Very-High-Temperature Corrosion of Chromia- and Alumina-Forming Alloys in Coal Combustion Systems

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Introduction

To increase national energy self-sufficiency for the near future, power systems will be required to fire low-grade fuels more efficiently than is currently possible. The typical coal-fired steam cycle used at present is limited to a maximum steam temperature of 540°C and a conversion efficiency of 35%. Higher working-fluid temperatures are required to boost efficiency, exposing subsystems to very corrosive conditions. To initially evaluate the suitability of a new material for use in a fossil energy system and to determine appropriate alterations in material composition or processing during the development stage, short-term tests of the corrosion resistance of the material and the corrosion mechanisms must be performed.

The University of North Dakota Energy & Environmental Research Center (EERC) is working with the Oak Ridge National Laboratory (ORNL) and the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) to provide technical assistance and products of coal utilization to the Fossil Energy Materials Program investigating materials failure due to corrosion in fossil energy systems. This work serves DOE goals of advancing the efficiency and reducing the emissions of coal-fired power plants by providing inexpensive and rapid initial tests of the corrosion resistance of newly developed advanced materials. The information is most useful in the development stage so that the potential of the material for use in a fossil energy system can be quickly assessed and so that modifications can be made to the material or its processing in order to increase its corrosion resistance. Upon successful testing under this program, the materials developer will be able to produce a more corrosion-resistant material, recommend appropriate uses for the material in a fossil energy system, and choose appropriate long-term testing scenarios under other programs.

The EERC has two pilot-scale solid-fuel systems available for exposure of materials coupons. The slagging furnace system (SFS) was built under the DOE Combustion 2000 Program as a testing facility for advanced high-temperature heat exchanger (HTHX) subsystems. It is a 2.5-MMBtu/hr solid-fuel combustion system with exit temperatures of 1500° to 1600°C to ensure the ash in the main combustion is molten and flowing. Sample coupons may be exposed in the system either within the slagging zone, near the convective air heater (CAH) at 1000°C, or in an elbow following a heat exchanger at 700°C. The results of coupon exposures and analyses are presented in the first part of this paper.

Two main configurations of a single radiant heat exchanger have been tested extensively in the slagging combustion. The heat exchanger is composed of three 6-foot-long by 2 ½-inch-o.d. tubes of MA 754 and nickel/chrome-based oxide-dispersion-strengthened (ODS) alloy. The first configuration is that developed by the United Technologies Research Center (UTRC) during Combustion 2000 testing. This “tubes-in-a-box” design has

the three tubes held within a ceramic brick-lined box to prevent the products of combustion from direct contact with the alloy. Process air at 950°C and 150 psig was routinely produced with this configuration for over 2000 hours of testing. For a short time, conditions of up to 1100°C and 100 psig were reached. However, the ceramic tiles forming the face of the heat exchanger were prone to corrosion and thermal shock. Therefore, the EERC performed laboratory corrosion tests on the alloy which indicated very low surface recessions when the alloy was exposed directly to ash and gas at up to 1150°C. Based on these results, the EERC has begun testing the heat exchanger in a second configuration, exposing the alloy tubes directly to the products of combustion.

In addition to the MA 754 work, another ODS alloy, MA 956, is being tested. It is an iron/chrome/aluminum material with an even higher melting point and lower static corrosion rate than for the MA 754. Based on the excellent corrosion resistance measured in laboratory and pilot-scale testing, one of the tubes in the original bare-tube heat exchanger is currently being replaced by MA 956. Also, in order to better understand the corrosion resistance of the materials under the most extreme conditions, that of flowing slag falling directly on the surface of the alloys, bench-scale tests simulating the conditions of dynamic corrosion by a flowing slag have been initiated for both alloys. The results of the initial tests of this bare-tube heat exchanger and the corrosion resistance of the ODS materials under both static and dynamic conditions are described in the second part of this paper.

