TASK 6.1 – CORROSION OF HIGH-TEMPERATURE ALLOYS

Final Topical Report

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TASK 6.1 – CORROSION OF HIGH-TEMPERATURE ALLOYS

1.0 BACKGROUND

The maximum-use temperature and the specific impacts of gas and ash composition, alloy type, and temperature on the magnitude and rate of corrosion of alloys used in the construction of advanced supercritical boiler high-temperature components are not well understood.

Ultrasupercritical (USC) boilers, employing higher temperatures and pressures than conventional coal-fired boilers, require improved materials to achieve high performance and long life. The steam cycle in a typical conventional power system is limited to a maximum pressure of 175 bar and a metal temperature of 550°C, with efficiencies of approximately 35%. To boost the efficiency to 50%, which would reduce greenhouse gas production by 40%, working pressures and temperatures of 325 bar and 625°C are necessary, exposing the metal components to a much more corrosive environment. USC parameters have already been incorporated into two liquefied natural gas-fired units at Kawagoe, Japan, which have been operating extremely well since they were commissioned in 1989 and 1990. Two USC units have been built in Denmark.

The use of biomass to produce electrical power in these units is an application that continues to expand in scope. Countries like Denmark are investigating concepts for the combustion of straw in blends with coal. The products of biomass combustion contain chlorine and alkali metals that are highly corrosive to typical alloys. The main properties necessary for alloys used in these systems are ash corrosion resistance, chlorine resistance, and creep rupture strength. Knowledge of the expected integrity of alloys over time is crucial to the success of combined coal–biomass supercritical boilers.

2.0 OBJECTIVES

In previous work at the EERC, alloys accepted by commercial industry as candidate materials for USC systems were assembled, a furnace system was prepared, and preliminary corrosion testing was performed (1). The objective of Task 6.1 was to continue the corrosion testing to determine the effects of sulfur dioxide and chlorine gas concentration on the corrosion of the alloys coated with coal slag and potassium sulfate (K_2SO_4) to simulate the addition of biomass to a USC system.

3.0 STATEMENT OF WORK

The ash corrosion studies involved five alloys, two of which were previously tested: TP347HFG, HR3C, RA85H, RA310, and TP310. All of these alloys have been attractive to boiler vendors and operators because of their high creep strength and good resistance to corrosion and oxidation. Previous alloy work focused on the impacts of three different

temperatures using one slag composition, Illinois No. 6 coal. Work performed this year involved using the same slag type, with the addition of K_2SO_4 to simulate biomass and the addition of chlorine gas to the simulated gas atmosphere.

The experimental work involved cutting test-size coupons of each of the alloys, which were then coated with the same type of Illinois No. 6 slag and K_2SO_4 . Corrosion rates were determined by heating the weighed coupons in a tube furnace to a characteristic USC metal skin temperature of 630°C and passing the gas over the coupons. Two corrosion runs were conducted: the first with oxidizing gas and water vapor, the second with oxidizing gas, water vapor, and hydrochloric (HCl) acid vapor. The coupons were then weighed, cross-sectioned, and analyzed by scanning electron microscopy (SEM).

The specific deliverables are a report and a conference paper describing the impact of sulfur dioxide and chlorine gases on relative corrosion rates and mechanisms of corrosion of the alloys under USC conditions.

4.0 ACCOMPLISHMENTS

Previous work at the EERC revealed two facts: First, the alloys that had moderate to extensive attack formed an iron oxide scale, as opposed to a chrome oxide scale; second, there does not appear to be a relationship between the degree of attack and the Cr:Ni ratio. It should be noted that the alloy with the greatest chromium content had minimal attack, while the alloy with the greatest nickel content had extensive attack.

