Volume I

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

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ABSTRACT

This report describes the result of the first eight months of effort on a project directed at improving metallic interconnect materials for solid oxide fuel cells (SOFCs). The results include cyclic oxidation studies of a group of ferritic alloys, which are candidate interconnect materials. The exposures have been carried out in simulated fuel cell atmospheres. The oxidation morphologies have been characterized and the ASR has been measured for the oxide scales. The effect of fuel cell electric current density on chromia growth rates has been considered

The thermomechanical behavior of the scales has been investigated by stress measurements using x-ray diffraction and interfacial fracture toughness measurements using indentation. The ultimate goal of this thrust is to use knowledge of changes in oxide thickness, stress and adhesion to develop accelerated testing methods for evaluating SOFC interconnect alloys.

Finally a theoretical assessment of the potential for use of “new” metallic materials as interconnect materials has been conducted and is presented in this report. Alloys being considered 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.

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INTRODUCTION

Solid oxide fuel cells provide a potential way to generate electricity with high efficiency and low pollution. The operating principles of fuel cells have been known for over 100 years and low-temperature fuel cells provided the electric power on all the Gemini and Apollo spacecraft. However, fuel cells have not achieved widespread commercial use for a number of economic and technical reasons.

One of the most important technical challenges for solid oxide fuel cells, which operate in the temperature range 700-900°C, is the design of interconnects (current collectors). These components, in addition to drawing off the electric current, must separate the anode compartment of one cell from the cathode compartment of the adjacent cell. This means that one side of an interconnect is exposed to the fuel, typically hydrogen or hydrocarbons in which the oxygen partial pressure is low, and the other side is exposed to the oxidant, which is typically air. The requirements for interconnects have been reviewed recently [1,2]. Interconnect material requirements include a variety of physical, chemical, and electrical properties. The optimal interconnect material would have the following properties:

1. Low electrical resistivity.
2. Impermeability to anode and cathode gases.
3. Stability in both anode and cathode gases under thermal cycling conditions.
4. Chemical compatibility with other cell components.
5. Close match in coefficient of thermal expansion with other components.
6. Good mechanical properties.
7. High thermal conductivity.
8. Ease of fabrication.
9. Low cost.

Ceramic interconnects usually have favorable values of properties 2, 3, 4, and 5. However, they are usually deficient in the other desired properties. Metallic interconnects are attractive in that they have favorable values of properties 2, 6, 7, 8, and 9. Metallic materials also have low electrical resistance but they react with the gases to form oxide layers, which generally have high electrical resistivity. Oxidation resistant alloys are designed to form one of three protective oxides: alumina, silica, or chromia. Of these the electrical resistivities of alumina and silica are much too high for interconnect applications. Metals cover a range of thermal expansion coefficients but many are compatible with the ceramic components of SOFCs. Metals are usually stable in contact with the other cell components but this is not always the case.

Current Status of Metallic Interconnect Materials

A number of studies have been conducted on potential metallic interconnect materials, particularly with regard to their stability in the cathode and anode gases. Virtually all of these materials form chromia scales in both gases.

Cathode Gas

The cathode gas provides the oxidant for the cell and will generally consist of air. England and Vircar [3] oxidized thin foils of the commercial Ni-base alloys Inconel 625,

Inconel 718, Hastelloy X, and Haynes 230 in air under isothermal conditions at temperatures between 800 and 1100°C. All the alloys formed scales consisting essentially of chromia and the apparent parabolic rate constants varied over more than an order of magnitude e.g. between 1×10^{-15} and $2.8 \times 10^{-14} \text{ g}^2/\text{cm}^4\text{s}$ at 800°C. Such isothermal data must be supplemented for applications in which the temperature is cycled. Figure 1 shows data for a similar group of chromia-forming alloys [4] which exhibit a wide range of behavior under thermal cycling conditions. These data also illustrate an important point that extrapolation of short term test data to long term behavior is difficult: after 180 days ($\approx 4000 \text{ h}$) there are no apparent differences in the oxidation kinetics of the three alloys whereas at longer times profound differences develop. **Clearly, oxidation testing must be done under cyclic conditions and a mechanism-based accelerated testing protocol is needed for interconnects in SOFCs.**

Quadakkers et al [5] have studied chromium-based alloys since they have lower coefficients of thermal expansion than the nickel based alloys. The addition of a Y_2O_3 dispersion improved the mechanical strength and lowered the oxidation rates of the

Figure 1 Long term cyclic oxidation data for three chromia forming alloys in air at 982°C from Ref. 4.

alloys. A significant problem with Cr (and chromia-forming alloys) which has been recognized for many years [6] is the reactive evaporation of chromia scales. This is a particular problem in the cathode gas since the CrO_3 partial pressure increases with oxygen partial pressure, as illustrated in Figure 2 [7]. The volatile species are reduced at electrochemically active sites on the cathode during SOFC operation, which inhibits the

required oxygen reduction [8]. Analysis of the Cr vapor species [9] indicates water contents above about 0.1% in air result in partial pressures of $\text{CrO}_2(\text{OH})_2$ which exceed the partial pressure of CrO_3 . Thus, maintaining the cathode gas as dry as possible is desirable. **Notwithstanding, the issue of evaporation of Cr-containing species must be addressed.**

A number of investigators have studied the behavior of ferritic stainless steels as interconnect materials since they have a good thermal expansion match with typical ceramic components of SOFCs. Huang et al [10] studied the isothermal oxidation of ferritic Fe – 26 wt% Cr alloys in air reporting a k_p of $8.8 \times 10^{-14} \text{ g}^2/\text{cm}^4\text{s}$ at 800°C . Brylewski et al [11] reported a similar value of $8.5 \times 10^{-14} \text{ g}^2/\text{cm}^4\text{s}$ for Fe-16 wt% Cr. Quadakkers et al [12, 13] have developed model alloys based on the philosophy of:

- i. Using La additions to slow the growth rate of the chromia scale and improve the adherence of the scale to the alloy.
- ii. Making additions of Ti and Mn to form spinels on the chromia scale to reduce CrO_3 evaporation.
- iii. Maintaining Al and Si levels as low as possible to prevent the formation of electrically insulating alumina or silica layers.

(The last point is quite important in that many commercial Fe- and Ni-base alloys, which are nominally chromia-formers, contain sufficient Al and/or Si so that, under certain exposure conditions, alumina or silica can form between the chromia layer and the alloy.)

Coatings of $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$ have also been applied to ferritic alloys to limit CrO_3 evaporation [14].

The ASR was reported in Ref. [10] for scales formed during 24 hour exposures in air at 900°C . The ASR measured at 900°C with Ag electrodes was on the order of $0.02 \Omega\text{cm}^2$. Quadakkers et al [12] performed in-situ measurements of the ASR of chromia scales forming on one of the modified ferritic alloy alloys described above. The ASR after 100 hours of oxidation was approximately $0.01 \Omega\text{cm}^2$ and increased to approximately $0.1 \Omega\text{cm}^2$ after 8000 hours.

The ferritic alloys have suitable potential to justify studies to optimize their properties as SOFC interconnects.

Figure 2. Vapor species diagram for the Cr-O system at 1250 K from Ref. 7.

Anode Gas

The anode gas consists of the fuel (typically hydrogen or hydrocarbons) and the products of combustion (water vapor and, possibly, CO and CO₂). England and Vircar [15] oxidized thin foils of the commercial Ni-base alloys Inconel 625, Inconel 718, Hastelloy X, and Haynes 230 in hydrogen, which was saturated with water at 40°C under isothermal conditions at temperatures between 700 and 1100°C. The growth rate of the chromia scales at 800°C were higher than those observed in air [3] for the same alloys and the electrical resistance of the scales was higher than for those formed in air.

Quadakkers et al [16-18] have studied pure Cr and yttria-dispersed Cr at 950 and 1000°C in Ar/H₂/H₂O mixtures. They too observed larger mass gains in H₂/H₂O mixtures but correctly point out that this is the result of mass losses from CrO₃ evaporation in air, which are minimal at the reduced oxygen partial pressures in H₂/H₂O mixtures. One rather surprising result of this study was that the chromia scales were substantially more adherent when formed in H₂/H₂O mixtures than in dry air. It is well

documented that spallation of alumina scales is accelerated by water vapor [19] so these results for chromia are in need of further study.

Quadakkers et al reported the chromia scales formed on ferritic stainless steels in simulated anode gas at 800°C were thinner than those formed in air [12, 13]. Brylewski et al [11] reported similar values of k_p for oxidation in 94H₂/6H₂O and air.

