IV.D.2 Interfacial Strength and Interconnect Life Quantification Using an Integrated Experimental/Modeling Approach

Mohammad A. Khaleel (Primary Contact), Xin Sun, Wenning Liu, Elizabeth Stephens, Kurt Recknagle and Brian Koeppel
Pacific Northwest National Laboratory (PNNL)
902 Battelle Blvd.
Richland, WA 99352
Phone: (509) 375-2438; Fax: (509) 375-4392
E-mail: moe.khaleel@pnl.gov

DOE Project Manager: Travis Shultz
Phone: (304) 285-1370
E-mail: Travis.Shultz@netl.doe.gov

Objectives

- To develop a systematic methodology for quantifying the interfacial strength between oxide scale and interconnect substrate.
- To report the quantified interfacial strength developed by the combined experimental/modeling technique.
- To predict possible debonding/delamination and subsequent spallation at the scale/substrate interface for Crofer 22 APU, therefore indicating the possible interconnect life under isothermal cooling or thermal cycling conditions.

Accomplishments

- Identified the driving force for delaminations during indentation tests.
- Developed a coupled experimental/analytical approach for quantifying oxide/substrate interfacial strength.
- Applied the developed interfacial strength quantification method in predicting interconnect life upon isothermal cooling.

Introduction

Interconnects (IC) in solid oxide fuel cells (SOFCs) provide cell-to-cell electrical connection and also serve as gas separator for the separation of the fuel (anode) from the oxidant (cathode). Recently, Solid State Energy Conversion Alliance (SECA) funded interconnect materials development has been mostly focusing on ferritic stainless steels. Compared to chromium-based alloys, iron-based alloys have advantages in terms of high ductility, good workability and low-cost [1]. By far, iron-based alloys, especially Cr-Fe-based alloy, e.g. Crofer 22 APU, are the most attractive metallic interconnect material for SOFCs [2, 3].

It should be noted that the oxidation reaction of the metallic interconnect in the SOFC working environments is unavoidable. Appearance and growth of the oxide scale will cause growth stress in the oxide scale [2, 3]. In addition, thermal expansion coefficient mismatch between the oxide and the substrate creates stresses in the scale and on the scale/substrate interface during cooling [4], leading to scale delamination/buckling and eventual spallation. The interfacial strength between the oxide scale and substrate is therefore crucial to the reliability and durability of the metallic interconnect in SOFC operating environments. The objectives of the current work are: 1) to develop a methodology for quantifying the interfacial strength between oxide scale and interconnect substrate; 2) to report the quantified interfacial strength developed by the combined experimental/modeling technique; and 3) to predict possible delamination and subsequent spallation at the scale/substrate interface therefore indicating the possible interconnect life under isothermal cooling or thermal cycling conditions.

Approach

First, finite element fracture mechanics analyses of the micro-indentation test are performed with preexisting cracks at the oxide scale/Crofer substrate interface for various crack length, location and scale thickness. It is found that the interfacial crack tips are mainly mode II dominant, with very low ratios of K_I/K_{II}. From these results, one can conclude that the interfacial shear stress can indeed be considered the driving force for interfacial failure, and that this strength-based failure criterion is similar in many ways to the conventionally used fracture toughness criterion. The critical shear strength of the interface is then quantified by an integrated experimental/analytical approach. The predicted interfacial strength along with the predicted interfacial shear stress generated during the isothermal cooling process is used to determine the critical oxide scale thickness. The critical oxide scale thickness is next used in conjunction with the experimentally determined oxidization kinetics law for bare Crofer to predict IC life under normal operating temperature of 800°C.

Results

Evolution of Interfacial Shear Stress during Indentation

Figure 1 shows the cross-sectional microstructures of Crofer 22 APU after oxidation at 800°C for 1,200 hours. The thickness of the oxide scale is assumed uniform in the analyses. Temperature dependent material property is used for Crofer 22 APU. Taking advantage of the structural symmetry of an indentation test, an axisymmetric model is used. The total thickness of the substrate and its scale is kept constant at 0.5 mm. Figure 2 shows the predicted stress distribution in the scale during indentation process. It shows that a field of very high shear stress is generated by the indentation process, at the interface of the scale/substrate, right outside the contact radius of the indenter with the scale. The location and magnitude of the maximum shear stress on the interface evolve with the indentation depth and the thickness of the oxide scale. This high interfacial shear stress can be considered as the driving force for interfacial failure.