An attempt was made to correlate the resistance to attack to the predicted microstructure of the alloys. Microstructural predictions are based on the ability of certain alloying elements to stabilize ferrite, while other alloying elements will stabilize austenite. The procedure is quantified by multiplying previously determined weighting factors by the percentage of each ferrite or austenite stabilizer. As an example, niobium has a ferrite-stabilizing factor of 1.75, meaning that each percentage of niobium present in the alloy is equivalent to 1.75% chromium in its ability to stabilize ferrite. Carbon, on the other hand, is a powerful austenite stabilizer, with a weighing factor of 30. To predict metallurgical structure from the composition, the ferrite stabilizers (expressed as equivalent chrome) are plotted against the austenite stabilizers (expressed as equivalent nickel) on a Schaeffler diagram, which shows areas of stability as a function of concentration. Table 1 shows the elemental composition of the alloy, the ferritizing or austenizing factor that applies for the element, the equivalent chrome or nickel for each alloy, and the predicted structure for each alloy previously tested.

Examination of the data presented in Table 1 show that the alloy with the least attack, Alloy HR3C, and the alloy with the greatest attack, Alloy 800HT, are both predicted to have a microstructure composed entirely of austenite. The remaining two alloys, TP347HFG and RA253MA, are predicted to have a microstructure composed of austenite plus ferrite. The predicted microstructure evidently does not relate to resistance to slag attack.

TABLE 1

Alloys Tested in Previous Corrosion Work						
Element	Ferritizing Factor	Austenizing Factor	HR3C	RA253MA	800HT	TP347HFG
Chromium	1.00		25.00	21.03	21.00	18.00
Nickel		1.00	20.00	10.97	33.00	10.00
Carbon		30.00	0.07	0.09	0.08	0.07
Silicon	2.00		0.75	1.67	0.50	0.75
Manganese		0.50	2.00	0.56	0.08	2.00
Phosphorus			0.03	0.03		0.05
Nitrogen		25.00	0.25	0.17		
Sulfur			0.03		0.01	0.03
Cerium				0.05		
Molybdenum	1.50			0.20		
Cobalt		1.00		0.14		
Copper		0.30		0.18	0.40	
Titanium	1.50				0.40	
Aluminum	5.50			0.01	0.40	
Niobium	1.75		0.40	0.01		0.70
Iron			Balance	Balance	Balance	Balance
Cr:Ni Ratio			1.25	1.92	0.64	1.80
Chrome Equivalent			27.20	24.73	24.80	20.73
Chrome Equivalent – Chrome			2.20	3.70	3.80	2.73
Nickel Equivalent			29.35	18.39	35.41	13.10
Nickel Equivalent – Nickel			9.35	7.42	2.41	3.1
Predicted Structure			Austenite	Austenite + Ferrite	Austenite	Austenite + Ferrite

The difference between the equivalent chromium and the actual chromium for each alloy is also shown in Table 1. This would indicate whether ferritizing would be caused mostly by chromium (in which case the difference would be zero) or is caused by the addition of other ferrite-stabilizing elements. The alloy with the greatest resistance, Alloy HR3C, has the least amount of its ferritizing effect due to minor alloy additions. Conversely, the alloy with the least resistance, Alloy 800HT, has the greatest amount of its ferritizing effect due to minor alloy additions. However, the differences are so small that the results are probably not significant. There appears to be no correlation between resistance to corrosion and the quantity of minor austenite-stabilizing elements.

For further investigation of any correlation between composition or microstructure, five alloys were chosen for testing. Their compositions, chromium and nickel equivalents, and predicted microstructure are shown in Table 2. Alloys RA310, TP310, and HR3C can all be generally characterized as 25:20 (Cr:Ni) “superstainless,” compared to an 18:8 composition for typical stainless steels. Alloy HR3C contains niobium which aids in preventing high-temperature creep. This alloy has been tested previously. Alloy TP310 has twice the nominal silicon content as the other two, which will impart some corrosion resistance and high-temperature strength.