If hydrocarbons, e. g. natural gas, are used in place of hydrogen as the fuel in an SOFC, the presence of carbon can result in additional reactions with the interconnect materials. In stainless steels and superalloys carbon results in the formation of carbides based on chromium and other alloying elements. Excessive carburization can result in the removal from solution of protective elements such as chromium. This can seriously reduce the corrosion resistance of the component, particularly at grain boundaries. This is illustrated in Figure 3 [20]. The oxidation of Fe-15Cr is very slow in pure O₂ because it forms a continuous chromia film. However, in CO₂ the oxidation rate is rapid because the Cr is tied up as carbides and a scale of iron oxides forms even though the oxygen partial pressure is low.

If the hydrocarbons are injected directly into the cell, carbon deposition can occur. If deposition does not occur conditions are set up which can allow a very serious, often catastrophic, form of degradation known as metal dusting [21, 22]. In this reaction, the carbon activity in the gas must be greater than unity and it appears that the carbon from the atmosphere gas species dissolves into the metal faster than it can nucleate as soot on the metal surface. This produces high carbon activities in the metal and leads to the growth of metastable carbides, which subsequently decompose to a powdery product. These reactions occur typically in the temperature range 450-800°C.

Much of the work on the dusting attack of alloys has been carried out on nickel and iron based stainless systems similar to those used in reforming reactions where the phenomenon is a significant problem [23 –25]. The reaction is also dangerous in that it can lead to the perforation of tubes and thin sheets very rapidly, within a few hours, and it is found generally where metal components are in contact with gases which are typically CO-H₂ mixtures or atmospheres containing organic gases. Because the carbon activity of the atmosphere exceeds unity and because of the difficulty in nucleating graphite on the metal surface, without a catalyst, it is possible for metastable carbides of the type M₃C and M₂₃C₆ to form. These metastable carbides later decompose to metal and carbon. Thus, the corrosion products of metal dusting attack are powdery mixtures of fine metal powder and carbon. The alloy is quite uniformly attacked in the case of low alloy steels, but involves pitting in the cases of alloy steels and nickel based alloys.

Metal dusting of iron proceeds in five stages. (1) carbon dissolves in the metal to a degree of supersaturation. (2) cementite precipitates at the metal surface and in grain boundaries. (3) graphite deposits from the atmosphere on to the cementite. (4) the cementite begins to decompose forming graphite and metal particles. (5) further graphite deposition proceeds, catalyzed by the metal particles. Similar mechanisms are thought to be valid for low alloy steels.

In the case of alloys that contain high concentrations of chromium, a protective scale is formed of chromium oxides. Where this scale fails locally, the dusting sequence can proceed. This results in the formation of a pitted surface, beginning with small pits which widen to larger hemispherical sites with time. It is feasible that, if the chromia scale could be made more stable, the alloy would show improved resistance to metal

dusting. It should be recognized, however, that this increased resistance is not stable and that failure would be swift, once the sequence of dusting is begun. Pure chromium and chromium-based alloys have been found to be quite resistant to metal dusting [25].

There is a clear need to evaluate potential interconnect materials for their susceptibility to carburization and metal dusting and to determine the effects of water vapor on the oxidation kinetics and oxide properties.

Figure 3. Effect of CO₂ on the isothermal oxidation rates of Fe-Cr alloys Ref. 16.

EXECUTIVE SUMMARY

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 report describes the results of the first eight months of this project.

This 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.

The cyclic oxidation behavior of three ferritic alloys (E-Brite, AL 453 and Crofer22 APU) has been measured in an accelerated test using 2000 one-hour thermal cycles at 900°C. (This test is designed to give similar amounts of oxide growth as exposures at 800°C lasting for approximately 20,000 hours.) Three exposure atmospheres were used: simulated anode gas (SAG), simulated cathode gas, and air+10% H₂O (to simulate cathode gas if there was a small amount of seal leakage). The most severe degradation was observed in air+10% H₂O, which produced severe scale spalling from E-brite and excessively rapid scale growth on Crofer and AL 453. The degradation microstructures and oxide thicknesses for all the alloys have been carefully characterized. Cyclic exposures at 700°C are now in progress.

The area specific resistance (ASR) for the specimens exposed at 900°C was measured by Dr. C. Johnson at NETL. The ASR scaled essentially with scale thickness. Calculations to evaluate the effect of electric current flow on the growth of chromia scales on the interconnects have been performed. These indicate the current flow will accelerate oxide growth on the anode side and retard it on the cathode side. Under some conditions these effects can be considerable and should be investigated experimentally.

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. In this thrust, 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 thrust is to use knowledge of changes in oxide thickness, stress and adhesion to develop accelerated testing methods for evaluating SOFC interconnect alloys.

The goal of first year indentation testing and modeling has been to confirm the potential of the test method in characterizing the adhesion of SOFC interconnect alloy interfaces. Specifically, testing has been performed on exposed bare alloys and alloys with chromite coatings applied to them as a means of controlling chromia evaporation. The testing approach shows much promise. It has been successful at inducing debonding in uncoated and coated chromia scale systems and has highlighted differences in adhesion in uncoated specimens exposed in wet air and SAG environments. It has also demonstrated changes in adhesion behavior with exposure in uncoated and coated systems. Methods for analysis of the tests (extracting debond sizes or debond density distributions) have been established and preliminary modeling work has been completed to allow quantitative results to be extracted from the tests. Modeling work will combine results from the indentation tests, thickness measurements and XRD stress measurements to give insight into dominant mechanisms leading to scale spallation. This is a critical step in the development of accelerated test methods for 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 thrusts 1 and 2 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. The Phase I activities have involved a theoretical assessment of these systems, which is presented in this report.

A supplemental benefit of this grant is the education of a significant number of students with knowledge of fuel cell technology. The SECA grant is supporting one graduate student at the University of Pittsburgh and one at Carnegie Mellon University. One undergraduate Senior Design Project is being supported each year at the University of Pittsburgh. An additional graduate student is being supported at the University of Pittsburgh on an NETL Partnership Fellowship. This student is conducting research on coatings, which will constitute an extension of the first and second research thrusts, mentioned above. Dr. Christopher Johnson is serving as his NETL Mentor.

PROJECT DESCRIPTION

The University of Pittsburgh and Carnegie Mellon University, in collaboration with investigators at several National Laboratories, are teaming in a study directed at improving interconnect materials for solid oxide fuel cells (SOFCs). The program has three major thrusts. The first is to develop mechanism-based evaluation procedures for the durability of interconnect materials and to use these procedures to study and modify a group of alloys, which have already been identified as candidate interconnect materials. This involves studies of interface reactions in fuel cells for which the electrical characteristics have been established during operation and the development of procedures for evaluating the behavior of metallic interconnect materials which develop chromia scales during high-temperature exposure. This includes studies of “Growth Rates of Chromia Scales on Cr and Ferritic Alloys”, “Adhesion of Chromia Scales”, “Complex Atmosphere Testing”, and “Oxide Evaporation”. Many of the procedures being used are based on their successful application by the PIs in the area of Thermal Barrier Coatings where many of the key issues are analogous to those being faced with SOFCs.

The second thrust is to investigate the fundamental thermo-mechanical aspects of SOFC interconnects and coatings applied to the interconnects. This involves “Stress Measurement by X-ray Diffraction” and “Indentation Testing of Interface Adhesion” and development of “Accelerated Testing Procedures”.

The third thrust is to investigate the potential for the application of “new” metallic materials as interconnect materials. These 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.

A supplemental benefit of this grant will be the education of a significant number of students with knowledge of fuel cell technology. The SECA grant is supporting one graduate student at the University of Pittsburgh and one at Carnegie Mellon University. One undergraduate Senior Design Project is being supported each year at the University of Pittsburgh. In addition, an additional graduate student is being supported at the University of Pittsburgh on an NETL Partnership Fellowship. This student, Mr. Scot Laney, is conducting research on coatings, which will constitute an extension of the first and second research thrusts, mentioned above. Dr. Christopher Johnson is serving as his NETL Mentor.