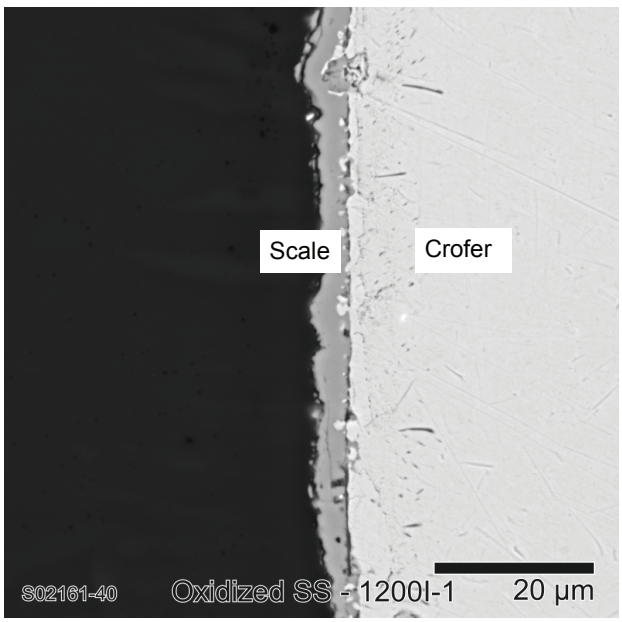

FIGURE 1. Cross-Sectional Microstructures of Crofer 22 APU after Oxidation at 800°C for 1,200 Hours

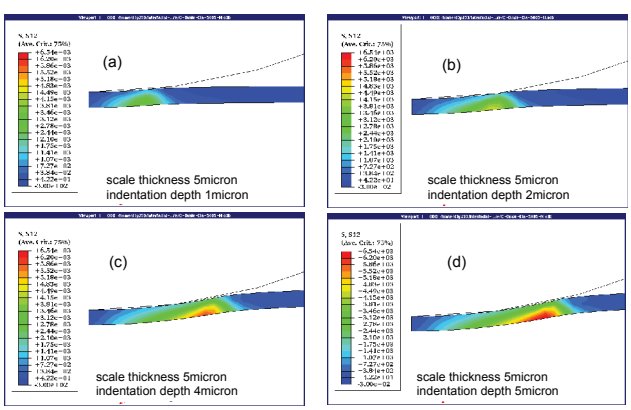

FIGURE 2. Development of Shear Stress Contours in 5-micron Thick Scale during Indentation

Crack Tip Mode Mixture for Pre-Existing Interfacial Crack during Indentation

In order to verify that interfacial shear stress is the driving force for delamination, finite element fracture mechanics analyses of the micro-indentation test are performed with preexisting cracks at the oxide scale/Crofer substrate interface for various crack length, location and scale thickness. Figure 3 shows the schematic of axisymmetric model for the indentation test. A Brale-C indenter with 0.2 mm tip radius is used. The indenter tip angle is 120°. A preexisting interfacial crack with length a is placed on the scale/substrate interface at distance L from the center of the indenter. The predicted stress intensity factor ratio, K_I/K_{II}, is plotted over the entire indentation depth of 10 microns for different initial crack length and different scale thickness. See Figure 3 for example of scale thickness of 5 microns. For all the scale thicknesses examined, the results clearly indicate that the interfacial crack tips have much higher stress intensity factor K_{II} than K_I. In other words, the interfacial crack tips are mostly mode II dominant. This is true for both the left and the right crack tips.

Experimental Indentation Test

Room temperature indentation tests were then performed on oxidized Crofer specimens in quantifying the interfacial strength between the oxide scale and the Crofer substrate. A hardness tester was used to apply the load utilizing a Rockwell 1/16”-diameter ball indenter to penetrate the oxide scale on the Crofer material. The loads were stair-stepped between 60 kgf and 150 kgf to determine the load that spallation occurred on each specimen. When spallation was observed, the load was typically reduced and the indentation repeated, continually increasing the load with each indent until failure was observed again. The load that spallation occurred along with the corresponding oxide scale thickness measured were inputted into the model to determine the interfacial shear strength of the interface.

