MEASUREMENTS OF THE CORROSION OF TWO ODS ALLOYS BY FLOWING COAL SLAG

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ABSTRACT

The High-Performance Power System, or HiPPS, Program was started by the U.S. Department of Energy to encourage the development of a coal-fired power system that would employ an indirectly fired combined-cycle that is one-third more efficient than existing power plants while producing only one-tenth of the emissions. One concept for a HiPPS plant proposed by the United Technologies Research Center employed a very-high-temperature heat exchanger composed of ODS alloys that would have to withstand corrosion by flowing coal slag. The University of North Dakota Energy & Environmental Research Center was a major subcontractor on that project, building and operating both pilot- and bench-scale systems for testing the heat exchanger and other subsytems key to the operation of such a plant.

In this paper, we present the results of corrosion tests of two ODS alloys cooled to 1000°, 1100°, and 1200°C while exposed to flowing coal slag at 1500°C. The alloys are MA754, a nickel-based chromia former, and MA956, an iron–chromium alumina former. The tests were performed in a bench-scale system in air for 100 hours each.

INTRODUCTION

Advanced coal-fired power plants employing an indirectly fired combined-cycle (IFCC) promise significant increases in plant efficiency and reductions in plant emissions. This type of plant will use a heat exchanger to produce very-high-temperature but low-pressure clean air to turn an advanced gas turbine. The waste heat will be used to produce high-pressure but lower-temperature steam to turn a steam turbine. Under the High-Performance Power System, or HiPPS, Program, the U.S. Department of Energy (DOE) worked with industry in the development of key technologies for this type of power plant. The goals for the HiPPS system were 47% efficiency, with only one-tenth of the particulate, SO_x, and NO_x emissions allowed under the New Source Performance Standards, while reducing the cost of electricity (COE) by 10%(1–3). The Energy &

Environmental Research Center (EERC) worked with a team led by United Technologies Research Center (UTRC) in the development of one system concept.

The heart of the UTRC IFCC system is a high-temperature heat exchanger (HTHX) to produce clean pressurized air to turn an aeroderivative turbine. The overall system design is like that of a combined-cycle gas turbine system, except that a pulverized-coal (pc)-fired furnace containing the HTHX is used to preheat the air entering the gas turbine. Conversion efficiencies of 45% higher heating value (HHV) can be reached by such a system while firing on coal. To achieve the highest temperatures and efficiencies of over 50%, a gas-fired duct burner can be used to further heat gas entering the turbine 1430°C and 1.7 MPa. Because of the extremely high temperatures, only advanced oxide dispersion-strengthened (ODS) alloys or ceramics can be used to carry the high-temperature gases. Early in the program, the EERC and UTRC determined that the current state-of-the-art-technology for ceramic heat exchangers was insufficient to use in reaching near-term objectives. Therefore, UTRC turned primarily to the ODS alloys because of their superior high-temperature creep resistance as compared to superalloys. ODS alloys typically contain 0.5% of an oxide such as yttria dispersed throughout the material. The oxide particles help to pin grain boundaries, reducing their ability to creep at high temperatures.

The EERC role in the UTRC HiPPS Program, as well as in subsequent DOE-funded programs, has been to design, construct, and operate laboratory-, bench-, and pilot-scale equipment to test key subsystems of the IFCC concept. Pilot-scale tests of the initial ODS heat exchanger typically produced 950°C air at 1.0 MPa for over 2000 h of operation. For a short duration, air up to 1090°C was produced, which is believed to be a record for a coal-fired system. Detailed results of the pilot-scale testing have been presented in other technical papers (4–6). The initial heat exchanger used ceramic panels to separate the alloy tubes from the products of coal combustion in order to reduce corrosion. Although the panels were effective in this role, they also significantly reduced the heat-transfer rates and were prone to thermal shock. Subsequent testing of a bare-tube design showed that removing the ceramic panels from the heat exchanger increases the heat removal rate by nearly a factor of five. This means that the heat exchanger could be as small as one-fifth of that originally proposed. Factoring in the price reduction due to the smaller size and lack of ceramic panels, the unprotected heat exchanger panel could cost as little as one-tenth as much as the original tubes-in-a-box design. However, corrosion of the alloys then becomes the primary concern. Therefore, in order to determine if the alloys could be exposed directly to the coal flame for commercially significant periods of time, laboratory- and bench-scale tests are being performed under carefully controlled conditions. In this paper, we present the results of corrosion tests of two ODS alloys cooled to 1000°, 1100°, and 1200°C while exposed to flowing coal slag at 1500°C. The alloys are MA754, a nickel-based chromia former, and MA956, an iron–chromium alumina former.