EXPERIMENTAL

Cyclic Oxidation

The cyclic oxidation of three ferritic stainless steels has been evaluated under a range of conditions pertinent to fuel cell operation. The alloys were: (Compositions in Wt%)

- E-BRITE (Fe-26 Cr-1 Mo - 0.2 Si)
- AL 453 (Fe-22 Cr-0.6 Al-0.3 Mn + 0.1Ce/La)
- Crofer22 APU (Fe-22Cr-0.5Mn-0.08 Ti-0.016P-0.06 La)

The exposure conditions included:

- T = 900°C and 700°C
- One-Hour Cycles (45 min. hot, 15 min.cold)
- Atmospheres
 - Dry Air (Simulated Cathode Gas)
 - Air + 0.1 atm H₂O (Simulated Moist Cathode Gas)
 - Ar/H₂/H₂O (Simulated Anode Gas)(p_{O2} = 10⁻¹⁷ atm at 900°C and 10⁻²⁰ at 700°C)

The exposure apparatus used for these exposures is shown schematically in Figure 4

Figure 4 Schematic diagram of the apparatus used for cyclic oxidation exposures with controlled partial pressures of water vapor.

Coated Specimens

Coated specimens have been tested using the indentation technique described below in the as coated condition. The specimens consist of a sputtered LaCrO_3 (some were also Sr doped) layer on ferritic and Ni based alloy substrates. The substrates are as follows:

- E-Brite (same as above)
- AL 453 (same as above)
- 29-4C (29Cr, 4 Mo, 0.5 Mn, 0.3 Ni, 0.35 Si)
- Type 446 stainless steel (similar to E-Brite)
- Inconel 600 (Ni based, 14-17 Cr, 6-1 Fe, max 1 Mn)

X-ray diffraction showed that these coatings are amorphous in the as coated condition. E-Brite and T-446 specimens were exposed in a dry air (simulated cathode gas) atmosphere at 900°C for 100 hours to crystallize the coating and to form a chromia layer. These specimens were then indented. The results are described below.

Indentation Testing

The use of indentation as a means for inducing chromia scale spallation from interconnect alloys builds upon previous research by the PIs involving indentation of thermal barrier coating (TBC) systems [26, 27]. Testing goals in TBC and interconnect alloy systems are similar, where an understanding of mechanisms leading to coating spallation is needed, as are methods for accelerating cyclic thermal testing to evaluate new coating/substrate systems.

The test for SOFC interconnects currently involves indenting the specimen using a Rockwell hardness tester and a conically-shaped brale indenter. The chromia scale is penetrated by the indenter and the interconnect alloy substrate is plastically deformed. This plastic deformation induces compressive radial strains in the substrate, which are transferred to the chromia scale (there is a match of in-plane strains across the interface). This causes an axisymmetric region of spallation, either in the form of intermittent flaking of the scale or as an intact peeling of the scale from the substrate. The radial extent of the debonding or its density as a function of radial distance can be related (through fracture modeling) to the fracture toughness or distribution of fracture toughness of the chromia/alloy interface. Micrographs of debonds resulting from indentation are given in the section on Indentation Testing of Interface Adhesion.

This type of test can be applied to other brittle coating systems deposited or grown on comparatively ductile substrates. As part of this program, chromite-coated interconnect alloys are being tested, where indentation can induce spallation of the chromite coating and a chromia layer growing beneath it. Similarly, this type of test may be applicable to the testing of other SOFC interfaces, such as those between sealant glasses and interconnect materials and those between electrolyte and anode layers in anode-supported cell structures. Finally, although the concept is the same, use of different indenter shapes and sizes will yield different indentation strain fields and different types of debonding behavior. As part of this program, the PIs will consider changes in indenter shapes and sizes to optimize the testing of interconnect alloy systems.

To date, indentation testing has been performed for the following alloy systems and exposure conditions, which parallel cyclic oxidation experiments described above:

- E-BRITE in Air + 0.1 atm H₂O: 100 Hrs. and 200 Hrs. @ 900°C
- E-BRITE in Ar/H₂/H₂O (SAG): 264 Hrs, 364 Hrs. and 464 Hrs. @ 900°C
- La_{0.8}Sr_{0.2}CrO₃ on E-BRITE, AL 453 and AL 29-4C (from PNNL): As Processed
- LaCrO₃ on Inconel and SS 446 (from Drexel/NETL): As Processed
- La_{0.8}Sr_{0.2}CrO₃ on E-BRITE and LaCrO₃ on SS 446: 100 Hrs. @ 900°C
- Indentation tests on interconnect specimens exposed at 700°C is currently underway.

A full description of these tests and their relation to cyclic oxidation testing is provided in the sections on Indentation Testing of Interface Adhesion and Accelerated Testing

Conductivity Measurements

The area specific resistance (ASR) of the oxide scales formed at 900°C was 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.

RESULTS AND DISCUSSION

Task 1. Mechanism-based Evaluation Procedures

Task 1.1 Characterization of Exposed Fuel Cell Interfaces

There has been little progress made on this subtask because of the unavailability of specimens from actual cells.

Task 1.2 Growth Rates of Chromia Scales on Cr and Ferritic Alloys

This section will also describe results from Task 1.3 as the oxidation tests were carried out under cyclic conditions.

Cyclic oxidation at 900°C

The experiments at 900°C were designed as *accelerated tests*. The duration of the test was 2000 cycles, which corresponded to the specimens being at 900°C for 1500 hours (i.e. hot time). Based on the temperature dependence of the parabolic rate constants reported for oxidation of Fe-26 wt% Cr in air [10], exposure for 1500 hours at 900°C should result in a chromia scale thickness comparable to that formed after about 16,000 hours at 800°C. Thus, if one can assume the same oxidation mechanisms at 800 and 900°C, these experiments should simulate an exposure at 800°C for 16,000 hours of hot time. In the latter case 2000 cycles would correspond to the specimen being cycled to room temperature with a frequency of approximately twice per day. Since cyclic degradation can depend on cycle frequency, it is not clear how many cycles at 800°C would produce similar degradation. Correlation between the accelerated test with operating conditions is an ongoing theme of this project.

The oxidation kinetics for exposure in dry air (simulated cathode gas) are presented in Figure 5. The mass gains for Crofer22 APU correspond to literature values for the isothermal oxidation of ferritic alloys in air [10] while the mass gains for E-brite are somewhat smaller and those for Al 453 are somewhat larger. The oxidation curves do not give evidence for substantial scale spallation.

Figure 6 presents the corresponding oxidation kinetics in simulated anode gas. The mass gains for E-brite and Crofer are similar and are similar to those reported for isothermal oxidation of ferritic alloys in hydrogen-water vapor atmospheres [11]. The mass gains for AL 453 are larger.

Figure 5. Weight Change Vs Time plots for duplicate specimens of three ferritic alloys exposed in dry air (simulated cathode gas) at 900°C using one-hour cycles.

Figure 6. Weight Change Vs Time plots for duplicate specimens of three ferritic alloys exposed in Ar/H₂/H₂O (simulated anode gas) at 900°C using one-hour cycles.

Figure 7 presents the oxidation kinetics in air containing 10% water vapor. This gas does not directly simulate a planned fuel cell atmosphere. However, in the event of the use of air, which has not been dried or small seal leakages it is not unreasonable to anticipate that the cathode gas may contain water vapor in some situations. The mass changes for E-brite are similar to those in dry air. However, the mass gains are far larger

for Crofer and AL 453 than those observed in either of the other two atmospheres. These observations are consistent with measurements of oxide thickness (presented in Table 1) and metallographic observations to be described below.

Figure 7. Weight Change Vs Time plots for duplicate specimens of three ferritic alloys exposed in air + 10% H₂O (simulated moistened cathode gas) at 900°C using one-hour cycles.

Alloy	Atmosphere	Time (hours)	Average Oxide Thickness (μm)	Calculated Δm/A (mg/cm ²)	Measured Δm/A (mg/cm ²)
Crofer	Ar/H ₂ /H ₂ O	2000	8	1.3201	2.1916
Crofer	dry air	2000	13.5	2.2276	1.9964
Crofer	air + 0.1atm H ₂ O	2005	20	3.3001	11.2230
E-brite	Ar/H ₂ /H ₂ O	2000	8.75	1.4444	2.5033
E-brite	dry air	2000	7.5	1.2375	1.0790
E-brite	air + 0.1atm H ₂ O	2005	11.5	1.8976	0.7079
AL453	Ar/H ₂ /H ₂ O	2000	4.5	0.7425	3.4825
AL453	dry air	2000	6	0.9900	3.0840
AL453	air + 0.1atm H ₂ O	2005	8.5	1.4025	6.1166

Table 1: Comparison of oxide thicknesses and weight gains per area for three ferritic alloys exposed in Ar/H₂/H₂O, air, and air + 10% H₂O

Figure 8 presents cross-section micrographs of E-brite after exposures in all three atmospheres at 900°C. The scales are similar and are consistent with the similar oxidation kinetics observed in the three environments. The external scale consists of Cr_2O_3 and there is a fine distribution of Al-rich precipitates in the alloy below the scale. Aluminum is not listed as a component of E-brite but must be present as a dilute impurity. Figure 9 shows more detail of the alloy/scale interface for E-brite. There is a substantial amount of silica at this interface. It is not clear if this phase was responsible for the lack of acceleration of scale growth for exposures in air + 10% H_2O . However, it is believed that oxide spallation is primarily responsible for the thinner scales observed on E-brite in this atmosphere. Figure 10 shows a macroscopic surface photograph of E-brite after 847 cycles showing circular spalled areas. Other areas were also observed where there were circular areas of thin oxide, which appeared to have reformed in spalled areas on subsequent cycles. Spalling is also consistent with the data in Table 1. The experimental mass gain for E-brite in wet air is substantially smaller than that calculated from the oxide thickness.

