Corrosion Tests of MA956 ODS Tube Specimens

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Presented at
34th International Technical Conference on Coal Utilization
Clearwater, FL
May 31 – June 4, 2009

TP_Metal_09_02

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ABSTRACT

Two corrosion probes have been installed in a coal-fired electric utility boiler under Phase III of the Oak Ridge National Laboratory Project “Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coatings, and Claddings.” The probes incorporate tubular specimens of both wrought and oxide-dispersion-strengthened (ODS) alloys. The two probes contain uncooled material specimens that are being exposed to flue gas temperatures ranging from 1093°C to 1204°C (2000°F to 2200°F) for time periods of one and two years respectively. After removal, the material specimens will be metallurgically examined to assess their resistance to fire-side corrosion and evaluate their suitability for the construction of high temperature heat exchangers for advanced-cycle power plants.

INTRODUCTION

Boiler-steam turbine based Rankine cycles are the primary means for electric power generation in the United States and for most of the world. In these plants the boiler superheater and reheater tubes typically operate with outside tube metal temperatures that are 55°C-111°C (100°F-200°F) hotter than their inside steam temperatures. Although steam turbine inlet temperatures remained relatively constant for many years at about 538°C (1000°F), in the late 1990s advanced designs were introduced that raised steam temperatures to as high as 621°C (1150°F). Since higher steam temperatures will further increase efficiencies, R&D programs are underway to develop new, high-creep-strength materials that will allow operation at steam temperatures as high as 760°C (1400°F). In addition to possessing high-creep-strength, these new materials must resist the corrosive conditions that will exist on their outside tube surfaces (fire-side corrosion).

Since gas turbines operate at much higher temperatures than steam turbines, they are more thermodynamically efficient and can be integrated with the latter to form combined cycle power generating plants. In this arrangement the gas turbine operates as the topping cycle, discharges its exhaust heat to the steam turbine bottoming cycle, and yields a plant efficiency that can greatly exceed that of a simple Rankine cycle plant. With inlet temperatures well above 1093°C (2000°F) gas turbines are susceptible to corrosion and must operate with clean gases such as natural gas. Since natural gas can be expensive and in short supply, there is a desire to operate gas turbines with coal. One approach to coal firing is the indirect-fired gas turbine cycle. In this cycle coal combustion gases are passed over tubes that are cooled with clean, high pressure air; the tubes heat the air to temperatures above 1093°C (2000°F) and the hot air is used to drive the gas turbine. Although the air pressure may be up to an order of magnitude lower than that of current supercritical pressure steam turbines, its 1093°C (2000°F) plus temperatures require the development of even more advanced, high-creep-strength, corrosion resistant materials. Oxide dispersion strengthened (ODS) alloys are prime candidates for this high temperature application.

LABORATORY TESTING

Under U.S. Department of Energy (DOE) Contract DE-FC26-05NT42238 coupons of Incoloy MA956 and Haynes 230 were coated with ashes representative of high sulfur and low sulfur coals and exposed to high temperature gases in electrically heated furnaces to evaluate material susceptibility to fire-side corrosion. The compositions of the coupons are given in Table 1 and the tests were conducted at 1093°C, 1149°C, and 1204°C (2000°F, 2100°F, and 2200°F) with two different gas compositions and two different ashes each for 1000 hours. The tests were conducted in 100 hour segments to allow specimens to be inspected and their ashes replenished. The gases were synthesized from gas cylinders to simulate the combustion exhaust gases from Western (low sulfur) and Eastern (high sulfur) coals.

Table 1 Composition of Laboratory Test Materials

Material	C	Si	Mn	Al	Co	Cr	Ni	Mo	Ti	Fe	W	Other
MA956	0.014	0.02	0.07	4.74	0.02	18.7	0.04	----	0.37	Bal	----	0.48 Y_2O_3
230	0.10	0.40	0.50	0.30	5.0 max	22.0	57.0	2.0	----	3.0 max	14.0	0.02-La, 0.015 max B

The active wastage mechanism observed in the electric furnace tests was sulfidation / oxidation preceded by hot corrosion from the sulfur in the ashes and gases. Although the chromium levels of the two materials were comparable, the MA956 possessed a much higher level of aluminum--an element known to form a very protective barrier (Al_2O_3) against oxidation at temperatures above 1200°C (2192°F). The formation of Al_2O_3 on the outside tube surface during the test enabled the MA956 to perform much better than the 230. Examination of the 1000-hour MA956 samples revealed fragments of a chrome-rich scale on top of an almost continuous layer of aluminum-rich oxide with pitting occurring where the latter had been breached by the molten slag.