EXPERIMENTAL

The EERC bench-scale dynamic slag application furnace (DSAF) was modified to permit measuring the corrosion rates of sections of cooled alloy pipe to flowing slag. Figure 1 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 into the furnace system as sandlike grains where it drops into a platinum melting pan. The slag was collected from a commercial slagging boiler system burning Illinois No. 6 coal. The major components in the slag were determined by x-ray fluorescence. Reported as oxide weight percents, the composition is approximately 55% silica, 19% alumina, 16% iron oxide, and 7% calcia normalized to a closure of 100%. After melting in the platinum pan, the slag 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 its 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. Two ODS alloys have been tested to date at 1000°C, 1100°C, and

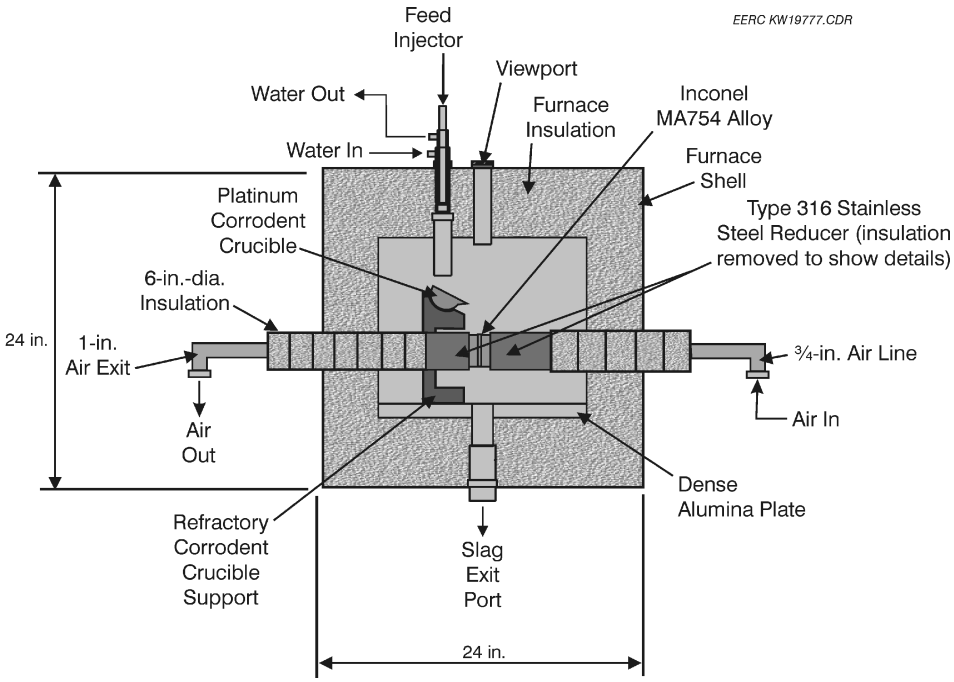

Figure 1. The DSAF system modified for flowing slag corrosion testing of air-cooled alloy tube sections.

1200°C. The alloys are the nickel–chrome MA754 used in the heat exchanger tested at the EERC in the high-temperature heat exchanger and MA956, an iron–chrome–aluminum alloy. Each contain approximately ½% yttria particles. Figure 2 shows the surfaces of the alloy tube sections after each test. 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.

