

Fundamental Studies of the Durability of Materials for Interconnects in Solid Oxide Fuel Cells

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Objectives

- To develop mechanism-based procedures for evaluating the durability of solid oxide fuel cell (SOFC) interconnect materials, and to use these

procedures to study a group of alloys already identified as candidate interconnect materials.

- To gain an understanding of the fundamental aspects of the thermo-mechanical behavior of SOFC interconnect alloys, and to use this understanding to develop accelerated testing methods.
- To use the understanding and test methods developed from the first two objectives to propose and evaluate “new” alloys as SOFC interconnect materials.

Key Milestones

- Evaluated the cyclic oxidation resistance of three ferritic stainless steels (E-BRITE, AL 453 and Crofer) under a range of conditions pertinent to fuel cell operation.
- Initiated electrical conductivity measurements of oxide scales grown on ferritic stainless steels during cyclic oxidation.
- Utilized indentation testing to evaluate oxide scale adherence on specimens of ferritic stainless steels exposed in wet air and simulated anode gas, including chromate-coated specimens designed to reduce Cr contamination of other fuel cell components.

Approach

The University of Pittsburgh and Carnegie Mellon University, in collaboration with investigators at several DOE national laboratories, are teaming in a study directed at improving metallic interconnect materials for solid oxide fuel cells (SOFCs). Durable metallic interconnects are essential to the development of low-cost, lower operating temperature SOFCs. Durable metallic interconnects must maintain a consistent resistance over time, and resistance changes are related to the rate of growth and adherence of oxide scales forming on the alloys.

This recently-initiated program has three thrusts. The first is to develop mechanism-based testing procedures for evaluating the durability of interconnect materials, and to use these procedures to study a group of alloys already identified as candidate interconnect materials.

This involves developing procedures for evaluating the oxidation resistance of metallic interconnect materials which develop chromia scales during high-temperature exposure. Oxidation resistance in such alloys is tied to chromia/alloy interface reactions and transport in chromia, which determine chromia scale structure, growth rates and adhesion. The effects of simulated atmospheres (in addition to dry air) and the role of chromia evaporation are being investigated. Electrical resistivity is also being measured to tie oxidation resistance to conductivity changes due to thermal exposure. Many of the procedures being used are based on successful application by the authors in the area of thermal barrier coatings (TBCs), where many of the key issues are analogous to those being faced with SOFCs [1].

The second thrust is to investigate in-depth the fundamental aspects of the thermo-mechanical behavior of SOFC interconnect alloys. The failure event linked to a loss of oxidation resistance is the spallation or decoherence of the chromia scale, which in turn can greatly increase the resistance of an interconnect in a cell stack. The energy driving chromia scale spallation is determined by its residual stress and thickness, and the resistance to spallation is determined by the toughness or adhesion of the chromia/alloy interface. Oxide thicknesses are being measured via sectioning and microscopy and residual stresses are being measured by x-ray diffraction. Mechanical testing (e.g. indentation tests) is being used to measure interface adhesion. It is expected that losses in adhesion due to short-term high temperature exposures can be used to infer a loss of spallation resistance from long-term high temperature exposures. The ultimate goal of this research is to use knowledge of changes in oxide thickness, stress, and adhesion to develop accelerated testing methods for evaluating SOFC interconnect alloys.

The third thrust of this program is to investigate the potential use of “new” metallic materials as interconnect materials, where knowledge and test methods developed in the other areas will be used to rapidly evaluate candidate alloys. Alloys to be investigated will include materials based on pure nickel, materials based on the “Invar” concept, and coated materials to optimize properties in both the anode and cathode gases.

Results

The cyclic oxidation resistance of three ferritic stainless steels has been evaluated under a range of conditions pertinent to fuel cell operation. The alloys investigated are E-BRITE (26 Cr-1 Mo), AL 453 (22 Cr + Ce/La), and Crofer. Thus far, specimens have been exposed using 1-hour cycles at 900 °C to rapidly obtain comparative results; however, 1-hour cyclic tests at the more realistic operating temperature of 700 °C have been initiated. Specimens have been exposed in dry air (simulated cathode gas), air with 0.1 atm H₂O, and (simulated anode gas) Ar/H₂/H₂O (P_{O₂} = 10⁻¹⁷ atm).

The exposure apparatus used for these exposures is shown schematically in Figure 1. Figure 2 presents typical weight change versus time data for duplicate specimens of the three alloys exposed in dry air. Similar data were generated in the other atmospheres. Extensive microstructural analysis has been performed for all the exposed specimens. The results of the cyclic oxidation tests may be summarized as follows:

- All three alloys formed continuous chromia scales in all three environments.
- E-BRITE exhibited similar oxidation kinetics in all three environments, with small amounts of oxide spalling observed.
- AL 453 and Crofer exhibited oxidation rates similar to E-BRITE in dry air and simulated anode gas, but exhibited greatly accelerated oxide growth in wet air (0.1 atm H₂O).
- The oxide thicknesses for these alloys were consistent with weight change data.
- No oxide spallation from Crofer was observed in any of the environments.