The unique chemistry of MA956 enabled it to perform well in the electric furnace tests; the material contained enough chromium (18%) to quickly form a protective chromia layer at the low and intermediate temperatures. This chromia layer not only protected the sample as it progressed through the higher temperature regions but it also provided corrosion protection during the time needed for the slower forming Al_2O_3 scale to form beneath it. Even with spalling (during test cycling) and possible volatilization of the chromia layers, the MA956 was protected by the remaining Al_2O_3 layer.

FIELD EXPOSURE TESTING

While laboratory electric furnace tests are a valuable screening tool and have shown MA956 to be a promising candidate for high temperature coal-fired applications, they are not able to address a variety of field-related variables because:

- The actual composition of the deposits formed on the tubes is more complex than the composition of simulated laboratory ash.
- The SO_3 concentration formed by heterogeneous reaction on cooled surfaces is variable.
- The temperature gradients that occur within the ash deposits are very large.
- The ash and flue gas move past tubes at high velocity; the rate varies with design.
- The composition of the corrosive deposits changes over time.
- The temperatures are not constant.
- The effect of fly ash erosion results in the removal of the protective oxides from the tube and replenishes the metal surface with fresh corrosive ash.

As a result, two probes containing ODS specimens were designed, fabricated, and installed in a coal-fired boiler under DOE Contract DE-AC05-00OR22726. The two probes are being tested in a 625 MWe boiler that fires a blend of Illinois Basin coals with an as-received sulfur content typically ranging from 2.8 to 3.3%. The probes have been inserted in the boiler flue gas near the top of the furnace via two existing wall penetrations. The first is an observation door, whereas, the second is a 5 inch ID nozzle located slightly below and approximately 18 feet to the right of the first. At these locations the flue gas temperature ranges from 1093°C (2000°F) to 1204°C (2200°F) at full load.

Probe Description

The two corrosion probes are identical, L shaped, and possess a single, 90 degree, 356 mm (14 inch) bend radius that facilitates entry through either boiler wall penetration.

Each probe contains a total of 14 tubular shaped material specimens in its approximately 1.60 m (63 inch) long vertical, down leg. The materials installed in the probes are listed in Table 2; the specimens consist of wrought nickel based alloys 602 and 693 and oxide dispersion strengthened iron based alloys PM2000 and MA956 and their nominal compositions are given in Table 3. The MA956 specimens were provided in commercial annealed (CA suffix) or modified annealed (MA suffix) conditions. The cold drawn, commercial annealed specimens had been held at 1293°C (2360°F) for 6 hours to allow recrystallization to occur, whereas, the MA suffix, a FW designation, identifies material that was only held for one hour at 1121°C (2050°F). In addition to the above, the specimen arrays contain sections of MA956 that have been joined by either Inertia Welding or Flash Butt Welding, thereby permitting an evaluation of both base metals and weld zones.

The specimens have nominal outside and inside diameters of 63.5 mm and 50.8 mm (2 ½ inch and 2 inch) respectively and threads have been machined into their ends (see Figure 1). Each specimen array was screwed together, match marked, indexed, dissembled, their wall thicknesses measured relative to their indexing, and screwed back together. To prevent the specimens from possibly separating during testing, they were also tack welded together and then welded to a 2 inch Incoloy 800 HT pipe that forms the balance of the "L" shape. To give the probe strength, each probe contains an internal air cooled pipe / core section. The air enters through the branch of a 2 inch tee and ultimately discharges into the boiler at the bottom of the L. The annulus formed by the specimens and the core pipe is packed with insulation and enables the specimens to operate at the temperature of the flue gas sweeping over it.