For both alloys, as the surface temperature increased, the slag wetted the surface more broadly and flowed farther around the circumference before dripping off (the surface coating of slag on the 1000°C MA956 sample was because of splashing from the slag melting pan). However, the surface temperatures of the alloys in all tests were below the solidus temperature of the slag, so immediately adjacent to the alloy, the slag was frozen into a very high viscosity aluminosilicate glass with some intermittent crystallization, primarily of iron oxide-rich species. In all tests, the ribbon of slag frozen to the surface fell off upon cooling. In the case of the MA754, the slag ribbon broke from the alloy at the slag–chromia interface, leaving no slag behind and removing a small amount of chromia in the slag that spalled off on cooling. The chromia content of the frozen slag increased as the slag flowed around the tube. During operation of a power plant, temperature cycling would be expected, so the loss of the chromia with the slag upon cooling would be detrimental to alloy lifetime because the chromia layer provides protection and reduces the oxidation rate of the alloy. Figure 3 is an SEM image of a cross section of the surface of the MA754 tube directly below the spot on which the slag dropped after the test at 1200°C. It shows 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 constituents dissolved into the alloy but that a small amount of the chromia did dissolve into the adjacent slag.

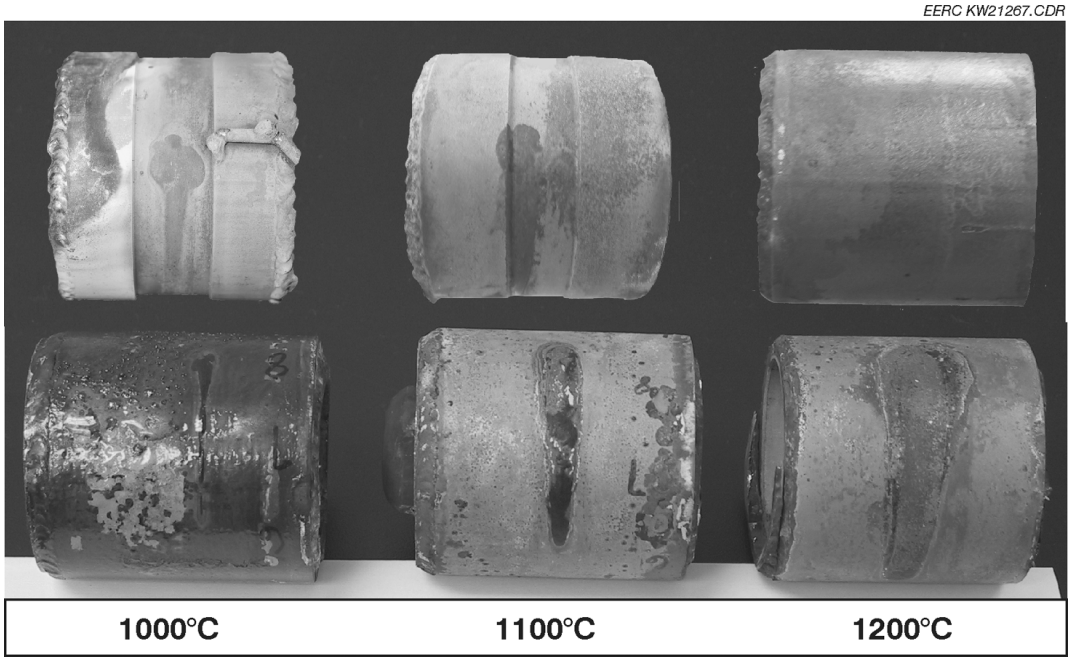

Figure 2. The surfaces of the MA754 (top row) and MA956 (bottom row) tube sections after flowing slag corrosion testing in the DSAF.