Figure 8. Cross-section micrographs of E-brite after exposure in three different atmospheres at 900°C.

Figure 9. Cross-section micrographs of E-brite after exposure in three different atmospheres at 900°C showing details of the alloy/scale interface

Figure 10. Macroscopic photograph showing freshly spalled and re-grown areas on the surface of E-brite (847 cycles, 1/10atm H_2O)

Figure 11 presents cross-section micrographs of Crofer after exposure in all three environments. The specimen exposed in dry air had a continuous layer of MnCr_2O_4 at the scale/gas interface with a chromia layer beneath. Figure 12 indicates some internal oxidation below the chromia layer. These oxides were found to be Al-rich, although Al is not listed as an intentional component of this alloy. The specimen exposed in wet air exhibited a very thick scale, which is consistent with the large mass gain in this atmosphere. However, The MnCr_2O_4 is present as discontinuous particles at the scale/gas interface rather than as a continuous layer. Figure 13 shows a macroscopic photograph of a Crofer specimen oxidized in wet air. This specimen is severely warped, presumably because of the extensive oxidation. Specimens exposed in dry air and simulated anode gas did not exhibit this deformation. The specimen exposed in simulated anode gas showed very little MnCr_2O_4 at the scale/gas interface and the chromia scale appeared somewhat 'friable'. The micrograph of this specimen in Figure 11 also shows an inclusion running parallel to the rolling direction of the sheet. This was identified as a La-rich oxide. Similar inclusions, as well as Ti-nitrides were found throughout the as-received alloy.

Figures 14 and 15 present cross-section micrographs of AL 453 exposed in the three environments. The striking feature in all environments is the extensive internal oxidation of Al below the chromia scale. Table 1 indicates the measured mass gain of this alloy in all three environments is substantially larger than that calculated from the thickness of the external scale. The oxygen uptake in forming the internal oxides is responsible for this difference. An additional feature of this alloy is the appearance of a layer of relatively pure Fe between the internal oxidation zone and the external chromia scale. The origin of this layer has not yet been determined. One possibility is extrusion of metal out from the zone of internal oxidation as the alumina precipitates form.

In summary, accelerated cyclic oxidation testing at 900°C has been investigated. The most detrimental environment was found to be air with 10% water vapor. This resulted in excessive oxide spallation from E-brite and rapid scale growth on Crofer22 APU and AL 453. These results indicate a need for the cathode gas to be dry, which will require highly effective seals in the fuel cells.

Figure 11. Cross-section micrographs of Crofer after exposure in three different atmospheres at 900°C.

Figure 12. Cross-section micrographs of Crofer after exposure in three different atmospheres at 900°C, showing more detail of the scales.

Figure 13. Macroscopic photograph of a Crofer specimen exposed in air +10% H₂O showing extensive warpage.

Figure 14. Cross-section micrographs of AL453 after exposure in three different atmospheres at 900°C.

Figure 15. Cross-section micrographs of AL453 after exposure in three different atmospheres at 900°C, showing more detail of the scales.

Cyclic Oxidation at 700°C

Figure 16 presents the mass change results for cyclic oxidation of E-brite, Crofer22 APU, and AL 453 in simulated anode gas at 700°C. These experiments are ongoing so no microstructural observations have been made.

Electrical Resistivity Measurements

The Area Specific Resistance for alloys exposed at 900°C are presented in Figure 17. Crofer in air + 0.1 atm H₂O at 900°C after 2005 hours had an oxide thickness of 14-26 µm and an area specific resistance (ASR) at 900°C of 1.301 ohms cm², which increased to 4.550 ohms cm² at 700°C. AL453 in dry air at 900°C after 2000 hours had an oxide thickness of 4-8 µm 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 2000 hours had an oxide thickness of 11-15 µm and an ASR at 900°C of 0.435 ohms cm². At 700°C, the ASR increased to 2.061 ohms cm². AL453 in Ar/H₂/H₂O at 900°C for 822 hours had an oxide thickness of 2-5 µm 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 2005 hours had an oxide thickness of 8-15 µm 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 2000 hours had an oxide thickness of 5-11 µm and an ASR at 900°C of 0.054 ohms cm², which increased

to 0.204 ohms cm² at 700°C. These results were qualitatively consistent with data in Ref. [12] for specimens exposed at 800°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.

Figure 16. Weight Change Vs Time plots for duplicate specimens of three ferritic alloys exposed in Ar/H₂/H₂O (simulated anode gas) at 700°C using one-hour cycles.

Effect of Electric Current on the Growth of Chromia Scales

Since the growth of an oxide generally involves the transport of charged particles, the growth of an oxide can be affected if an electric field is applied across its thickness, i.e. if an electric current is flowing in the oxide. In the case of fuel cell interconnects the current density, which should be on the order of one amp/cm², will accelerate the oxide growth on the anode side and retard it on the cathode side. A theoretical analysis of this problem, starting from Wagner's theory of parabolic oxidation [28], is presented in Appendix A. The results depend on the value used for the electronic conductivity of the chromia scale. Park and Natesan [29] have measured the conductivity of chromia scales but the difference between values measured using a two-probe and a four-probe system differ by two orders of magnitude i.e. at 900°C $\kappa_e \approx 10^{-2}$ (ohm cm)⁻¹ for four point measurements and $\kappa_e \approx 10^{-4}$ (ohm cm)⁻¹ for two point measurements. The values extracted from ASR measurements in the present study give $\kappa_e \approx 10^{-3}$ (ohm cm)⁻¹. Using the lower values of κ_e Appendix A indicates that there could be a significant effect of current density on chromia growth on interconnects. However, chromia grows primarily

by grain boundary diffusion. It is not certain that the passage of electrical current will affect grain boundary transport in the same way it does bulk diffusion.

Figure 17 Area Specific Resistance for specimens oxidized at 900°C as a function of measurement temperature.

Task 1.3 Adhesion of Chromia Scales

Results for this Task have been described under Task 1.2

Task 1.4 Oxide Evaporation

The experiments to directly measure oxide evaporation have not yet been initiated.

Task 1.5 Complex Atmosphere Testing

The experiments to study the effects of hydrocarbons on the degradation of interconnect materials have not yet been initiated. Figure 18 presents a schematic of the apparatus in which these exposures will be performed. . The atmospheres to be studied will be Ar-CO-CO₂ (low carbon activity) and Ar-H₂-CH₄ (high carbon activity). Exposure temperatures will be in the the range 700 -900°C. The degradation microstructures will be examined buy OM and SEM to assess the extent of accelerated oxidation, in the low carbon activity gas, and metal dusting, in the high carbon activity gas.

Figure 18. Schematic diagram of complex atmosphere furnace.

Task 2. *Fundamental Aspects of Thermomechanical Behavior*

Task 2.1. XRD Stress Measurements

XRD stress measurements are based on the determination of the strain by measuring the d-spacing of specific lattice planes. The following relationship, which is subject to several experimentally verifiable assumptions, including a biaxial stress state (see [30]), exists between strain and stress:

$$\varepsilon_{\psi} = \frac{d_{\psi} - d_0}{d_0} = \frac{1}{2} S_2(hkl) \sigma \sin^2 \Psi + 2S_1(hkl) \sigma \quad (1)$$

where ε_{ψ} is the strain measured for a particular set of (hkl) planes in a laboratory coordinate system, d_{ψ} is the lattice spacing of (hkl) planes when the specimen is tilted by the angle ψ , d_0 is the strain-free lattice spacing and σ is the stress. $S_1(hkl)$ and $S_2(hkl)$ are the X-ray elastic constants. In this $\sin^2\psi$ technique the stress is calculated from the slope of the d_{ψ} vs. $\sin^2\psi$ plot.