The area specific resistance (ASR) of the oxide scales formed at 900 °C were measured by Dr. Chris Johnson at NETL, Morgantown. To make the electrodes for conductivity measurements, about half a micron of platinum was sputtered onto the surfaces. Platinum paste was used to hold down a small piece of platinum mesh, onto which silver wires were welded. Conductivity measurements were made at 900 °C, and when the voltage drop stabilized, the temperature was dropped in 50 °C increments to 700 °C. The voltage drop across the samples was recorded for each temperature. The current was constant at 10mA.

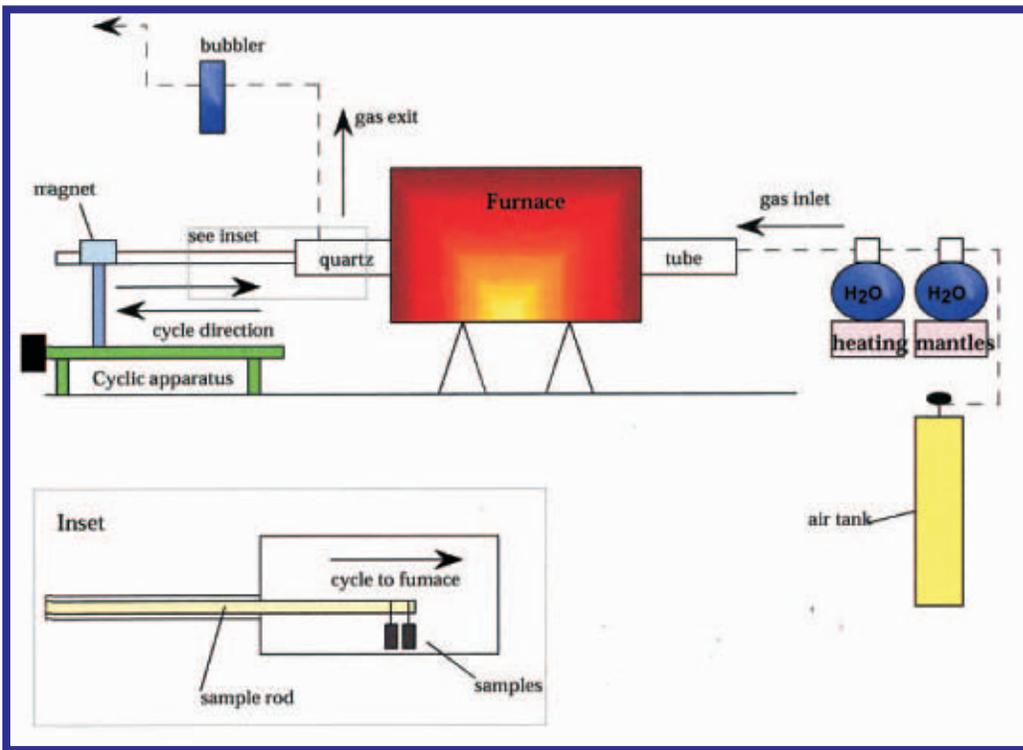


Figure 1. Diagram of the Cyclic Oxidation Exposure Apparatus.

Time vs. Mass Change / Area for Crofer, E-brite, and AL453 Samples (900°C, Dry Air)