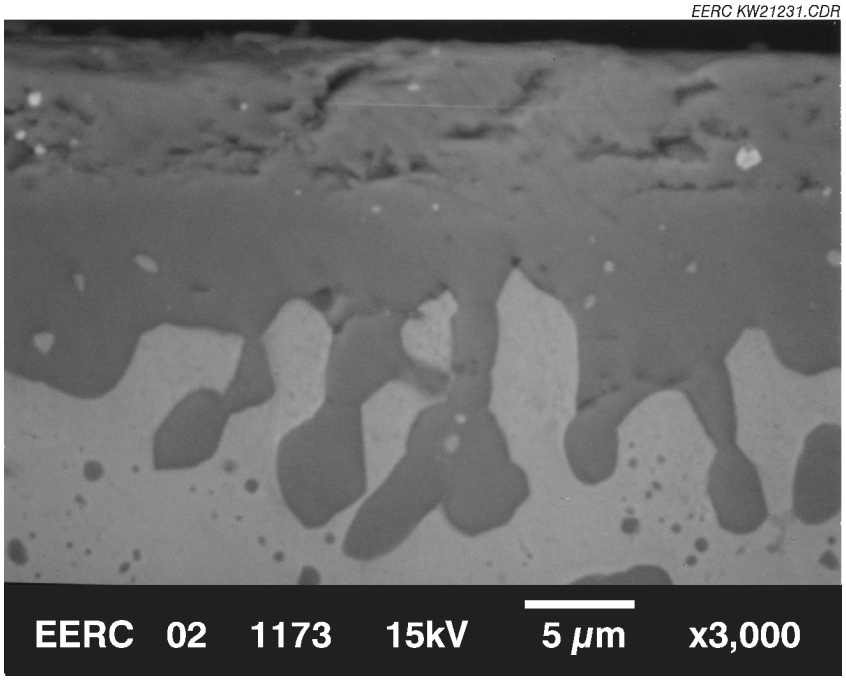

Figure 3. SEM image of a cross section of the surface of the MA754 tube directly below the spot on which the slag dropped after the test at 1200°C.

In contrast, during cooling of the MA956, 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 4 is an SEM image of a cross section of the surface of the MA956 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 the slag remaining on the surface was significantly enriched in alumina indicating that some of the alumina protective layer had dissolved into the slag, but that the slag that spalled off was not enriched. The intergrown fingers of alumina into the remaining slag 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 MA956 surface shows that the protective oxide layer is not lost through spallation during thermal cycling and that up to 1200°C no measurable alumina is lost into the spalled slag.

In addition to imaging the slag–scale interface, the SEM was used with energy dispersive x-ray analysis to measure the depletion of scale-forming elements as a function of depth within the alloys. The analyses were performed in 10-µm-square areas starting at the top of the scale and moving into the alloy perpendicular to the surface. Figure 5 shows a semilog plot of the concentration of chromium within the MA754 samples as functions of depth for the 1100° and 1200°C samples directly below where the slag was dropped, as well as for an unexposed sample, and just upstream of where the slag was dropped (no slag). The graph shows that, relative to the unexposed alloy, the samples corroded in the DSAF show a significant depletion of chromium down to a depth of approximately 400 µm below the slag at 1100°C and 500 µm at 1200°C. Significantly, the amount