The $\sin^2\psi$ method allows the calculation of the stress without measuring d_0 , which could yield great errors with one point methods. In order to calculate the stress from the slope of d vs. $\sin^2\psi$ plots the knowledge of $S_2(hkl)$ is sufficient. For randomly oriented grains S_2 can be calculated from single crystal data using the Reuss, Voigt and other approximations [30].

Standard techniques based on equation (1) are the Rocking and Tilting methods. In the Tilting technique, the tilt axis is the intersection of the sample surface with the diffraction plane. The diffraction plane is fixed and by definition contains the incident and reflected X-ray beams. The angle ψ is zero when the normal to the sample surface is within the diffraction plane. ψ increases as the sample is tilted and its surface normal is rotated out of the diffraction plane. In the Rocking technique the sample normal is tilted within the diffraction plane and ψ is the angle between the surface normal and the normal [hkl] of the measured set of (hkl) planes. In both techniques only one selected set of (hkl) planes is used for the measurement. To achieve high accuracy during stress measurements, only reflections with high $2\theta_B$ (Bragg angle) can be used, since errors in the measurement of d decrease with increasing θ_B [30].

The PIs have used these techniques extensively for measuring the stresses in alumina scales both at room temperature (residual stress) and at elevated temperatures (growth stresses) [31, 32] and have demonstrated that the same techniques work for chromia films, which have the same crystal structure as α -alumina [33]. Extensive studies of stresses in chromia films have also been performed by Shores and coworkers [34-34] on Ni-base alloys. In this project the residual stresses in chromia films formed on ferritic interconnect alloys are being measured after the exposures to simulated fuel cell environments, described above. This will allow evaluation of the effect of exposure atmosphere and surface preparation on the residual stress in the chromia films, which is the driving force for delamination.

Figure 19 is a $\sin^2\psi$ plots for Crofer22 APU exposed at 900°C for 100 cycles in air +10% H₂O. These data were obtained using the “tilting technique”. The stresses in the scales were compressive with values of -2.27 GPa in dry air and -1.90 GPa in moist air. These values compare with calculated thermal stresses of -2.22 GPa.

Figure 19. $\sin^2\psi$ plots for Crofer22 APU exposed at 900°C for 100 cycles in air +10% H₂O.

Task 2.2. Indentation Testing of Interface Adhesion

Indentation fracture tests have been performed on a subset of the specimens subjected to cyclic oxidation testing. A listing of tests performed to date is given in the EXPERIMENTAL section of this report. The primary goals of this testing are to evaluate the effectiveness of existing indentation testing methods as they are applied to a variety of interconnect systems, and to identify aspects of the current test (originally developed for use on TBC systems) that could be changed to tailor it to the evaluation of interconnect alloys.

Chromia Scale Systems: E-BRITE Exposed in Wet Air and Simulated Anode Gas

Testing of chromia scale systems has thus far involved exposure and indentation of E-BRITE in Wet Air (Air + 0.1 atm H₂O) and simulated anode gas (SAG) (Ar/H₂/H₂O) at 900°C (although exposures at 700°C have been initiated). Indentation has been performed at 100 hrs. and 200 hrs. in wet air and at 264 hrs., 364 hrs. and 464 hrs. in SAG.

Figure 20 shows SEM micrographs of indentations on E-BRITE specimens exposed in Wet Air and SAG. White areas in each micrograph indicate exposed alloy due to chromia scale spallation. The circular shaded region in the center of each micrograph is the indentation induced by the test. For both types of exposures, mechanical loading of the substrate via indentation has induced spalls at early exposure times; however, significant differences are seen in the debonding behavior for the two types of exposures. The wet air specimens exhibit a nonuniform flaking of the chromia scale, with the density of the flaking decreasing with increasing distance from the center of the indentation. Clearly, this behavior is indicative of a non-uniform interfacial toughness, where at different radial distances from the center of the indent (corresponding to different values of applied energy release rate or stress intensity factor) a different percentage of the surface area has debonded. In contrast, SAG-exposed specimens show a more uniform peeling of an intact chromia scale. This debonding behavior is perhaps indicative poorer adhesion at the interface. Interfacial toughness may also be nonuniform in this case; however, the average toughness is low enough that the scale is able to peel away without breaking up.

These qualitative behaviors are consistent with the results of long-term weight gain measurements on E-BRITE, where weight gains in SAG were significantly greater than those in wet air. The debonding behavior of the specimens exposed in wet air could also explain the relatively flat mass change vs. time plot for this case. The nonuniform toughness allows weakly bonded portions of the scale to spall at relatively early times, keeping weight gain increases small.

Figure 20. E-BRITE indentation results (SEM images as viewed from above) for 100 hrs. in wet air at 900°C (left) and 264 hrs. in SAG at 900°C (right).

Testing Analysis Procedures for Chromia Scale Systems

For SAG-exposed specimens, the fact that the chromia scale peels as an intact layer means that the radial extent of the debonding can be used to quantify the interfacial toughness of the specimen. SEM images in Figure 21 represent a first attempt at this. The figure shows images from indentation of SAG-exposed E-BRITE at 264 and 364 hours. To roughly quantify the size of the debonds, a dashed circle centered at the center of the indentation has been drawn enclosing the debonded areas. It is clear that the debond size has increased from 264 to 364 hours of exposure.

In quantifying the fracture toughness of the chromia scale/E-BRITE interface, it is the ratio of the debond radius, R , to indent radius, a , that is important. The ratio R/a is roughly 2 for the specimen exposed for 264 hours and closer to 2.5 for the specimen exposed at 364 hrs. From a fracture mechanics standpoint, this increase in debond size could be due to an increase in scale thickness or a loss of adhesion at the interface or even an increase in scale residual stress. In order to diagnose this further, oxide thickness and XRD residual stress measurements are needed. However, weight gain measurements suggest that the oxide scale has thickened considerably from 264 to 364 hours.

Figure 21. E-BRITE indentation results (SEM images as viewed from above) for 264 hrs. in SAG at 900°C (left) and 364 hrs. in SAG at 900°C (right).

A key issue in analyzing the tests on SAG-exposed specimens is accurate quantification of the extent of chromia scale debonding. If the extent of the debond is simply indicated by the area of exposed metal, then image analysis can yield a precise debond area and an effective or average radius of debonding. However, it is possible that debonding has occurred beneath some of the scale left on the specimen after indentation. To investigate this issue, the PIs have employed a surface tinting procedure to rigorously image debonded areas. The images given in Figure 22 demonstrate the results of this procedure.

Figure 22 shows results from two indent tests after 464 Hours at 900°C. The image on the left was generated by indentation with a 60 kg load. The image on the right was generated by an additional tinting exposure of 10min at 700 °C, followed by a 150 kg indent at the same location as the 60 kg indent. The result of the second indentation is an increase in indent size and corresponding increase in debond size (a mechanics analysis of the indent problem shows that increasing the applied load only increases the size scale of the indent and debond but does not change R/a). What the debonding from the second indent has done, however, is to reveal the tinted surface from the first indent, showing the shape of the original debond.

The micrographs of Figure 22 demonstrate two things. First, the ratio of debond to indent radius in the first and second indents is very similar –as is the shape of the debond (based on the size and shape of the exposed metal). Thus the test appears to be yielding consistent results. More importantly, the true extent of the debond from the first indent (as indicated by the tinted shape in the second image) is not much different than the shape of the exposed metal in the first image. Some sharp edges of the debond in the first image are not replicated in the shape of the tinted metal in the second image, but the differences are minor. As a result, the size of the exposed metal after indentation appears to be a reasonable estimate of the size of the actual indentation-induced debond.

Figure 22. E-BRITE indentation results (SEM images as viewed from above) for 464 hrs. in SAG at 900°C after indentation with a 60 kg load (left) and after tinting and indentation at the same location with a 150 kg load (right).

For wet air-exposed specimens, the nonuniform flaking of the chromia scale caused by indentation makes analysis of the indent tests more difficult. Clearly, characterizing the adhesion of the scale using a single average toughness of the scale/alloy interface is not appropriate. However, the PIs have initiated a test analysis procedure based on image analysis that is more appropriate for these specimens.

This procedure is illustrated in Figure 23, where a single debond image has been decomposed into (in this case) 3 concentric rings. For each ring (with an average radius, R), image analysis can yield a percentage of debonded area, yielding a plot of percent debond area vs. normalized radius, R/a (where a is the indent radius). Fracture modeling of the indent problem can yield a plot of energy release rate or stress intensity factor vs. R/a (a description of modeling work is provided in the next section). Combining these plots can yield a plot of energy release rate vs. percent debonded area, based on this one image.