TABLE 2

Nominal Alloy Compositions, wt%							
Element	Ferritizing g Factor	Austenizing Factor	RA310	TP310	HR3C	RA85H	TP347HFG
Chromium	1.00		25.00	25.00	25.00	18.00	18.00
Nickel		1.00	20.50	20.50	20.00	15.00	10.00
Carbon		30.00	0.08	0.07	0.07	0.20	0.07
Silicon	2.00		0.75	1.50	0.75	3.60	0.75
Manganese		0.50	2.00	2.00	2.00	2.00	2.00
Phosphorus			0.04	0.05	0.03	0.03	0.05
Nitrogen		25.00			0.25	0.01	
Sulfur			0.03	0.03	0.03	0.03	0.03
Cerium			0.07				
Molybdenum	1.50		0.75				
Cobalt		1.00	0.22				
Copper		0.30	0.50			0.02	
Aluminum	5.50					1.20	
Niobium	1.75				0.40	Trace	0.70
Iron			Balance	Balance	Balance	Balance	Balance
Cr:Ni Ratio			1.22	1.22	1.25	1.20	1.80
Chrome Equivalent			27.63	28.00	27.20	31.80	20.73
Chrome Equivalent – Chromium			2.63	2.20	2.20	3.00	2.73
Nickel Equivalent			24.27	23.60	29.35	22.26	13.10
Nickel Equivalent – Nickel			3.77	3.10	9.35	7.26	3.10
Predicted Structure			Austenite + Ferrite	Austenite + Ferrite	Austenite	Austenite + Ferrite	Austenite + Ferrite

Alloy RA85H contains 15% nickel, so its Cr:Ni ratio is similar to that of the superstainless but at lower total levels. This alloy contains higher silicon and carbon contents which provide corrosion and high-temperature creep resistance. These additions may also provide protection in reducing atmospheres. Alloy TP347HFG can be characterized as an enhanced 18:8 stainless, with 2% added nickel. It also contains niobium for creep resistance. Alloy TP347HFG has also been tested previously. The modest nickel contents will limit the cost of the alloys and make them attractive to industrial clients. Two of the alloys have been used with success in previous tests and will provide a ready comparison with the new test conditions. Coupons for Alloys TP310, HR3C, and TP347HFG were cut from tubes, and coupons for Alloys RA310 and RA85H were cut from plates.

The alloys were cut into coupons, with the approximate size of 25 mm by 15 mm, then prepared and cleaned as described in the American Society for Testing and Materials (ASTM) Procedure G1-88, Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens. All samples were weighed before testing. A layer of K_2SO_4 followed by a layer of Illinois No. 6 powdered slag were added to each coupon, each approximately 1.5 mm in thickness. The coupons were then placed on trays and set into the center of the tube furnace.

The tube furnace ends were capped and valved to allow control of the testing atmosphere. A synthetic combustion gas with a nominal composition of 14% CO₂, 4% O₂, 1000 ppm SO₂, and the balance N₂ was allowed to flow into the tube at a rate of 14.2 L/hr. Water was added to the system using a micropump to give an equivalent steam flow rate of 1.4 L/hr, or 10% of the gas flow rate. In the second run, 1000 ppm of hydrochloric acid was added to the water to introduce chlorine into the system. Testing was conducted at 630°C and held constant. A coupon of each alloy was removed after 200, 600, and 1000 hours for mass wastage calculations. After 1000 hours, samples were removed and mounted for SEM examination.

Alloy coupons removed for mass wastage calculations were cleaned by the method described in ASTM Procedure G1-88. This procedure involves cleaning the samples through a series of chemical baths to remove corrosion products and then weighing the samples to determine the mass lost during testing. The mass loss can then be related to an equivalent metal penetration or depth.

5.0 RESULTS

5.1 Alloy Corrosion Measurements

The results of corrosion depth calculations are shown in Figures 1 and 2. The superstainless Alloys HR3C and RA310 displayed corrosion depths that varied little with the addition of

Figure 1. Cumulative corrosion depth versus time for alloys tested in the presence of water vapor.