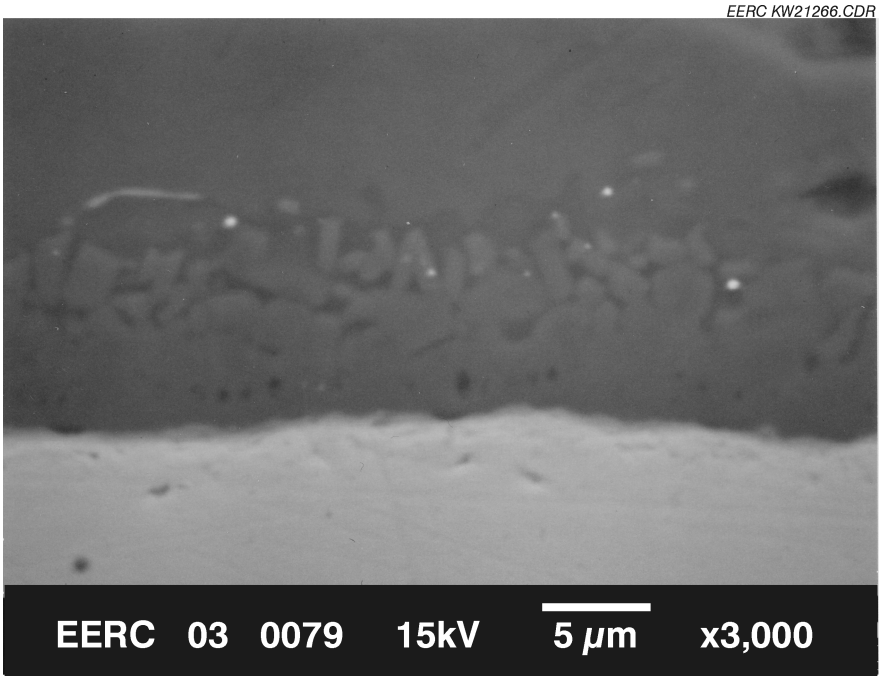

Figure 4. SEM image of a cross section of the surface of the MA956 tube directly below the spot on which the slag dropped after the test at 1200°C.

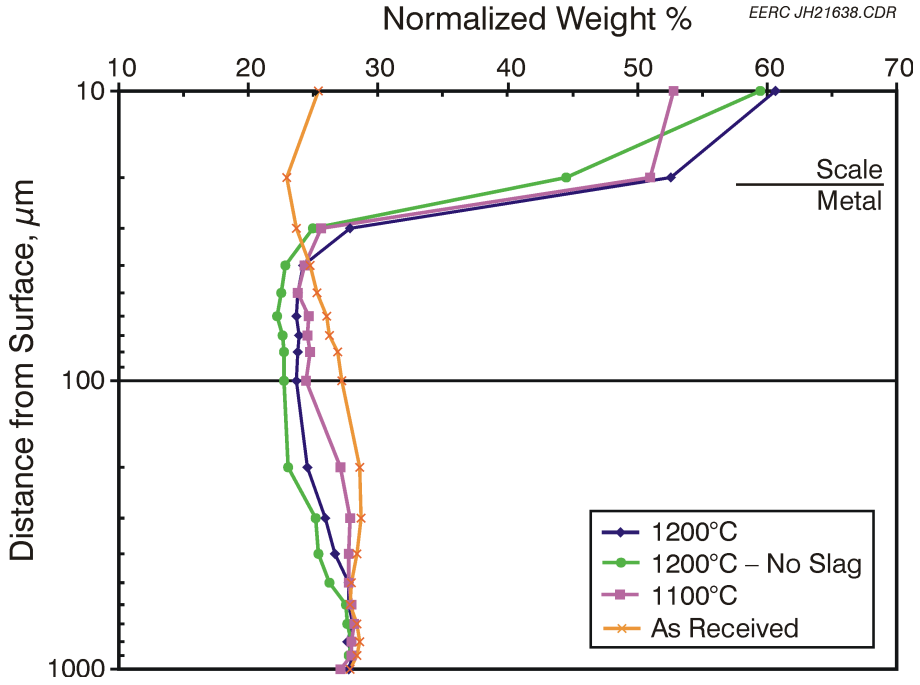

Figure 5. Chromium content in MA754 as functions of depth for an unexposed sample and two samples exposed in the DSAF.