Analogous plots of energy release rate vs. percent debonded area can be generated for indent images taken after other cyclic oxidation exposures. If XRD residual stress data and oxide thickness data are included in calculating the energy release rates, any changes in the energy release rate vs. percent debonded area plot with exposure will reflect a true change in the distribution of toughness at the interface. In short, the goal of this test analysis approach will be to not only track a change in average toughness with exposure (and help pinpoint mechanisms causing it) as is planned for SAG-exposed specimens, but will also be to track how the distribution of toughness across the interface changes with exposure.

Figure 23. Decomposition of wet air-exposed indentation results into rings having decreasing densities of debonding with increasing radius.

Indent Test Modeling

Fracture modeling of the indentation test involves finite element modeling of the indentation problem to determine mechanically applied in-plane strains on the surface of the specimen. Because the chromate coating is thin compared to the interconnect alloy substrate, the in-plane strains on the surface of the alloy are matched in the chromia scale – and it is these strains in the chromia scale (in addition to any residual strains) which drive its debonding. Strains in the loaded coating from the finite element simulations are then combined with residual strains and used in the formula:

$$\frac{2G(1-\nu^2)}{E(t_{\text{chromia}})} = \left[\varepsilon_r + \nu \varepsilon_\theta \right]^2, \quad (2)$$

where ε_r and ε_θ are the combined applied and residual radial and tangential in-plane strains, ν and E are the Poisson's ratio and elastic modulus of the chromia scale, t_{chromia} is the scale thickness and G is the energy release rate for debonding of the scale.

By definition, the energy release rate is the elastic strain energy released by debonding of the scale, per unit newly created debond area. The energy release rate is proportional to the combined applied and residual stress in the scale squared. Toughness results can be equivalently expressed in terms of a critical energy release rate to cause debonding (G_c) or in terms of a critical stress intensity factor to cause debonding (K_c)

(there is a straightforward conversion between the two quantities). An advantage of expressing results in terms of K_c is that K_c is linearly dependent on the stress in the scale.

Figure 24 presents a preliminary set of results from modeling of indentation fracture testing of E-BRITE, where stress vs. strain behavior of the E-BRITE substrate was approximated based on elastic modulus, yield stress, ultimate stress and percent elongation data taken from the technical data bluesheet for this alloy provided by Allegheny Ludlum. An elastic Poisson's ratio of 0.28 was taken for both the alloy and the scale, the elastic modulus of the scale was taken as 273 GPa and the biaxial compressive residual stress in the coating was taken as constant, with a value of -1.3 GPa. In the results presented in Figure 24, frictionless contact is assumed between the indenter and the substrate and the substrate is assumed to be thick compared to the indent depth. Work is currently underway to consider the effects of contact friction and finite substrate thickness on the modeling results. An image of the near-indent region in the axisymmetric finite element model is provided in Figure 24, along with a plot of K (stress intensity factor for interfacial debonding) vs. normalized distance from the center of the indentation, R/a (where R is the debond radius and a is the contact radius). The graph includes data for multiple values of chromia scale thickness.

In using the plot of Figure 24, a radius of debonding (or an average or effective radius for a non-circular debond like that seen in Fig. 21) is taken from the test, as is a radius of indentation. This gives a value of R/a . Combining this with a value of scale thickness (and an assumed value of residual stress) yields a value of K . Since that is the value of K at which debonding stops, that $K = K_c$, the critical value of interface stress intensity factor or interfacial toughness. For instance, for a value of $R/a = 2.5$ and $t_{\text{chromia}} = 2\mu\text{m}$ yields a value of $K_c = 3\text{ MPa}\sqrt{\text{m}}$. Converting this value to a critical value of energy release rate yields $G_c = 35\text{ J/m}^2$.

It should be noted that although the plot in Figure 24 is generated assuming a residual stress in the scale of -1.3 GPa, plots for other values of stress in the scale are readily generated. The constant values of K on the right side of the graph represent the stress intensity factor due to residual stresses only. Because K is proportional to the coating stress, a fixed percent change in residual stress will change the constant values of K on the right side of the graph by the same percentage. This change in K due to a change in residual stress is independent of R/a , so that the full K vs. R/a curve for a different value of residual stress will simply be one of the existing curves in the plot, with K offset by this constant value.

Figure 24. Preliminary results from modeling of the indentation test for interfacial fracture toughness.

Chromite Coated Specimens

As previously mentioned, the concept of indentation testing can be applied to a wide range of brittle coating/ductile substrate SOFC systems. As part of this project, a first round of indentation tests have been performed on chromite coated specimens, where the debonding layer consists of the chromite coating and any chromia scale that may have grown under the coating due to cyclic thermal exposure. The specific coating systems studied are 1) a $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ coating on E-BRITE, AL 453 or AL 29-4C from PNNL and 2) a LaCrO_3 Coating on Inconel or SS 446 from Drexel and NETL. Of interest is how the addition of a chromite coating might add to the stored energy acting to drive chromia scale spallation, and how the effect of the coating on chromia scale growth and evaporation rates during exposure will affect spallation resistance (by also changing the stored energy in the chromia layer).

Figures 25 and 26 show SEM images from indentation of these two types of coatings in the as-processed state (with no chromia scale between the coating and alloy). In the as-processed state, the results for each type of coating are consistent, and roughly independent of the alloy the coatings were deposited upon. The $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ coating consistently showed some susceptibility to debonding; however, the radial extent of the debonding is not large. In contrast, the LaCrO_3 coating did not debond at all, though some radial tensile cracks were seen in the coating deposited onto Inconel, suggesting that the coating itself may be brittle. This difference in behavior may be due to the difference in thickness for the two coatings. The $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ coatings were each on the order of $4\text{ }\mu\text{m}$ thick. The LaCrO_3 coatings were each less than $1\text{ }\mu\text{m}$ thick.

Figure 25 SEM images after indentation of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ coating on E-BRITE, AL 453 and AL 29-4C in the as-processed state.

Figure 26 SEM images after indentation of LaCrO_3 Coating on Inconel and SS 446 in the as-processed state.

Figure 27 provides a comparison of two of the five coating systems from figures 25 and 26 (one with an $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ coating and one with an LaCrO_3 coating) in the as-processed state and after cyclic thermal exposure for 100 hours at 900°C . It is clear that thermal exposure has resulted in both types of coating systems becoming more susceptible to debonding. The $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ on E-BRITE system now exhibits more complete debonding than was exhibited in the as-processed state, though the radial extent of the debonding is still not large. The LaCrO_3 on SS 446 system is now experiencing some flaking of the coating from the substrate, in contrast to the lack of debonding in the as-processed state. These results are consistent with an increase in debonded coating thickness caused by chromia scale growth beneath the chromite coatings. SEM/EDS analysis of the debonded portions of the exposed specimens confirms that the debonding has exposed the bare metal in both coating systems. Exposed flakes of chromia have also been found in the debonded portions of the coating, confirming that a chromia scale has grown beneath the chromite coating. These specimens will be sectioned to image the thickness and structure of the chromia scales.

As Processed:

Exposed 100hr 900°C:

Figure 27 Comparison of indentation images from as-processed and exposed chromite coated specimens.

Summary of Progress on Indentation Testing

The goal of first year indentation testing and modeling has been to confirm the potential of the test method in characterizing the adhesion of SOFC interconnect alloy interfaces. Specifically, testing has been performed on exposed bare alloys and alloys with chromite coatings applied to them as a means of controlling chromia evaporation. The testing approach shows much promise. It has been successful at inducing debonding in uncoated and coated chromia scale systems and has highlighted differences in adhesion in uncoated specimens exposed in wet air and SAG environments. It has also demonstrated changes in adhesion behavior with exposure in uncoated and coated systems. Methods for analysis of the tests (extracting debond sizes or debond density distributions) have been established and preliminary modeling work has been completed to allow quantitative results to be extracted from the tests. Modeling work will combine results from the indentation tests, thickness measurements and XRD stress measurements to give insight into dominant mechanisms leading to scale spallation. This is a critical step in the development of accelerated tests methods for SOFC interconnect alloys, which is the subject of the next section.

Task 2.3 Accelerated Testing

A primary goal of indentation fracture toughness testing is to use fracture mechanics-based tests to understand mechanisms leading to chromia scale spallation in SOFC interconnect alloys. This will allow the design of accelerated testing protocols that ensure that the spallation mechanisms dominant from exposures in a fuel cell stack are also those dominating spallation in the accelerated test. Accelerated testing can take the form of tests at elevated temperatures or tests at increased thermal cycle frequency.