After match marking, two 2.4 mm (3/32 inches) deep slots located 180 degrees apart were machined in the outside walls of 4 specimens (see Table 2 for locations). Each slot contained a 4.8 mm (3/16 inch) diameter hole that enabled a thermocouple to be slid from the core section into the slot. After positioning a thermocouple in each slot, a pad was welded over each slot to seal it from the flue gas. In addition to the above eight thermocouples, two more were installed 180 degrees apart on the walls of the core pipe immediately downstream of the 90 degree bend; the 10 thermocouples allow the specimen and core temperatures to be monitored / recorded and used to develop time-temperature correlation of the test data. From the specimens and 90 degree bend region the thermocouples enter the core pipe and eventually exit from the horizontal end of the probe. Figure 2 shows a specimen assembly and Figure 3 shows a fully assembled probe.

Table 2 Probe Material Specimens

Specimen Number	Specimen Material	Approx Length (inches)	Thermo-couple
1 (Top)	602CA	1 3/8	Yes
2	MA956CA	2 5/8	
3	MA956MA	2 5/8	
4	PM2000	2 5/8	
5	693	1 3/8	Yes
6	Inertia Welded 956CA	3 3/4	
7	Flash Welded 956CA	3 3/4	
8	602CA	1 3/8	Yes
9	MA956CA	2 5/8	
10	MA956MA	2 5/8	
11	PM2000	2 5/8	
12	693	1 3/8	Yes
13	Inertia Welded 956CA	3 3/4	
14 (Btm)	Flash Welded 956CA	3 3/4	

Table 2 Nominal Compositions of Probe Specimens

Alloy	Supplier	Cr	Ni	Fe	Al	Ti	C	Y2O3	Zr	Others
602CA	Krupp VDM	25.0	62.2	9.5	2.1	0.2	0.2	0.1	0.1	0.7
Inconel 693	Special Metals	29.0	54.1	9.0	3.3	1.0	0.2			3.5
MA956	Special Metals	20.0		74.0	4.5	0.5	0.1	0.5		0.5
PM2000	Schwarzkopf Plansee	19.0		74.5	5.5	0.5		0.5		