Experimental Conditions

The Pilot-Scale Slagging Furnace System

Figure 1 is a simplified illustration of the pilot-scale SFS. It was constructed with funding from the DOE Combustion 2000 Program through a subcontract with UTRC to support testing and development of subsystems to be used in a high-temperature advanced furnace. It consists of eight main components: 1) slagging furnace, 2) slag screen/slag tap, 3) dilution-quench zone, 4) process air preheaters, 5) CAH section, 6) radiant air heater (RAH) panel, 7) tube-and-shell heat exchangers, and 8) pulse-jet baghouse. The SFS design is intended to be as fuel-flexible as possible, with maximum furnace exit temperatures of 1480°–1590°C to maintain the desired heat transfer to the RAH panel and slag flow. The furnace has a nominal firing rate of 2.6×10^6 kJ/hr and a range of 2.1 to 3.2×10^6 kJ/hr using a single burner. The furnace design was based on Illinois No. 6 bituminous coal (25,800 kJ/kg) and a nominal furnace residence time of 3.5 s. The EERC oriented the furnace vertically (downfired) so that slag would not interfere with the operation of the burner. Internal dimensions are 119 cm in diameter by roughly 4.9 m in total length. It is lined with three layers of refractory totaling 30 cm thick to minimize heat loss. This insulation keeps the wall surface temperature near that of the gas stream. The inner layer is composed of an alumina castable, developed by the EERC in cooperation with the Plibrico Company, that has been shown in bench and pilot tests to be extremely resistant to slag corrosion at the high wall temperatures.

Material sample coupons can be inserted into the system either through ports in the main combustion, in the slag screen, on racks in the convective pass downstream of the CAH, or in an elbow following the first tube-and-shell heat exchanger. Most samples were inserted downstream of the CAH. Near that subsystem, gas temperatures are maintained at 980°C, but they drop farther back in the system to approximately 175°C as the gas enters the exit stack. To be included in SFS tests, materials coupons should be no more than 5 cm wide and be able to slip onto a 1.2-cm-thick Inconel support rod.

Bench-Scale Dynamic Corrosion Testing

In a commercial power system, the HTHX tubes may be exposed to coal slag dripping directly onto the tubes. Therefore, the EERC bench-scale dynamic slag application furnace (DSAF) was modified to permit measuring

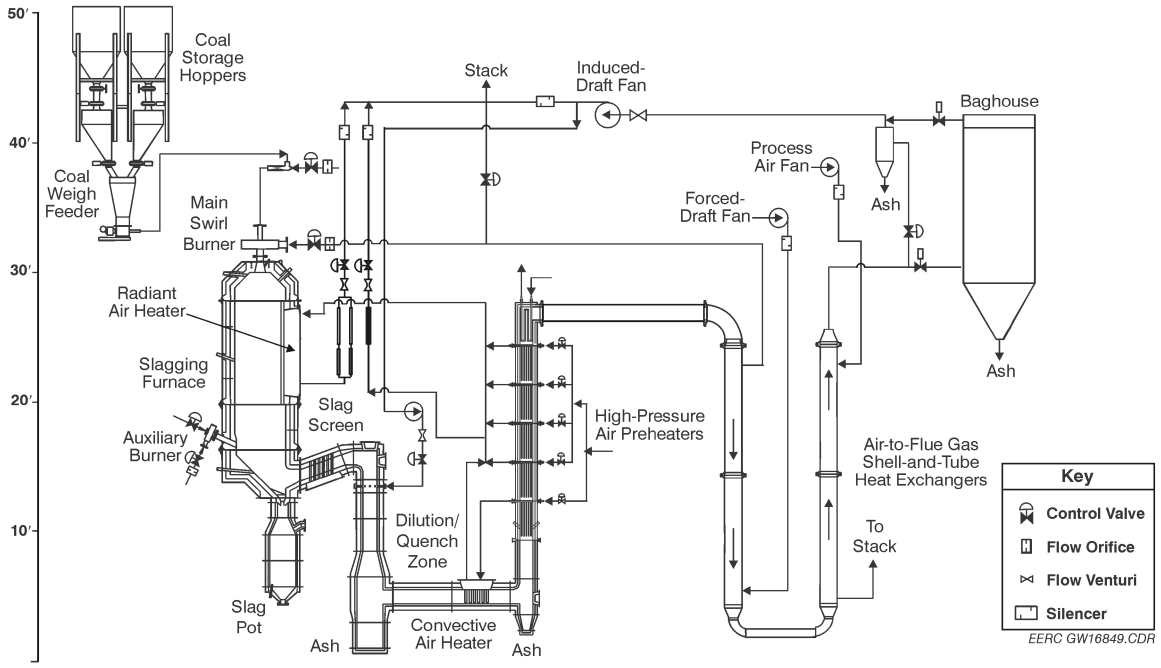

Figure 1. The EERC slagging furnace system.