Another type of accelerated test would be indentation testing itself, where mechanical loads applied to the interconnect alloy induce spallation at times much earlier than those at which residual stress-driven spallation occurs due to cyclic thermal exposure.

Figure 28 illustrates this approach, combining a number of images from this report related to the cyclic oxidation of E-BRITE exposed to SAG. The standard test for evaluating oxidation resistance is weight gain measurement; however, the test data plotted in Fig. 28 is already being performed under accelerated conditions of an elevated test temperature of 900°C and increased cycle frequency of one cycle per hour. Even under these conditions meant to decrease testing time, all three alloys in the plot (Al 453, E-BRITE and Crofer) are still gaining weight with exposure after 1000 hours of testing.

As seen in Fig. 28, weight gain measurements indicate that the performance of E-BRITE lies between that of Al 453 and Crofer. Sectioning and SEM imaging has shown that at 822 hours the chromia scale grown on E-BRITE is much thicker than E-BRITE specimens exposed in either dry air or water vapor. Compared to exposures in other environments, the chromia scale does not seem to be well-bonded to the alloy (evidenced by the debonding of the scale as a result of the sectioning operation). Measured weight gains can be compared to predictions of weight gain based on chromia scale thickening rates to determine the exposure time at which scale spallation has begun; however, this requires that weight gain measurements continue at least until spontaneous spallation occurs.

A key goal of this project is to consider how the use of mechanically induced spallations at early times can further accelerate interconnect alloy testing. In Fig. 28, images are shown of indentations performed on E-BRITE at the relatively early times of 264 and 364 hours. The peeling of the chromia scale from the substrate as an intact layer suggests a much thicker scale and perhaps less adhesion to the substrate, consistent with the observations from sectioning at 822 hours. Furthermore, multiple indentation measurements at early times, coupled with residual stress and scale thickness measurements will allow a prediction of when residual stresses and scale thickness will be sufficient to cause peeling of the scale. In other words, by tracking toughness degradation at early times, a prediction of the initiation of spallation can be made without having to wait for it to occur spontaneously.

Indent fracture testing can also give insight into the validity of the more traditional acceleration techniques of elevating temperature and thermal cycle frequency. Indentation tests are now being initiated on specimens exposed at 700°C. The goal is to compare degradation mechanisms at 700°C and 900°C to verify that they are indeed the same. Measurements of oxide thickening, residual stress and interfacial toughness can indicate whether spallation is induced by growth of the oxide scale, changes in residual stress in the scale, changes in the actual adhesion (toughness) of the interface or combinations of all three. Furthermore SEM imaging can indicate whether changes in adhesion are due to mechanical damage or structural or compositional changes at the interface.

Thermogravimetric Analysis (Longer-Term Tests)

Characterization of Chromia/Alloy Interfaces and Phases

Accelerated Tests: Indentation Debond Measurements of Chromia/Alloy Interfacial Toughness

Figure 28 Accelerated testing concepts.

Task 3. Alternative Material Choices

The third objective of this project is to evaluate the possibility of using metallic materials other than chromia-formers as interconnects as the operating temperature of SOFCs are reduced. The approach that is being used is to perform a theoretical analysis of potential interconnect materials during Phase I. Based on this analysis the most attractive one (or two) systems will be fabricated and tested under fuel cell operating conditions during Phase II. The following is a summary of the theoretical analysis that has been formed to date and the results of preliminary experiments.

Task 3.1. Pure Ni

Nickel has several advantages over chromia-forming alloys. Its only oxide, NiO, has no vapor species with high partial pressures and it has a higher electrical conductivity than chromia. Also, NiO should not even form in the anode gas. Table 2 indicates that the dissociation pressure of NiO is approximately 10^{-12} atm at 900°C so that NiO would not be stable in a typical anode gas where the oxygen partial pressure is expected to be on the order of 10^{-20} atm. Also, Table 2 indicates the vapor pressure of metallic Ni is among the lowest of the common metals and should not be an issue. Also, as indicated in Table 3 the coefficient of thermal expansion (CTE) of Ni and NiO match very closely so that thermal stresses during cyclic oxidation should be small. One negative aspect of NiO, relative to chromia is its higher growth rate. However, the k_p for growth of pure NiO is

less than one order of magnitude greater than that typically observed for chromia. This growth rate can be reduced further if cation dopants with a +1 charge (e.g. Li, Cu) can be incorporated into the scale, which will also increase the electronic conductivity of the scale. As indicated in Table 4, the CTE of Ni is substantially larger than that of the typical ceramic components of SOFCs, which will need to be addressed. However, it also has a rather high thermal conductivity, which will be beneficial in maintaining a uniform temperature in the SOFC.

Figure 29 presents preliminary oxidation data for Ni exposed in a simulated anode gas under cyclic conditions at 700°C. The mass change of the specimen is extremely small compared to that for the ferritic alloys (See Figure 16). The fact that the specimen mass is increasing slightly may reflect dissolution of oxygen and hydrogen into the Ni.

Table 2. Selected Properties of Several Metals/Oxides

Metal/Oxide	p_{O_2} (atm) 900°C	p_{Metal} (atm) 900°C
Cr/Cr ₂ O ₃	10^{-25}	10^{-10}
Mn/MnO	10^{-26}	10^{-5}
Fe/FeO	10^{-17}	10^{-11}
Ni/NiO	10^{-12}	10^{-11}
Cu/Cu ₂ O	10^{-8}	10^{-9}

Table 3 Linear Coefficients of Thermal Expansion of Metals and Oxides⁷

System	Oxide Coefficient	Metal Coefficient	Ratio
Fe/FeO	12.2×10^{-6}	15.3×10^{-6}	1.25
Fe/Fe ₂ O ₃	14.9×10^{-6}	15.3×10^{-6}	1.03
Ni/NiO	17.1×10^{-6}	17.6×10^{-6}	1.03
Co/CoO	15.0×10^{-6}	14.0×10^{-6}	0.93
Cr/Cr ₂ O ₃	7.3×10^{-6}	9.5×10^{-6}	1.30
Cu/Cu ₂ O	4.3×10^{-6}	18.6×10^{-6}	4.32
Cu/CuO	9.3×10^{-6}	18.6×10^{-6}	2.00

Table 4 . Physical Properties of Various Materials

Material	CTE X 10^6 (K ⁻¹)	Therm. Cond. (W/mK)
Cu	18.6	370
Cr	9.5	70
Ni	17.6	65
St. Steel (Aust.)	18	21
St. Steel (Ferritic)	11	26
Invar (Fe-36%Ni)	2	13*
Hastelloy X	14	17
Electrolyte (YSZ)	10	2
Anode (Ni-YSZ)	11	-
Cathode (LSM)	12	-
Si-based glasses	3-8	1

Figure 29. Weight Change Vs Time plots for pure Ni exposed in Ar/H₂/H₂O (simulated anode gas) at 700°C using one-hour cycles.

Task 3.2. Dispersion-Strengthened Ni

The strength of Ni can be increased and its CTE decreased by incorporating an oxide dispersion. TD-Nickel contains ThO₂ as a dispersoid. However, the radiation hazards associated with thorium preclude the use of this material. An alternative might be dispersing Y₂O₃ in Ni or Li₂O, since the latter would also provide a potential source of Li⁺ cations to dope the NiO scale.

Task 3.3. Low CTE Fe-Ni Alloys (Invar)

Some Fe-Ni alloys, e.g. Fe-36Ni sold under the name Invar, have very low CTEs, as indicated in Table 4. In fact, the CTE of Invar is substantially lower than that of the typical ceramic components of SOFCs. This offers the opportunity to tailor the CTE of the interconnect, by increasing the Ni content above 36%, to closely match that of the ceramic components. Also, as indicated in Table 2, neither component of these alloys will form oxide in the anode gas. One potential issue will be the composition of the oxide formed in the cathode gas. If the Ni content of the alloy is high enough to prevent the formation of FeO, this oxide should also grow relatively slowly and have a high electronic conductivity.

Task 3.4. Coatings

If the oxidation rates of the Fe-Ni alloys with optimized CTE are too high, they can be decreased by coating the cathode side with Cr by pack cementation. This is a well established, economical coating technique which diffuses Cr into the alloy and produces a surface capable of forming a chromia scale [See for example Ref. 38]. This of course, leads to the issue of CrO_3 evaporation.