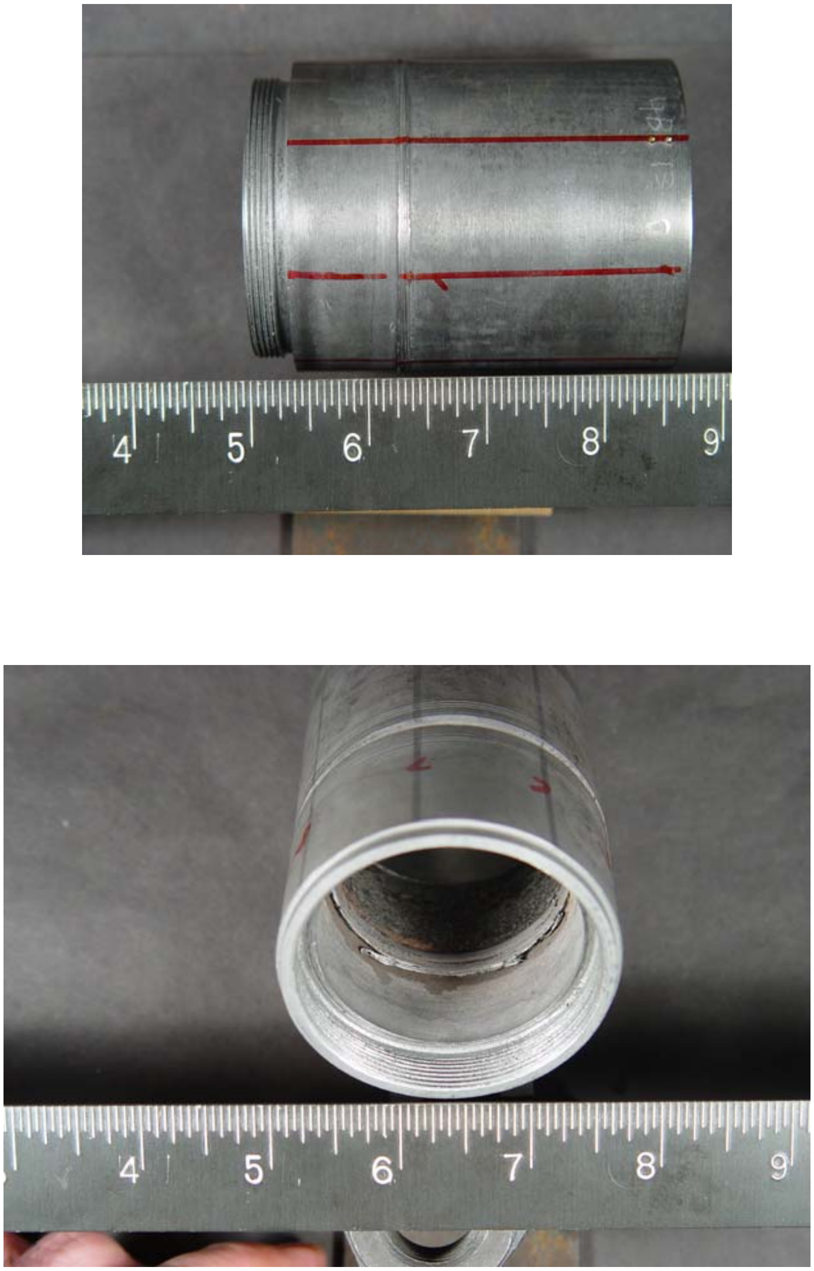

Figure 1 Welded Specimen with Machined Ends

Figure 2 Specimen Assembly

Figure 3 “L” Shaped Corrosion Probe

Each probe is provided with a manual screw mechanism that allows the 14 specimen down leg to be positioned between 0.35 to 0.91 m (14 to 36 inches) from the boiler inside wall. In addition, each probe can be rotated up to approximately 15 degrees from the vertical. By rotating the probe and by varying the insertion depth, a 111°C (200°F) gradient is planned to be induced along the specimens (~1093°C (2000°F) at the topmost and ~1204°C (2200°F) at the bottommost specimen); this will allow data to be collected at two different metal temperatures.

Balance of Probe System

The two probes are cooled with air supplied by a single, positive displacement, 480 volt blower; should that cooling air be lost, the probes can over heat and fail. To protect the probes from a loss of blower air, the latter is backed up with plant air that will automatically activate to maintain the probe core pipe at its design temperature. When the blower cooling air flow resumes, the plant air will automatically shut off. The probe instrumentation and control system operate with 120 volt power. Should that power be lost, a step down transformer will automatically supply power from the 480 volt line to keep the system operating and the probes supplied with cooling air. The probe temperatures and key system parameters are monitored by an on-site computer and the data transferred by modem to FW.

Probe Testing

The probes and their support system were installed in the 625 MWe boiler in October 2008. Testing commenced shortly thereafter and the first probe will be removed for evaluation after one year of exposure; the second probe will be removed after two years of exposure. After removal, the probe specimens will be photographed, the extent of ash deposits noted, and ash deposits sampled for analyses. Two ring sections encompassing the indexed points of the probe samples will be cut from each tubular specimen to facilitate macroscopic and microscopic analyses. Using one of the ring sections, gross wall loss will be quantified by measuring the wall thickness at the indexed points and comparing them to pre-test values. The second ring section from each specimen will be cut into metallographic cross sections, mounted, and dry polished to retain any possible water soluble species i.e. chlorides, etc. and to characterize the type and morphology of the oxide formed. The mounted sections will be microscopically examined to determine the extent of wall loss due and quantify the degree of subsurface penetration. SEM/EDS analysis will be employed to determine the composition of overlying deposits and to ascertain the nature of the penetrating species (if any). Based on the collected data the maximum metal wastage and corrosion rate of each material will be calculated and the materials ranked for their ability to resist corrosion induced by coal combustion gases and ashes at the temperatures tested.

ACKNOWLEDGEMENTS

The laboratory tests discussed herein were conducted under DOE Contract No. DE-FC26-05NT42238. Funding for the field tests was provided by Oak Ridge National Laboratory under DOE Contract No. DE-AC05-00OR22726.