the corrosion rates of sections of cooled alloy pipe to flowing slag. Figure 2 shows a schematic of the system. During a test, the furnace is heated to 1500°C while the surface of the alloy tube section is cooled to the desired temperature by an internal air flow. The slag is screw-fed as sand-like granules into the furnace system, where it drops into a platinum melting pan. After melting, it drips onto the surface of the cooled alloy tube section at approximately the 11 o'clock position. It then flows around the cooled tube and drips off the alloy and out of the furnace through a hole in the bottom. After 100 h of slag exposure, the DSAF is cooled, the alloy tube is removed and photographed, and its diameter is measured with a caliper. The surface is then sprayed with dilute epoxy to hold the remaining slag in place, and the tube section is cut into pieces, then embedded in epoxy, cross-sectioned, and polished for analysis in a scanning electron microscope (SEM).

The DSAF testing provides a worst-case-scenario type of test for the alloys because the corrosion mechanism is more severe than would be encountered by a heat exchanger in a power system. It is more severe because the slag is dripped directly onto the surface of the alloy, whereas in a power system the surface would be coated with a thin layer of less reactive fly ash before building to the thickness at which the slag would become molten.

Results and Discussion

Coupon Testing in the SFS

The EERC performed two 200-hr tests under separate DOE funding in the SFS in March and June of 2000, during which over 50 ceramic and alloy samples were exposed to coal combustion conditions. The conditions of those tests and results of analyses of the samples were reported previously in an annual report (1) and three technical papers (2–4). In this paper we present the test results of three high chromia alloys that along with 19

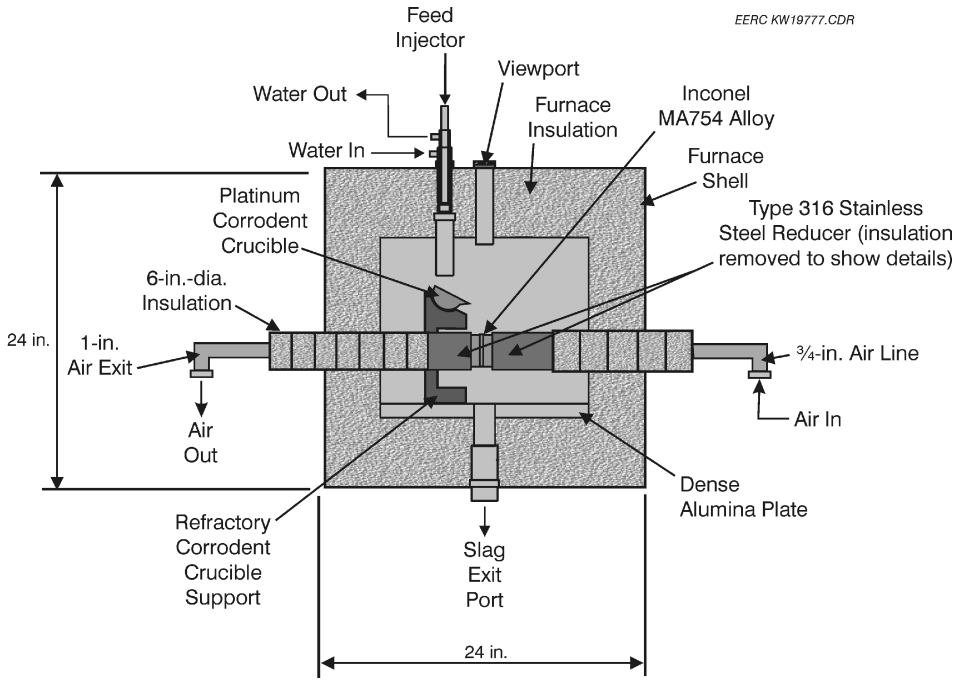

Figure 2. The DSAF system modified for flowing slag corrosion testing of air-cooled alloy tube sections.

other alloy and ceramic samples were exposed in the SFS during a 100-hr coal combustion test in November 2001.

The three high chromia alloys consisted of rings supplied by ORNL. Two of these contained chromium with iron, tantalum, molybdenum, titanium, and silicon. The remaining alloy contained chromium with magnesium oxide, tantalum, and lanthanum oxide. All samples were installed in the convective pass, where they were exposed to flue gas at an average temperature of 935°C while firing Illinois No. 6 bituminous coal. Brownish-gray scales covered with thick ash deposits were observed on all samples. No visible signs of erosion or major corrosion were observed on any of the alloys or ceramic rings. One sample from each type of chrome/tantalum alloy received from ORNL was analyzed by SEM, which verified the absence of major corrosion or erosion. The remaining 19 materials samples were returned to their prospective suppliers.

