergranular penetration of the substrates. The extent of attack is greatest in Types 304H and 316H stainless steel, lowest in Type 310 stainless steel, and somewhat intermediate in Alloy 253 MA. The trailing edge photographs for Types 304H and 316H stainless steel show that even with an exposure temperature of $\approx 516^{\circ}\text{C}$ (961°F), the alloys are susceptible to significant intergranular attack in the MHD-BOP environment. The grain-boundary phase is predominantly oxides of base metal constituents, but significant precipitation of sulfide particles is observed ahead of the grain-boundary oxidation front. The effect of these precipitates is to weaken the grain boundaries and lead to grain separation, as can be seen in some of the photographs, especially at lower exposure temperatures and under thermal cycling conditions.

Fig. 33. SEM photomicrographs of Type 304H stainless steel (7 ft from tubesheet, Pass 1) after 1500-h exposure at metal temperatures of 516-576°C (961-1067°F) in CFFF

Fig. 34. SEM photomicrographs of Type 316H stainless steel (7 ft from tubesheet, Pass 1) after 1500-h exposure at metal temperatures of 516-576°C (961-1067°F) in CFFF

Fig. 35. SEM photomicrographs of Type 310 stainless steel (7 ft from tubesheet, Pass 1) after 1500-h exposure at metal temperatures of 577-599°C (1070-1110°F) in CFFF

Fig. 36. SEM photomicrographs of 253 MA (7 ft from tubesheet, Pass 1) after 1500-h exposure at metal temperatures of 574-597°C (1066-1106°F) in CFFF

Figure 37 shows SEM photomicrographs of cross sections of Type 316H stainless steel after 2000 h of exposure in the LMF Train at 6 ft from the tubesheet in Pass 2 (near the U-bend of the tube). The tube at this location was exposed to temperatures 544-553°C (1012-1029°F) and the intergranular penetration and grain separation are clearly evident. Figure 38 shows SEM photomicrographs of cross sections of Type 316H stainless steel after 2000 h of exposure in the LMF Train at 1 ft from the tubesheet in Pass 2. The material was exposed to temperatures of 438-524°C (821-975°F). Significant intergranular cracking of the material is seen at all radial locations, as is grain-boundary penetration ahead of the brittle, cracked zones. Microstructural analysis indicates that even though alloys such as Types 304H and 316H stainless steels exhibit gross corrosion depths of 150-250 µm in 2000-h exposures, penetration of the grain boundaries, weakening of the bonding between grains, and onset of cleavage type fracture are subtle. Therefore, caution should be exercised in extrapolation of the short-term corrosion data to long-term service applications.

The mechanism of oxidation/sulfidation attack and the corrosion scale/penetration morphologies are similar for all the alloys tested, but the degree of attack is highest for Types 304 and 316 stainless steel and lowest for Type 310 stainless steel. Alloy 253 MA (which contains 1.8 wt.% Si) exhibited Si-rich areas in the grain boundaries ahead of crack fronts, especially at locations with higher metal temperatures; this seems to have reduced the depth of internal attack, but the corrosion mechanism is essentially the same. The oxidation/sulfidation attack of the materials observed in this test program is similar to that

Fig. 37. SEM photomicrographs of Type 316H stainless steel (6 ft from tubesheet, Pass 2) after 2000-h exposure at metal temperatures of 544-553°C (821-975°F) in CFFF

Fig. 38. SEM photomicrographs of Type 316H stainless steel (1 ft from tubesheet, Pass 2) after 2000-h exposure at metal temperatures of 438-524°C (821-975°F) in CFFF

Fig. 39
Schematic representation of
reaction sequence for high-
chromium alloys exposed to
combustion environments

reported for materials exposed to fluidized-bed combustion environments.⁷ Figure 39 is a schematic representation of corrosion scale development and morphological changes that occur in chromia-forming alloys exposed to combustion atmospheres at elevated temperatures. In these cases, the high-chromium alloys generally develop porous oxide scales, and some sulfides are also observed in the inner portions of the scale (in the vicinity of the scale/alloy interface). The sulfides form via reactions between substrate elements and sulfur that is released when chromium reacts with SO_2 to form an external oxide scale. Porosity in the scale enables further molecular transport of SO_2 in the gas phase to the scale/substrate alloy interface, leading to further corrosion by oxidation/sulfidation. The released sulfur is transported along the grain boundaries in the metal, leading to internal sulfidation of the alloy. Potassium and chlorine in the environment can exacerbate the corrosion process. Generally, the oxide scales are fairly thin on high-chromium alloys exposed to combustion atmospheres and are insensitive to exposure time. As a result, the acceptable lifetimes for these alloys exposed to combustion atmospheres are influenced by the depth of internal penetration, which is largely determined by the alloy chemistry, temperature, SO_2 content of the gas phase, and physical and chemical nature of the deposit.