Figure 2. Cumulative corrosion depth versus time for alloys tested in the presence of water vapor and HCl.

chlorine. The corrosion for Alloy TP310 did double. Corrosion for the enhanced stainless alloys was much more dramatic. Alloy RA85H experienced a fourfold increase of corrosion with the addition of chlorine. Alloy TP347HFG was shown to have the greatest measured corrosion rate of the five alloys tested. The addition of chlorine caused its corrosion rate to be over ten times that of the three superstainless alloys.

5.2 SEM Examination

At the conclusion of the 1000-hour tests, alloy coupons were removed from the furnace, mounted in epoxy, cross-sectioned, and polished for SEM analyses. Point analyses were collected to determine the morphology of the alloy surface layers. X-ray mapping was conducted on selected areas to examine the distribution of elements within the alloy and surrounding oxide layers.

5.2.1 Superstainless Alloys

Alloy RA310 showed limited pitting, and little scaling could be detected with the presence of just water vapor. The maximum depth of pits was approximately 30 microns. Intergranular attack was observed to a depth of 8 to 10 microns where pits were not present. X-ray mapping of pits revealed that they are composed mostly of chromium oxide, with a thin layer of iron oxide at the surface. Sulfur was present in the pits and increased in concentration from 0.5% at the top to 3.5% at the bottom, closest to the unreacted alloy. The material in the zones of intergranular attack was composed of chromium, oxygen, and sulfur. The surface oxide layer was composed of a mixture of chromium and iron oxides and was continuous across the coupon. Figure 3 is a micrograph showing a large pit on the surface of the sample.

Figure 3. SEM micrograph showing a large pit on the surface of Alloy RA310.

The alloy coupon tested with water and chlorine showed fewer isolated pits and limited scaling across the surface. The surface, however, was very rough. A 2- to 10-micron-thick, discontinuous chromium oxide layer was detected. Intergranular attack was observed to a depth of 5 to 7 microns from the surface. Small amounts of sulfur were present but were not detected above 0.5%.

Minor pitting of Alloy TP310 was observed in the presence of both water vapor and water vapor and chlorine. A chromium/iron oxide layer did form in the presence of water vapor and was approximately 3 microns thick at its maximum. Intergranular attack was restricted to a depth of only 2 to 3 microns from the surface where pitting did not occur. Pitted zones were composed mostly of chromium oxide with some sulfur. Sulfur content in these zones ranged from 0.3% to 2.0%. Figure 4 shows the x-ray mapping results of a pit formed in the presence of water vapor.

The addition of chlorine prevented the oxide layer from fully developing. Figure 5 shows the results of x-ray mapping. Neither chromium nor iron was concentrated at the surface. Oxygen and sulfur were attributed to the potassium sulfate material placed on the alloy and are not reaction products of the alloy. No pitting could be detected, and attack of the alloy was restricted to a depth of a few microns.

Figure 4. X-ray mapping showing elemental distribution of a pit formed in Alloy TP310. The field of view is 24 microns.

Figure 5. SEM x-ray maps of Alloy TP310 tested with water vapor and chlorine. The field of view is 24 microns.

The sample tested in water vapor was very similar to the sample tested in water vapor and chlorine. This alloy reacted with more generalized corrosion at the surface and only a few pits. Maximum pit depth was 11 microns. The pit material was composed of chromium oxide, with sulfur concentrations from 1.0% to 3.8%. Iron was concentrated at the base of the pit, where the highest concentrations of sulfur were detected. Intergranular attack was restricted to a depth of 3 microns. A chromium oxide layer did form on both samples which was 2 to 3 microns thick.

The appearance of Alloy HR3C was similar to Alloy TP310. Minor pitting and no spalling were observed in the presence of water vapor. Intergranular attack was detected to a depth of 3 microns and was composed of iron and chromium oxides. Sulfur was not detected within the alloy. A thin, chromium-rich, oxide layer formed, with a maximum thickness of approximately 2 microns.