Figure 3 shows SEM photographs of the interface between the alloy and the ash deposits after the tests. ORNL Cr-Ta ring C contained 82.75 wt% Cr, 9 wt% Ta, 5 wt% Mo, 3 wt% Si, 0.15 wt% La, and 0.1 wt% Ti. It is essentially a chromium matrix reinforced with a Cr-Ta intermetallic phase. ORNL Cr-35Fe coupon A is composed of 54.5 wt% Cr, 35 wt% Fe, 5.5 wt% Ta, 4 wt% Mo, 0.5 wt% Ti, and 0.3 wt% Si. The Cr-6MgO Coupon A sample is composed of 93.2 wt% Cr, 6 wt% MgO, 0.5 wt% Ti, and 0.3 wt% La_2O_3. It is composed of a chromium matrix with a La-rich phase and a Mg-rich phase.

As expected, all three alloys formed chromia layers on their surfaces during exposure. The chromia layers were more bonded to the ash deposit than to the alloy and tended to separate from the alloy with the ash deposit, leaving only a thin chromia layer behind. The chromia dissolved partially into the deposits, and limited amounts of ash constituents dissolved into the chromia layer. This is common for chromia layers formed on other alloy samples analyzed previously. The presence of hollow pores below the layer indicates the loss of alloy material, and the discontinuous nature of the layer further indicates lessened protection to the alloy, although there is much

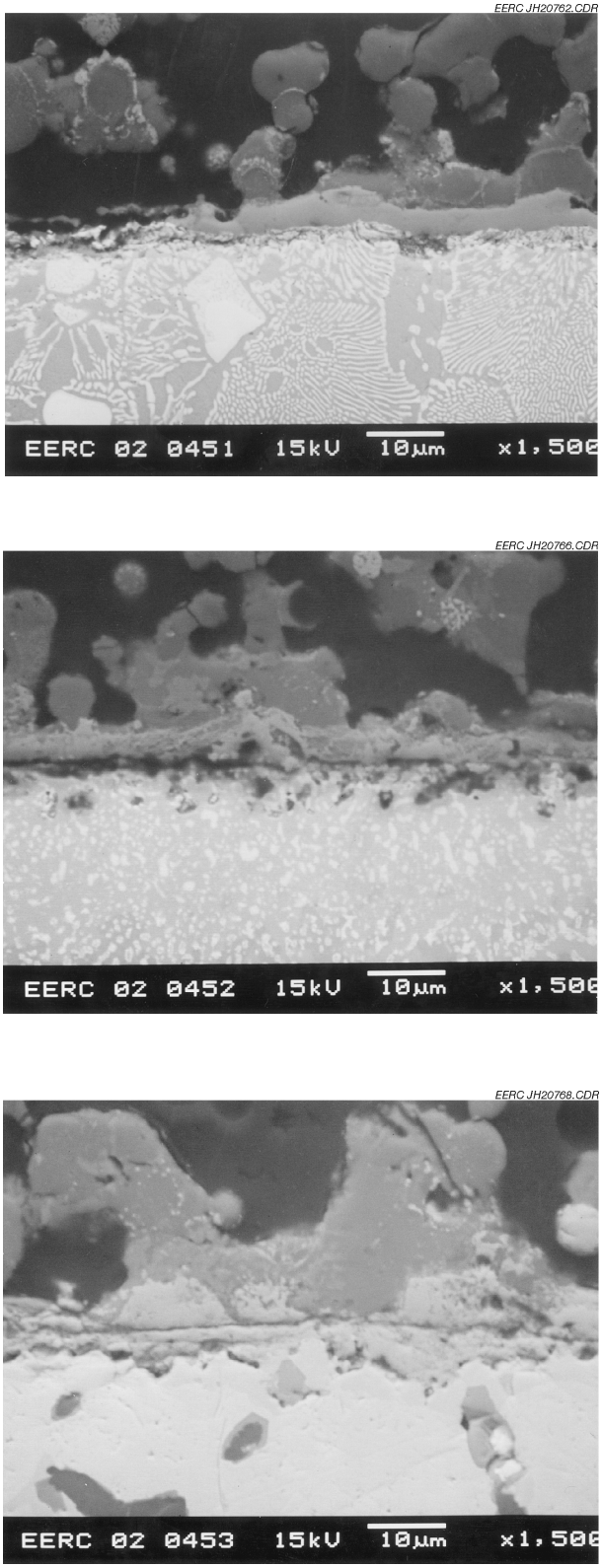

Figure 3. SEM photographs of the three high chromium ORNL samples after exposure in the SFS in November 2001. 1) Cr-Ta Coupon C. 2) Cr-35Fe Coupon A. 3) Cr-6MgO Coupon A.