Corrosion Rates

Corrosion information obtained for all test specimens with exposure times of 1500 and 2000 h were replotted as a function of exposure temperature to establish the adequacy of these alloys for use in MHD balance-of-plant environments. Figures 40 and 41 show the

data for all four alloys. Also shown are corrosion rates of 0.5 mm/y, based on linear and parabolic kinetics. The corrosion rates for the trailing edge are generally less than for the leading edges in all three austenitic stainless steels. Alloy 253 MA exhibited similar behavior at temperatures above $\approx 538^{\circ}\text{C}$ (1000°F); however, at lower temperatures, the Si in the alloy had no beneficial effect on corrosion rate and the rates were similar to those of Types 304 and 316 stainless steel. The results also indicate that only Type 310 stainless steel exhibits corrosion rates acceptable for long-term service in MHD environments.

Fig. 40
Corrosion loss data for Types 304H
and 316H stainless steel as a
function of exposure temperature

Fig. 41
Corrosion loss data for Type 310
stainless steel and Alloy 253 MA
as a function of exposure temperature

Analysis of ANL-Tested Materials

In the coal-fired MHD system, polarization of the slag layer along the cathode wall has been attributed to electrical shorting of electrodes. One of the strategies proposed to combat voltage nonuniformities in the cathode wall is to modify the local slag chemistry.⁹ This involves doping the slag layer with iron oxide, which seems to increase the electronic-to-ionic current transport ratio in the slag, leading to reduced slag polarization and cathode wall voltage nonuniformities. However, injection of iron oxide can also alter the deposit chemistry downstream of the channel in the steam bottoming plant and affect adversely the performance of heat transfer component materials. To evaluate the effect of iron oxide injection upstream, deposits with additions of 25 wt.% Fe_2O_3 were used for corrosion evaluation of the candidate materials.

In the ANL program, specimens were exposed for 2000 h in the presence of TS1 deposit (obtained from CFFF), TS1/25 wt.% Fe_2O_3 , pure K_2SO_4 , and K_2SO_4 /25 wt.% Fe_2O_3 . In addition to internally cooled ring specimens of several alloys and coatings (see Table 5 for chemical compositions), coupon specimens coated with different deposits were also exposed in these experiments. The metal temperature of the ring specimens was maintained at 762°C (1400°F), while the coupon specimens were exposed at the gas temperature of 982°C (1800°F). Figure 42 shows the macrophotographs of corrosion probes with ring and coupon specimens after 2000 h of tests conducted at ANL.

Fig. 42. Macrophotographs of specimens tested for 2000-h at ANL.

Among the advanced alloys listed in Table 5, RA 85H, Type 347 stainless steel, and Alloy 214 had chromium contents of <20 wt.%. Among these three, only RA 85H was tested in ring form at a metal temperature of 762°C (1400°F). The other two alloys were tested in coupon form at a metal temperature of 982°C (1800°F). Chromium contents of surface regions of chromized Type 304 stainless steel and Alloy 800 were 30-35 wt.%. A majority of these advanced alloys are chromia-formers when exposed to oxidizing environments. The exceptions are Alloys 8XX and 214, which contain sufficient aluminum to form alumina scale at elevated temperatures. Alloys such as RA 85H, 253 MA, and HR 160 contain silicon in the range of 1.8-3.5 wt.%, which enables the alloys to form silica scale at the interface between the outer chromia scale and the alloy substrate. Alloys 556 and HR 160 contained 20 and 27 wt.% cobalt, respectively.

Figures 43-53 show SEM microphotographs of cross sections of various specimens after 2000-h exposures in the presence of TS1 deposit and a mixture of TS1/25 wt.% Fe₂O₃. Figures 54-64 show SEM microphotographs of cross sections of various specimens after 2000-h exposures in the presence of K₂SO₄ deposit and a mixture of K₂SO₄/25 wt.% Fe₂O₃. In general, the thin scales in these alloys consisted of oxides. The depths of intergranular penetration of the substrates varied among the alloys, and the grain-boundary phases consisted of both oxides and some sulfides. Scale thicknesses in both chromia- and alumina-forming alloys were similar, but the latter alloys exhibited coarse precipitates of (Ni,Al) intermetallic compounds in the substrate (primarily due to long exposures at elevated temperatures), which can affect the mechanical properties of the material.