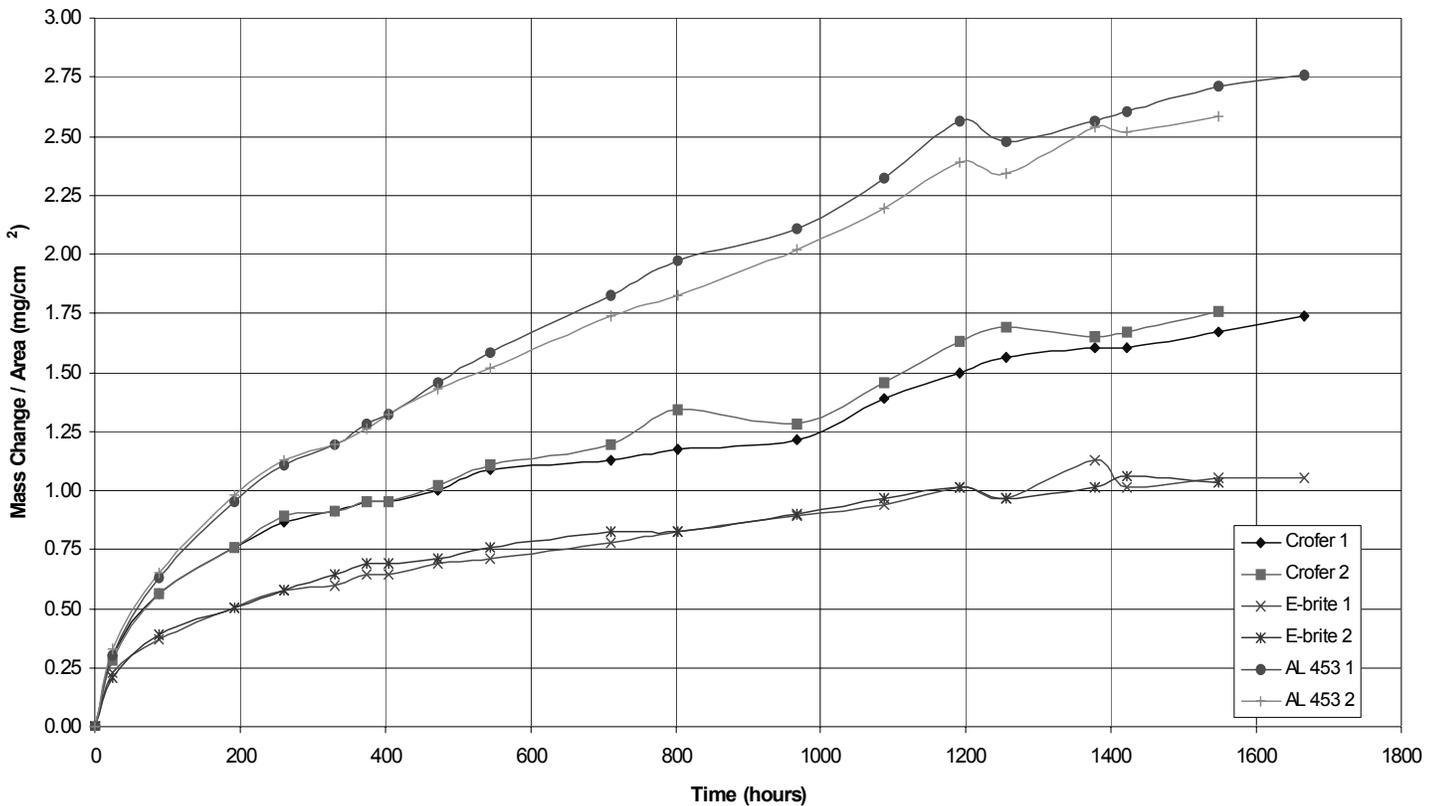


Figure 2. Cyclic Oxidation Results for Dry Air Exposures at 900 °C.

Crofer in air + 0.1 atm H₂O at 900 °C after 2,005 hours had an oxide thickness of 14-26 mm and an ASR at 900 °C of 1.301 ohms cm², which increased to 4.550 ohms cm² at 700 °C. AL 453 in dry air at 900 °C after 2,000 hours had an oxide thickness of 4-8 mm and an ASR at 900 °C of 1.015 ohms cm². This increased to an ASR of 5.612 ohms cm² at 700 °C. Crofer in dry air at 900 °C for 2,000 hours had an oxide thickness of 11-15 mm and an ASR at 900 °C of 0.435 ohms cm². At 700 °C, the ASR increased to 2.061 ohms cm². AL 453 in Ar/H₂/H₂O at 900 °C for 822 hours had an oxide thickness of 2-5 mm and an ASR at 900 °C of 0.238 ohms cm². This increased to an ASR of 0.996 ohms cm² at 700 °C. E-BRITE in air + 0.1 atm H₂O at 900 °C after 2,005 hours had an oxide thickness of 8-15 mm and an ASR at 900 °C of 0.222 ohms cm². At 700 °C, the ASR increased to 1.193 ohms cm². Crofer in Ar/H₂/H₂O at 900 °C after 2,000 hours had an oxide thickness of 5-11 mm and an ASR at 900 °C of 0.054 ohms cm², which increased to 0.204 ohms cm² at 700 °C.

The oxide scales were nonuniform in thickness but average thicknesses were used to compare the resistivity of the oxide scales on Crofer and E-BRITE after exposure in wet air. The resistivities, calculated at 700 °C, were 2500 and 1000 ohm-cm for Crofer and E-BRITE, respectively.