better protection then if no chromium were present. Sulfidation, halide attack, or ash constituent interaction directly with the alloys were not detected.

Bench-Scale Flowing Slag Corrosion of ODS Alloys

Both MA 754 and MA 956 have been tested to date at 1000°C, 1100°C, and 1200°C. In all cases, the surface recessions due to slag corrosion were not measurable with a caliper because they were so small and, in some cases, slag remained attached to the surface. With both alloys, as the surface temperature increased, the slag wetted the surface more broadly and flowed further around the circumference before dripping off. In all tests, the ribbon of slag frozen to the surface fell off upon cooling. In the case of MA 754, the slag ribbon broke from the alloy at the surface of the chromia oxidation layer, leaving no slag behind and removing a small amount of the chromia with the slag. Figure 4 is an SEM image of a cross section of the surface of the MA 754 tube directly below the spot on which the slag dropped after the test at 1200°C. During operation of a power plant, temperature cycling would be expected, so the loss of the chromia layer into the slag, and with the slag upon cooling, would be detrimental to alloy lifetime because the chromia layer provides protection and reduces the corrosion rate of the alloy. SEM analyses of this cross section of the surface of the MA 754 tube show that although some of the protective chromia layer was lost with the slag, a 10–15 μm-thick layer was left behind on the alloy. Analyses of composition variations within the alloy show that no slag or gas constituents dissolved into the alloy to the levels that could by detected by energy dispersive x-ray analysis.

In contrast, during cooling of the MA 956, the frozen slag broke from the alloy surface within the slag itself, leaving behind a layer 20 μm thick on the surface of the alloy. Figure 5 is an SEM image of a cross section of the surface of the MA 956 tube directly below the spot on which the slag dropped after the test at 1200°C. The figure shows the protective alumina layer, which is 5–10 μm thick, with the attached slag layer on top. SEM analyses showed that none of the slag constituents diffused into the alloy. A high alumina concentration in the slag

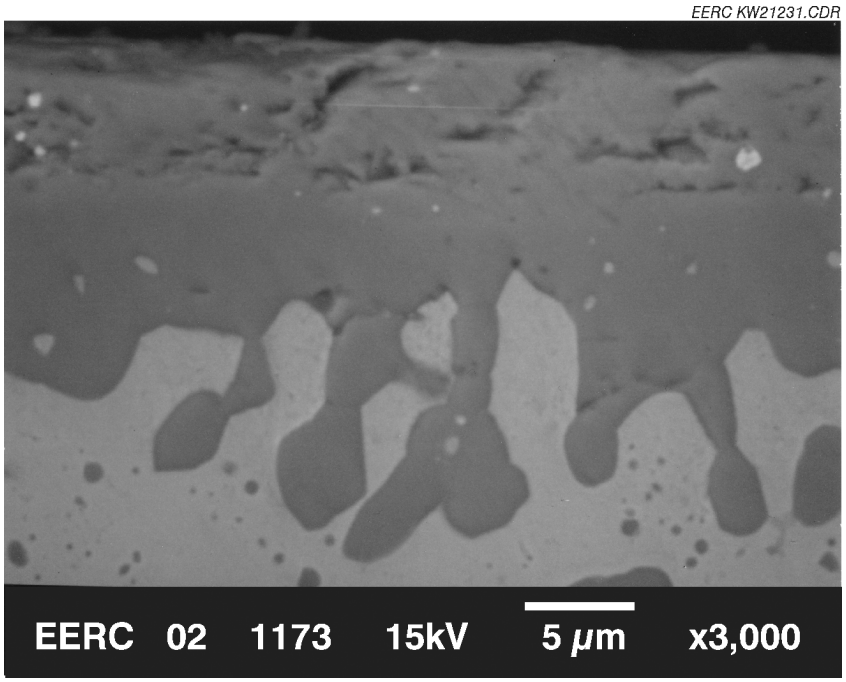

Figure 4. SEM image of a cross section of the surface of the MA 754 tube directly below the spot on which the slag dropped after the test at 1200°C.