Figures 65 and 66 show metal recession data developed in the present work on advanced alloys and coatings tested for 2000 h in the presence of TS1 and K₂SO₄ deposits with and without Fe₂O₃ additive. Also indicated in the figures are the corrosion limits of 0.5 mm/y calculated by either linear or parabolic kinetics for the corrosion process. The results show that all the tested materials exhibit corrosion losses of <0.5 mm/y even when calculated with the less conservative linear kinetics. The results also indicate that the corrosion performance of materials with TS1 deposit (which contains >80 wt.% K₂SO₄) is similar to that observed with pure K₂SO₄. Further, the presence of Fe₂O₃ additive in the deposit had a negligible effect on the corrosion behavior of alloys and coatings tested. Figures 67 and 68 show metal recession data for coupon materials tested at 982°C (1800°F) in the presence of various deposits. The measured corrosion losses are somewhat higher at this higher temperature and exceed the value of 0.5 mm/y limit (based on linear kinetics) for several candidate materials. However, the linear rate law for corrosion at the elevated temperatures is very conservative because alloys do develop oxide scales that are retained on the alloy surfaces, thereby invoking more parabolic (rather than linear) kinetics. Further, the ITAH temperatures will be in the range of 752-871°C (1400-1600°F) and this lower temperature range will also lead to adequate corrosion performance of these advanced alloys and coatings.

Fig. 43. Cross sections of Type 310 stainless steel specimens tested in presence of TS1 and TS1 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 44. Cross sections of Type RA 85H specimens tested in presence of TS1 and TS1 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 45. Cross sections of Alloy 556 specimens tested in presence of TS1 and TS1 plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 46. Cross sections of 253 MA specimens tested in presence of TS1 and TS1 plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 47. Cross sections of CR35A specimens tested in presence of TS1 and TS1 plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 48. Cross sections of CR30A specimens tested in presence of TS1 and TS1 plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 49. Cross sections of HR-120 specimens tested in presence of TS1 and TS1 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 50. Cross sections of HR-160 specimens tested in presence of TS1 and TS1 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 51. Cross sections of (top) Type 347 stainless steel and (bottom) Alloy 8XX specimens tested in presence of TS1 and TS1 plus Fe₂O₃ deposits at 982°C

Fig. 52. Cross sections of chromized Type 304 stainless steel specimens tested in presence of TS1 and TS1 plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 53. Cross sections of chromized Alloy 800 specimens tested in presence of TS1 and TS1 plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 54. Cross sections of Type 310 stainless steel specimens tested in presence of K₂SO₄ and K₂SO₄ plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 55. Cross sections of RA 85H specimens tested in presence of K_2SO_4 and K_2SO_4 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 56. Cross sections of Alloy 556 specimens tested in presence of K_2SO_4 and K_2SO_4 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 57. Cross sections of 253 MA specimens tested in presence of K_2SO_4 and K_2SO_4 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 58. Cross sections of CR35A specimens tested in presence of K_2SO_4 and K_2SO_4 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 59. Cross sections of CR30A specimens tested in presence of K_2SO_4 and K_2SO_4 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 60. Cross sections of HR-120 specimens tested in presence of K_2SO_4 and K_2SO_4 plus Fe_2O_3 deposits at (top) 762°C and (bottom) 982°C

Fig. 61. Cross sections of HR-160 specimens tested in presence of K₂SO₄ and K₂SO₄ plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 62. Cross sections of chromized Type 304 stainless steel specimens tested in presence of K₂SO₄ and K₂SO₄ plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 63. Cross sections of chromized Alloy 800 specimens tested in presence of K₂SO₄ and K₂SO₄ plus Fe₂O₃ deposits at (top) 762°C and (bottom) 982°C

Fig. 64. Cross sections of (top) Type 347 stainless steel, (middle) Alloy 8XX, and (bottom) Alloy 214 specimens tested in presence of K_2SO_4 and K_2SO_4 plus Fe_2O_3 deposits at 982°C

Fig. 65. Metal recession data for several advanced alloys and coatings in presence of TS1 deposit with and without iron oxide at 762°C

Fig. 66. Metal recession data for several advanced alloys and coatings in presence of K₂SO₄ deposit with and without iron oxide at 762°C

Fig. 67. Metal recession data for several advanced alloys and coatings in presence of TS1 deposit with and without iron oxide at 982°C

Fig. 68. Metal recession data for several advanced alloys and coatings in presence of K₂SO₄ deposit with and without iron oxide at 982°C

SUMMARY

Candidate heat exchanger materials tested in the Low Mass Flow Train at the Coal-Fired Flow Facility (CFFF) at Tullahoma, TN, were analyzed to evaluate their corrosion performance. Tube specimens obtained at each foot of the 14-ft-long U-bend pendants were analyzed for corrosion-scale morphologies, scale thicknesses, and internal penetration depths. Results developed on 500-, 1500- and 2000-h exposed specimens were correlated with exposure temperature. In addition, deposit materials collected at several locations in the CFFF were analyzed in detail to characterize the chemical and physical properties of the deposits and their influence on corrosion performance of tube materials. Further, a high-temperature corrosion program was conducted at ANL to evaluate the influence of K_2SO_4 -containing deposit materials on the corrosion behavior of commercially available, advanced metallic alloys and coatings under conditions that simulate the intermediate-temperature air heater (ITAH) of an MHD steam bottoming plant. Several conclusions can be drawn from these studies.