In the presence of water vapor and chlorine, the depth of intergranular attack was observed to be 6 to 8 microns. Little pitting or spalling was observed. Material between grains was composed of chromium oxide with some iron. Minor sulfur was detected in the sample at concentrations below 1.0%. An oxide layer did not form on this sample.

A potential problem with Alloy HR3C is the presence of niobium. The niobium addition intended to provide resistance to creep tended to be concentrated in nodules and was shown to provide conduits for corrosion. Niobium was found to be very susceptible to sulfidation and allowed a path for oxidation to depths of 60 microns. Figures 6 and 7 are a SEM micrograph and x-ray mapping results of areas demonstrating this effect.

Figure 6. SEM micrograph showing a niobium nodule (white area) near the surface of Alloy HR3C.

Figure 7. X-ray mapping showing the elemental distribution around niobium nodules. The field of view is 24 microns.

Figure 8. SEM micrograph showing the intergranular attack of Alloy RA85H.

5.2.2 Enhanced Stainless Alloys

Intergranular attack of Alloy RA85H tested with water vapor was quite extensive. The depth of the attack could be detected as deep as 50 microns from the surface. The material in between grains was composed of iron, chromium, and oxygen, with sulfur concentrations varying widely, in some areas measuring up to 10%. Figure 8 is a micrograph showing the intergranular attack. Extensive pitting of the sample could be observed, with pits as deep as 30 to 40 microns. Material in the pits was of a similar composition to that seen between grains.

The alloy sample tested in the presence of water vapor and chlorine displayed intergranular attack as deep as 100 microns. Sulfur concentrations in the zones of attack were only in the range of 1.0% to 2.0%. Excessive pitting was also observed, with pits as deep as 40 microns. The pit material was mostly iron oxide with some chromium and small amounts of sulfur.

Alloy TP347HFG generalized corrosion across the metal surface with limited pitting for the sample tested in the presence of water vapor. Pits were measured to be 20 to 25 microns deep, and minimal intergranular attack could be observed to a depth of 5 to 8 microns. Extremely high concentrations of sulfur reaching 20.0% were found in the pit material with chromium and iron oxides.

No pitting was observed in the alloy coupon tested in the presence of water vapor and chlorine. General surface corrosion, along with intergranular attack to a depth of over 20 microns,

gave the surface a rough texture. Sulfur content of the zones of attack ranged from 3.4% to 6.0%. The zones were composed mostly of iron oxide with chromium.

Like Alloy HR3C, Alloy TP347HFG displayed the same potential problems associated with its niobium content. The bulk of the niobium was found to be concentrated in nodules. Where these nodules were close to the metal surface, sulfidation occurred, providing conduits for further corrosion. Figure 9 is an example of niobium attack close to the surface.

Based on the SEM results, no correlations could be found between the corrosion resistance of the alloys and their Cr:Ni ratios, predicted microstructures, or quantity of minor austenite- and ferrite-stabilizing elements. All but one of the alloys' predicted microstructures were the same, yielding no correlations between microstructure and differences in corrosion resistance. Alloys TP347HFG and RA85H have the largest quantity of minor ferrite-stabilizing elements and were the most corroded, yet Alloy RA310 has a quantity only slightly less and performed among the best for corrosion resistance. Likewise, large quantities of minor austenite-stabilizing elements were not restricted to alloys with good corrosion resistance.

5.3 Role of Water Vapor, Sulfur, and Chlorine

The presence of water vapor increases the oxygen partial pressure potential of the combustion gas. For high-chromium alloys, this should increase the formation of protective chromium oxide layers (2). Metal, gas, and deposit compositions should be considered because water vapor can increase the dissolution of gaseous phases which can also disrupt protective oxide layers. For comparison, the cumulative corrosion depth versus time of Alloys HR3C

Figure 9. SEM micrograph showing niobium (white area) attack in Alloy TP347HFG.