Seven specimens oxidized at varying lengths of time were tested. All specimens were oxidized at 800°C. Metallography was performed to determine the oxide scale thickness for each specimen. Visual inspection was used to determine whether a specimen spalled after indenting. Typically, in the specimens with a

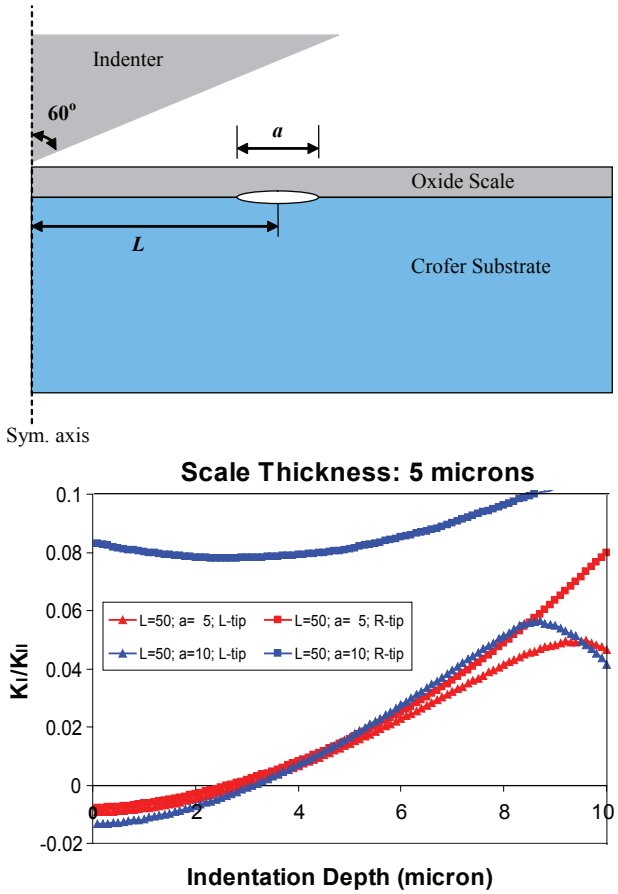

FIGURE 3. Schematic of the Indentation Test and Predicted K_I/K_{II} during Indentation

thicker scale layer, a full radial debonding of the scale was observed where as in specimens with a thinner oxide scale only partial flaking was observed. At a particular scale thickness, the number of spalled samples increases with indentation load. On the other hand, under a specific indentation load, more spalled samples are observed with increasing oxide scale thickness. Generally speaking, the results are quite consistent with some exceptions due to the statistical nature of the oxide layer thickness as well as the pre-existing interfacial flaws.

Quantification of Interfacial Strength

Summarizing the results from indentation tests, Figure 4 illustrates the numbers of non-spalled samples and spalled samples with increasing indentation load for the sample with oxide scale thickness of 2.41 microns. The sample was oxidized at 800°C for 1,500 hours. Clearly, with the resolution of the indentation load used, the critical indentation force to cause scale spallation is 100 kgf.

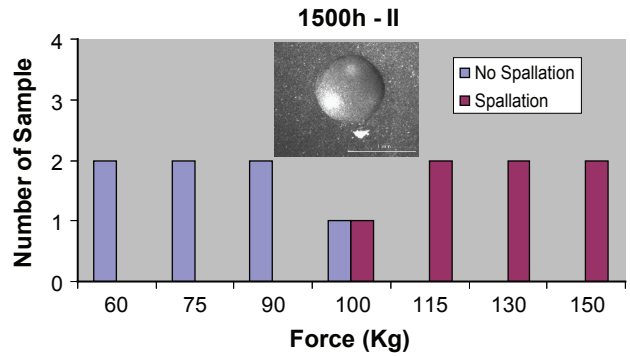

FIGURE 4. Number of Spalled and Non-Spalled Samples versus Indentation Force

Finite element simulation of the corresponding Rockwell 1/16”-diameter ball indentation test on 2.41-micron oxide scale/substrate system is then performed to quantify the interfacial shear stress at the critical indentation load of 100 kgf. The characteristic mesh size at the location for maximum shear stress is around 3 microns. At the critical applied force of 100 kgf, the corresponding maximum interface shear stress is 455 MPa. Therefore, the interfacial shear strength is quantified as 455 MPa for the oxide scale/substrate interface.