1. The deposits adjacent to the tube wall in the downstream components of the coal-fired MHD system will be predominantly K_2SO_4 . Ash builds up on top of the sulfate layer.
2. Detailed chemical and X-ray analysis of the deposit layers at several locations from the tube/deposit to gas/deposit interface showed that the influence of K_2/S ratio in the range of 1.1 to 1.3 was minimal in establishing the composition of the deposit.
3. Use of K_2CO_3 (instead of KOH) as a seed material increased the thickness of the deposit but had almost no effect on the composition of the deposit layer.
4. Thermal analysis of CFFF deposit showed that the thermal conductivity of the ash-dominant layer is ≈ 20 times that of the K_2SO_4 -dominated deposit adjacent to the tube wall. As a result, most of the temperature drop between the gas and the tube wall occurred across the sulfate layer.
5. Among the four alloys tested in CFFF, Type 310 stainless steel exhibited the least corrosive attack, while Types 304 and 316 stainless steel exhibited severe degradation. Performance of Alloy 253 MA was intermediate.
6. The corrosion-product layers were predominantly oxide in all four CFFF-exposed alloys. The scales were porous and offered little protection to the underlying alloy. Analysis of the alloys exposed at several locations along the pendant showed different degrees of intergranular penetration of the substrate alloys. Discrete sulfide particles were observed at grain boundaries in several locations.
7. The extent of corrosion in the trailing edge (lower metal temperature) of the alloy tube is generally less than that in the leading edge (higher metal temperature). Analysis of corrosion loss data as a function of metal temperature for the four CFFF-exposed alloys showed that only Type 310 stainless steel will meet corrosion rates of

<0.5 mm/y, based on linear kinetics. With parabolic kinetics, Alloy 253 MA may be acceptable; Types 304H and 316H stainless steel exhibited rates of >0.5 mm/y, especially at temperatures of 900-1100°F (482 to 593°C).

8. Corrosion tests of 2000 h were conducted at ANL with several commercially available, advanced alloys in the presence of K_2SO_4 or deposits collected from TS1 in CFFF. Corrosion tests were also conducted with an additive of 25 wt.% Fe_2O_3 to these deposits. Tests were conducted at metal temperatures of 762 and 982°C (1400 and 1800°F), respectively.
9. The corrosion mode of the advanced alloys was predominantly oxidation with some intergranular penetration of the substrate alloys. Grain-boundary precipitates were mixtures of oxides and sulfides. Corrosion occurred primarily as a solid-state reaction between the oxygen/sulfur in the environment and the alloy constituents. No liquid-phase corrosion product (similar to pyrosulfates or alkali-iron trisulfates in conventional coal-fired boilers) was observed in any of the specimens examined. The corrosion morphologies showed that the mechanism of corrosion is oxidation/sulfidation and is essentially similar to that observed for alloys exposed in CFFF and in earlier ANL material studies in support of steam bottoming plants.
10. A number of advanced alloys exhibited corrosion rates of <0.5 mm/y at 762°C (1400°F) and will be suitable for ITAH service. In particular, CR30A, CR35A, HR 120, HR 160, and chromized Type 304 stainless steel showed good corrosion resistance.
11. The ANL test results showed that the presence of Fe_2O_3 in the deposits (added to simulate deposits when iron oxide is injected into the MHD channel) had minimal influence on the corrosion performance of Type 310 stainless steel and other advanced alloys tested.
12. Evaluation of the corrosion performance of materials tested in this program showed that selection of an alloy for long-term application in MHD balance-of-plant service will be dictated by the extent of grain-boundary oxidation/sulfidation of the base alloy. Based on 2000-h laboratory test data, a number of advanced alloys can give acceptable performance in environments of the MHD steam bottoming plant.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Pittsburgh Energy Technology Center, under Contract W-31-109-Eng-38. The author is grateful to N. Johanson and M. K. White of the University of Tennessee Space Institute for supplying deposit materials and tube samples from the Coal-Fired Flow Facility. D. L. Rink assisted in the corrosion tests and in the microstructural analysis of exposed specimens.

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