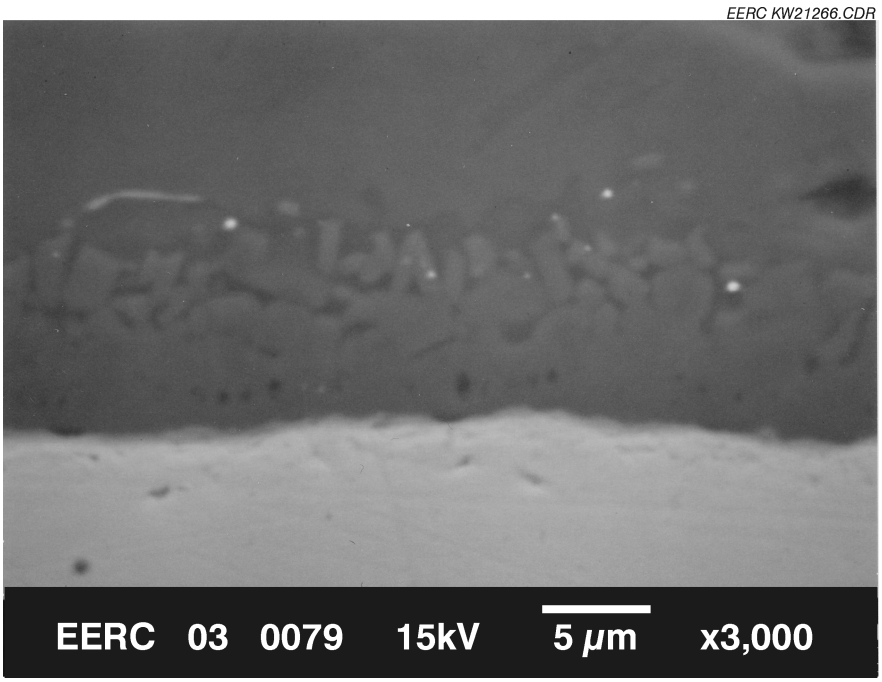

Figure 5. SEM image of a cross section of the surface of the MA 956 tube directly below the spot on which the slag dropped after the test at 1200°C.

showed that some of the alumina protective layer had dissolved into the slag. The intergrown fingers of alumina into the slag also indicate dissolution and recrystallization of the alumina at the interface of the alumina and slag. However, the fact that some of the slag remained attached to the MA 956 surface shows that the protective oxide layer is not lost through spallation during thermal cycling.

Conclusions

Bench- and pilot-scale tests of chromia-forming alloys at temperatures over 900°C have shown that although the chromia layers provide excellent protection against corrosion, they partially dissolve into the coal ash or slag during exposure. Also, the slag layer is completely lost on cooling, thereby eliminating it as a protective material. In very-high-temperature heat exchangers that thermally cycle often, the chromia dissolution may significantly shorten the lifetimes of the materials. In contrast, the tests with an ODS alumina-forming alloy at up to 1200°C show that although a small alumina enrichment is seen in the near slag layer, it remains with the alloy on thermal cycling. Therefore, the lifetime of the alloy should not be significantly shortened due to thermal cycling.

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References

1. Hurley, J. P.; Crocker, C.R. Support Services for Ceramic Fiber–Ceramic Matrix Composites. *Annual Technical Progress Report*, Oak Ridge National Laboratory/sub/94-SS112/06.

2. Hurley, J.P.; Crocker, C.R. High-Temperature Materials Testing in a Pilot-Scale Coal Combustion System. In *Proceedings of the 15th Annual Conference on Fossil Energy Materials*; Knoxville, TN, April 29–May 2, 2001.

3. Crocker, C.R.; Kay, J.P.; Hurley, J.P. Materials Testing in a Pilot-Scale Coal Combustion System. In *Proceedings of the 2001 ASM Materials Solutions, Combustion, and Analyses Conference*; Indianapolis, IN, Nov 5–8, 2001.

4. Hurley, J.P.; Crocker, C.R. Very-High-Temperature Materials and Heat Exchanger Testing in a Pilot-Scale Slagging Furnace. In *Proceedings of the 16th Annual Conference on Fossil Materials*; Pittsburgh, PA, April, 2002.