IC Life Prediction under Isothermal Cooling

In PNNL Report 15794 [4], it was reported that the interfacial shear stress will be generated during isothermal cooling from the operating temperature to room temperature, and the predicted cooling induced interfacial shear stress increases with the growth of the oxide scale thickness. The interfacial strength quantified can now be used to quantify the critical oxide scale thickness at which interfacial fracture/delamination will occur during isothermal cooling. For example, the critical oxide thickness corresponding to shear stress of 455 MPa is 14.2 microns under isothermal cooling for a 0.5 mm thick IC plate.

The critical oxide thickness can then be used together with the typical oxide growth kinetics law to estimate the interconnect life under normal operating temperature of 800°C. For example, the oxide growth kinetics for bare Crofer 22 APU can be expressed as the following experimental oxidation measurements: $h(in\ micron) = 0.15455 \cdot t^{1/2}(in\ hour) + 0.751$. Taking the critical oxide thickness as 14.2 microns, the lifetime for the bare Crofer is calculated as 7,570 hours.

Conclusions and Future Directions

In this report, we first use finite element fracture mechanics analysis to correlate the mode II dominance of interfacial crack tip, to the high shear stress levels at the interface between oxide/substrate during indentation process. A simplified, critical shear stress-based interfacial failure criterion is then proposed. The shear strength of the oxide/substrate interface is quantified using a combined experimental/analytical approach. Stair-stepping indentation tests are performed to quantify the critical indentation loads at which scale spallation occurs, for various scale thickness. Corresponding finite element indentation tests are then performed, to calculate the interfacial shear strength, at the critical indentation load. As an illustrative example, the interfacial strength is then compared to the shear stress predicted during isothermal cooling to determine the critical oxide scale thickness at which spallation will occur. The IC life is then determined using the oxide growth kinetics for bare Crofer.

It should be mentioned that the proposed approach is a deterministic approach, and it does not consider the statistical nature of the oxide thickness, as well as the interfacial flaw size and distribution. In addition, the critical shear strength quantified by this approach depends on the finite element mesh size used in the indentation simulation. In our analyses, we use equivalent mesh size in the subsequent isothermal cooling simulation, such that the influence of mesh size on predicted critical scale thickness, therefore IC life can be minimized.

In addition, the stair-stepping indentation tests, and the corresponding finite element indentation simulations are performed under room temperature. Therefore, high temperature interfacial strength quantification remains the subject for future study. Furthermore, we assumed that the interfacial strength is constant for various scale thickness. This will be subjected to further validations. Our future work will include identifying the delamination location, and quantifying the interfacial strength, for the spinel coating/oxide scale/Crofer substrate tri-layer system.

FY 2006 Publications/Presentations

1. Sun X, Liu W, Vetrano J, Yang ZG, Recknagle K and Khaleel MA, *Effects of Oxide Thickness on Scale and Interface Stresses under Isothermal Cooling and Micro-Indentation for Ferritic Stainless Steel Interconnect,* Poster Presentation at Fuel Cell Seminar 2006, Hawaii.

2. Sun X, Liu W, Stephens EV, Khaleel MA, *Interfacial Strength and IC Life Quantification using an Integrated Experimental/Modeling Approach,* PNNL Topical Report 16610, Pacific Northwest National Laboratory, Richland, WA 99354, May 2007.

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1. J. W. Fergus, Metallic interconnects for solid oxide fuel cells. *Materials Science & Engineering A (Structural Materials: Properties, Microstructure and Processing)*, 397(1-2), pp. 271-83, 2005.

2. Z. Yang, G. Xia, and J.W. Stevenson, Mn1.5Co1.5O4 spinel protection Layers on ferritic stainless steels for SOFC interconnect applications. *Electrochemical and Solid-State Letters*, 8(3), pp. 168-70, 2005.

3. Z. Yang, J.S. Hardy, M.S. Walker, G. Xia, S.P. Simner and J.W. Stevenson, Structure and Conductivity of Thermally Grown Scales on Ferritic Fe-Cr-Mn Steel for SOFC Interconnect Applications, *Journal of The Electrochemical Society*, 151(11), A1825-A1831, 2004.

4. X. Sun, W.N. Liu, P. Singh and M.A. Khaleel, *Effects of Oxide Thickness on Scale and Interface Stresses under Isothermal Cooling and Micro-Indentation*, PNNL Report 15794, Pacific Northwest National Laboratory, Richland, WA 99354, May 2006.