(superstainless) and TP347HFG (enhanced stainless) is shown with and without water vapor in Figure 10. Although the corrosion of Alloy HR3C was higher in the presence of water vapor, the increase was more significant in the enhanced stainless alloy. This suggests that vapor-induced dissolution is a more significant factor.

Sulfidation disrupts the formation of protective oxide scales by promoting localized reducing conditions that do not allow oxides to form (3). This effect can be increased in the presence water vapor. High chromium and nickel contents and the addition of silicon enhance an alloy's ability to withstand sulfide attack. Sulfide attack displayed in these tests appeared to be a secondary factor but was more abundant in Alloys HR3C, RA85H, and TP347HFG.

Halogen attack was by far the most significant corrosion factor. Chlorine is able to pass through the oxide surface layer and react with the metal, where chlorides are then formed (3). The chloride species can then have two effects. First, the formed chlorides between the metal and oxide layers will loosen the oxide layer, leaving behind a loosely bound, cracked, and sometimes porous layer that offers little or no protection. Second, the chlorides will diffuse slowly through the oxide layer and oxidize, freeing chlorine that will then cause further reaction with the metal (4–6). Chlorine has the strongest effect on iron in the alloy but can also react with chromium and nickel. To show the difference chlorine can have on the corrosion of alloys, Figure 11 shows a comparison of a superstainless alloy (HR3C) and an enhanced stainless alloy (TP347HFG) and their resistance to corrosion in both water vapor and water vapor and chlorine. The most dramatic effect can be seen in the enhanced stainless alloy.

Figure 10. Comparison of the cumulative corrosion depth versus time for Alloy HR3C and TP347HFG.

Figure 11. SEM micrographs comparing the effects of water vapor and chlorine on Alloy HR3C and Alloy TP347HFG.

6.0 CONCLUSIONS

Five alloys were tested in the presence of water vapor and water vapor with HCl for 1000 hours using simulated combustion gas. Samples were removed at intervals during each test and measured for determination of corrosion rates. One sample of each alloy was examined with a SEM after the completion of each test.

Cumulative corrosion depths were similar for the superstainless alloys. Corrosion for Alloy TP310 roughly doubled. Corrosion for the enhanced stainless alloys changed dramatically with the addition of chlorine. Corrosion for Alloy RA85H increased threefold, whereas Alloy TP347HFG showed an eightfold increase.

SEM examination of the alloys revealed that water vapor alone allowed the formation of chromium oxide protective layers on the superstainless alloys. The enhanced stainless alloys underwent more corrosion due to greater attack of sulfur. Iron-rich oxide layers were more likely to form, which do not provide protection from further corrosion. The addition of chlorine further increased the corrosion because of its ability to diffuse through the oxide layers and react with iron. This resulted in a broken, discontinuous, and loose oxide layer that offered less protection. Niobium, although added to aid in creep strength, was found to be detrimental to corrosion resistance. The niobium tended to be concentrated in nodules and was easily attacked through sulfidation, providing conduits for further corrosion deep into the alloy.

The alloys that displayed the best corrosion resistance were those which could produce chromium oxide protective layers. The predicted microstructure of all alloys except Alloy HR3C is the same and provided no further information relating to corrosion resistance. No correlation can be found relating corrosion resistance to the quantity of minor austenite-or ferrite-stabilizing elements. Also, there does not appear to be a correlation between corrosion resistance and the Cr:Ni ratio of the alloy.

These alloys were tested for their corrosion resistance alone. Strength and creep tests were not performed. Based only their corrosion resistance, Alloys RA310 and TP310 were shown to be the best suited to resist chlorine in a combustion environment. These alloys produced protective chromium oxide layers, displayed more general rather than localized corrosion, and their additives did not react to provide conduits for further corrosion.

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