Chromite coatings can, in principle, be used to reduce CrO_3 evaporation. The extent to which this occurs must still be measured experimentally. The thermomechanical properties of these coatings has been described in Task 2.

Task 3.5. Dispersion Strengthened Cu (Anode Side)/Cr (Cathode Side)

One rather revolutionary concept would be a bilayer interconnect consisting of dispersion-strengthened Cu on the cathode side and Cr on the anode side. Dispersion-strengthened Cu can be readily produced by internal oxidation [39]. A candidate starting alloy would be Cu-Ti (now sold commercially by Brush-Wellman) which could be formed into the desired shape and then internally oxidized to form TiO_2 precipitates in a matrix of virtually pure Cu. This alloy has high strength and the high electrical conductivity of Cu and will not oxidize in the anode gas (Table 2). The Cr layer could be applied to the cathode side by pack cementation. Chromium and copper are virtually insoluble in each other so interdiffusion of the layers during long term oxidation should not be an issue. The CTE mismatch between Cr and Cu would need to be addressed.

CONCLUSION

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, with the most significant changes 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 chromite 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.

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Appendix A: Oxidation Under Open Circuit Conditions

Figure A1. presents a schematic diagram of the growth of an oxide layer in the absence of an impressed current. This process has been described by Wagner [28]. In the growth of an oxide scale, metal ions and oxygen ions will tend to migrate across the scale in opposite directions. Because the ions are charged, this migration will cause an electric field to be set up across the scale resulting in consequent transport of electrons across the scale from metal to atmosphere. The relative migration rates of cations, anions, and electrons are, therefore, balanced and no net charge transfer occurs across the oxide layer as a result of ion migration. The gradients of chemical potential μ_i and electrical potential ϕ will result in a net drift velocity on charged particles through the scale

$$v_i = -\frac{B_i}{N_A} \left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x} \right) \text{ cm s}^{-1} \quad (\text{A1.})$$

where B_i is the particle mobility and is defined as the average drift velocity per unit force, $\frac{\text{particle} - \text{cm}^2}{\text{joule} - \text{s}}$. The flux of particles is obtained as follows,

$$j_i = C_i v_i = -\frac{C_i B_i}{N_A} \left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x} \right) \text{ moles cm}^{-2} \text{ s} \quad (\text{A2.})$$

where C_i is the concentration of i in $\text{moles} - \text{cm}^{-3}$.

Figure A1. Diagram of scale formation according to Wagner's model.

The mobility may be related to the conductivity κ_i and the self diffusion coefficient D_i of the particle by comparing equation (2) for limiting cases of zero electric potential gradient and zero chemical potential gradient to Fick's first law and Ohm's law, respectively. The following relationships are obtained,

$$kTB_i = D_i = \frac{N_A RT \kappa_i}{C_i (Z_i F)^2} \quad (\text{A3})$$

Replacing B_i in j_i yields

$$j_i = -\frac{\kappa_i}{Z_i^2 F^2} \left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x} \right) \quad (\text{A4})$$

Consider a scale growing by cations moving outward.

$$(\text{A.}) \quad j_c = -\frac{\kappa_c}{Z_c^2 F^2} \left(\frac{\partial \mu_c}{\partial x} + Z_c F \frac{\partial \phi}{\partial x} \right)$$

$$(\text{B.}) \quad j_e = -\frac{\kappa_e}{Z_e^2 F^2} \left(\frac{\partial \mu_e}{\partial x} + Z_e F \frac{\partial \phi}{\partial x} \right)$$

The condition for electrical neutrality is

$$(\text{C.}) \quad Z_c j_c + Z_e j_e = 0$$

and, using equations A, B, and C, it is now possible to eliminate $\frac{\partial \phi}{\partial x}$ as

$$\frac{\partial \phi}{\partial x} = -\frac{1}{F(\kappa_c + \kappa_e)} \left[\frac{\kappa_c}{Z_c} \frac{\partial \mu_c}{\partial x} + \frac{\kappa_e}{Z_e} \frac{\partial \mu_e}{\partial x} \right] \quad (\text{A5.})$$

The cation flux now becomes:

$$j_c = -\frac{\kappa_c \kappa_e}{Z_c^2 F^2 (\kappa_c + \kappa_e)} \left[\frac{\partial \mu_c}{\partial x} - \frac{Z_c}{Z_e} \frac{\partial \mu_e}{\partial x} \right] \quad (\text{A6.})$$

Considering ionic equilibrium and integrating across the oxide where j_c is assumed to be independent of x .

$$j_c = -\frac{1}{Z_c^2 F^2 x} \int_{\mu_M'}^{\mu_M''} \frac{\kappa_c \kappa_e}{\kappa_c + \kappa_e} d\mu_M \quad (\text{A7.})$$

If the concentration of metal in the oxide scale is $C_M \text{ mol cm}^{-3}$ then the flux may also be expressed by

$$j_c = C_M \frac{dx}{dt} \quad (\text{A8.})$$

Comparison with the parabolic rate equation

$$\frac{dx}{dt} = \frac{k'}{x} \quad (\text{A9.})$$

where k' is the parabolic rate constant in cm^2s^{-1} .

$$k' = \frac{1}{Z_c^2 F^2 C_M} \int_{\mu_M''}^{\mu_M'} \frac{\kappa_c \kappa_e}{\kappa_c + \kappa_e} d\mu_M \quad (\text{A10.})$$

This is the parabolic rate constant for open circuit conditions, k'_{oc}

Oxidation in the Presence of an Impressed Current

Equations (A) and (B) are unchanged. Equation (C) is written:

$$Z_c F j_c + Z_e F j_e = i$$

where i is the current density. The potential gradient now becomes:

$$\frac{\partial \phi}{\partial x} = -\frac{1}{F(\kappa_c + \kappa_e)} \left[\frac{\kappa_c}{Z_c} \frac{\partial \mu_c}{\partial x} + \frac{\kappa_e}{Z_e} \frac{\partial \mu_e}{\partial x} \right] - \frac{i}{(\kappa_c + \kappa_e)} \quad (\text{A11.})$$

The cation flux now becomes:

$$j_c = -\frac{\kappa_c \kappa_e}{Z_c^2 F^2 \kappa} \left[\frac{\partial \mu_c}{\partial x} - \frac{Z_c}{Z_e} \frac{\partial \mu_e}{\partial x} \right] + \frac{\kappa_c i}{Z_c F \kappa} \quad (\text{A12.})$$

Integrating across the oxide and setting $j_c = 0$ yields

$$i_0 = \frac{-\kappa_e}{Z_c F} \frac{\Delta \mu_M}{x} \quad (\text{A13.})$$

where i_0 is the current which will stop the growth of the oxide at oxide thickness $x = x_0$.

Note: If the external oxygen pressure is 1 atm, $\Delta \mu_M = \Delta G_{MO}^o$

At some intermediate current, combination of equations (A7.), (A8.), (A12.), and (A13.) or (A14) yields

$$k' = k'_{OC} \left[1 - \frac{i}{i_0} \right] \quad (A14)$$

There is some uncertainty regarding κ_e for chromia. At 900°C Park and Natesan, Ref. [29] give values of $\kappa_e = 10^{-2} \text{ (ohm cm)}^{-1}$ for four probe measurements and $\kappa_e = 10^{-4} \text{ (ohm cm)}^{-1}$ for two probe measurements. Values extracted from the ASR measurements of the present study also show some variability but seem to be consistent with values of κ_e on the order of $10^{-3} \text{ (ohm cm)}^{-1}$. Using this value and

$$\Delta G^\circ = -820,000 \text{ J/mole}$$

For a 1 μm thick oxide: $i_0 = 28 \text{ A/cm}^2$

For a typical Fuel Cell current density of 1 A/cm^2 , $k' \cong k'_{OC}$

However, for a 10 μm thick oxide, such as those formed on some specimens in the present study,

$$i_0 = 2.8 \text{ A/cm}^2$$

and $k' = 0.64k'_{OC}$ on one side of the interconnect and $k' = 1.36k'_{OC}$ on the other side. In fact at a current density of 1 A/cm^2 , if κ_e is smaller, i.e. closer to the two probe values of Park and Natesan [29] the effect of the electric current on scale growth would be more dramatic: $i_0 = 0.28 \text{ A/cm}^2$ for a 10 μm thick oxide or at $i = 1 \text{ A/cm}^2$, the oxide would stop growing on the cathode side of the interconnect when it reached a thickness of 2.8 μm .

It should be pointed out that chromia is known to grow primarily by grain boundary diffusion. It is expected, but not certain, that the effect of the electric current will be independent of diffusion mechanism.