An indentation technique has been used to evaluate the adherence of chromia scales on specimens of E-BRITE exposed in air and simulated anode gas, and of chromate coatings designed to reduce Cr evaporation. Details of the mechanics of the test and its application to TBC systems can be found in references [2] and [3]. A schematic of the technique applied to oxide scale

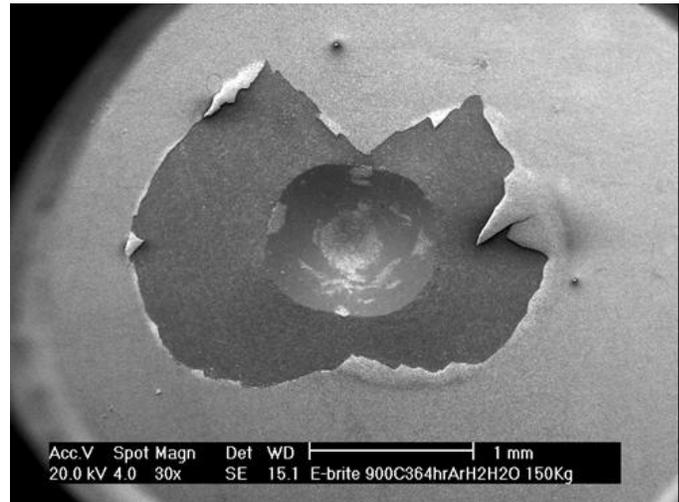
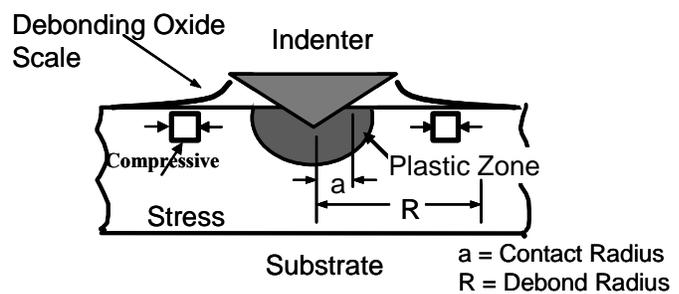


Figure 3. Schematic Diagram of the Indentation Test for Determining Interfacial Fracture Toughness in Oxide Scale Systems and a Typical Debond Induced in an E-BRITE Specimen Exposed to Simulated Anode Gas.

systems and a typical indent are presented in Figure 3. Indentation (currently by a conically-shaped brale indenter) produces plastic deformation in the substrate and compressive radial strains. Radial strains are transferred to the oxide scale, acting to drive oxide delamination. The radial extent of the oxide debonding produced by the indentation can be used as a measure of the oxide adherence to the substrate. The analysis of indentation data to date has indicated the following:

- Significant differences are seen in air with 0.1 atm H₂O vs. simulated anode gas (SAG) exposures at 900 °C at early times (100-264 hrs).
- These results are consistent with long-term weight change results, suggesting that indentation testing may be an effective means for accelerated evaluation of interconnect alloys.
- atm H₂O specimens show a non-uniform toughness, with the density of debonding decreasing with radial distance from the indent.
- SAG specimens show a peeling of an intact chromia scale, due to a thicker scale and/or poorer adhesion.
- SAG specimens also show an increase in debond size, from 264 to 364 hours of exposure, which could be due to an increase in scale thickness or loss of adhesion.
- Post-indentation heat-tinting of specimens has proven to be an accurate method for quantifying debond sizes in the SAG specimens.
- Chromate coatings show different resistances to debonding in the as-processed state, but debond resistance is consistently reduced with exposure.

Indentation model results, coupled with oxide thickness and XRD residual stress measurements will allow the tracking of interfacial toughness loss as a function of thermal exposure time. More specifically, the goal of combining these measurements is to gain an understanding of the dominant mechanisms leading to spallation. It is planned to use these testing techniques and the knowledge gained from them to develop accelerated testing protocols for SOFC interconnect materials. A key requirement is that the mechanism leading to spallation in the accelerated test (e.g. involving indentation-induced spallation, higher temperature exposures or higher cycling rates) must match that in the SOFC application.

Conclusions

Research completed thus far has already provided much-needed data on the oxidation resistance of three candidate interconnect alloys exposed to three different, simulative atmospheres at 900 °C. The response of each alloy was greatly affected by the testing atmosphere, and the most significant changes were seen in wet air exposures. Efforts are currently underway to perform weight gain measurements at 700 °C. The ASR for the scales formed at 900 °C, scaled approximately with oxide thickness. Indentation tests have been successful in inducing debonding of chromia scales on E-BRITE and debonding of chromate coatings in as-processed and exposed states. Differences in debonding behavior with short-term exposures are thus far consistent with observations from longer-term weight gain measurements for E-BRITE, suggesting the utility of indentation testing as an accelerated testing method. Coupling of indentation, stress and oxide thickness measurements will guide the development of accelerated test methods that capture long-term mechanisms causing durability loss.

References

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