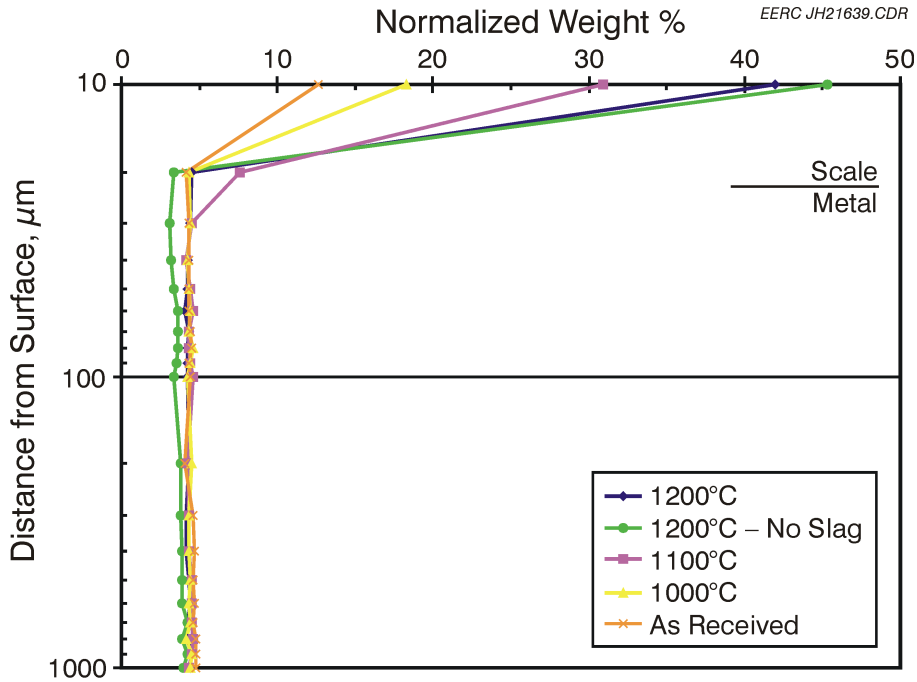

Figure 6. Aluminum content in MA956 as functions of depth for an unexposed sample and three samples exposed in the DSAF.

of depletion and depth of depletion is greatest at 1200°C where there is no slag, possibly indicating that the slag layer may protect the alloy by reducing the oxygen activity at the surface of the alloy.

Figure 6 shows a semilog plot of the concentration of aluminum within the MA956 samples as functions of depth for the 1000°, 1100°, and 1200°C samples directly below where the slag was dropped, as well as for an unexposed sample, and just upstream of where the slag was dropped (no slag). The graph shows that relative to the unexposed alloy, the samples corroded in the DSAF have a thicker alumina scale, but below the scale and the slag, there is no significant depletion of aluminum in the alloy in 100 h. In contrast, for the 1200°C sample upstream of where the slag was dropped, there is a small but measurable depletion of aluminum down to a depth of 100 µm. As may have been true for the MA754 samples, this may also indicate that the slag actually protects the alloy from oxidation by reducing the oxygen activity at the surface of the alloy.

SUMMARY AND CONCLUSIONS

The HiPPS Program testing of the UTRC original high-temperature heat exchanger enclosed in a ceramic box in the EERC slagging furnace system showed that it performed well, typically producing 954°C air at 150 psig for over 2000 h of operation. For a short duration, process air up to 1093°C was produced, which is believed to be a record for a coal-fired system. However, the ceramic panels were prone to failure through thermal shock and were significant impediments to heat flow. Subsequent testing of a

bare-tube design showed that removing the ceramic panels from the heat exchanger increases the heat removal rate by nearly a factor of five. This means that the heat exchanger could be as small as one-fifth of that originally proposed. Factoring in the price reduction due to the smaller size and lack of ceramic panels, the unprotected heat exchanger panel could cost as little as one-tenth as much as the original tubes-in-a-box design. Bench-scale testing of the resistance of two ODS alloys to corrosion by flowing slag showed that corrosion rates were very low and could not be measured by caliper over a 100-h test at temperatures up to 1200°C. Upon temperature cycling, the MA754 lost its slag coating along with a small amount of its protective chromia layer. The loss of the chromia layer will most likely reduce the lifetime of the alloy in cycling systems. In contrast, the slag remained attached to the MA956 alloy, indicating that temperature cycling should not shorten the lifetime of that alloy.

SEM analyses showed that relative to the unexposed alloy, the MA754 samples corroded in the DSAF show a significant depletion of chromium down to a depth of approximately 400 µm below the slag at 1100°C and 500 µm at 1200°C. Significantly, the amount of depletion and depth of depletion is greatest at 1200°C where there is no slag, possibly indicating that the slag layer may protect the alloy by reducing the oxygen activity at the surface of the alloy. A similar result was seen for the aluminum depletion in the MA956 sample at 1200°C. However, wherever slag covered the MA956 samples, no aluminum depletion could be measured in the alloy, showing that it may have a lifetime long enough to be commercially acceptable when used in an IFCC system.

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