Metal Interconnects for Solid Oxide Fuel Cell Power Systems

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ABSTRACT

Interconnect development is identified by the U.S. Department of Energy as a key technical area requiring focused research to meet the performance and cost goals under the Solid State Energy Conversion Alliance initiative. In the Phase I SECA Core Technology Program, Ceramatec investigated a commercial ferritic stainless steel composition for oxidation resistance properties by measuring the weight gain when exposed to air at the fuel cell operating temperature. A pre-treatment process that results in a dense, adherent scale was found to reduce the oxide scale growth rate significantly. A process for coating the surface of the alloy in order to reduce the in-plane resistance and potentially inhibit chromium oxide evaporation was also identified. The combination of treatments provided a very low resistance through the scale. The resistance measured was as low as 10 milliohm-cm² at 750°C in air. The oxide scale was also found to be stable in humidified air at 750°C. The resistance value was stable over several thermal cycles. A similar treatment and coating for the fuel side of the interconnect also showed an exceptionally low resistance of one milliohm-cm² in humidified hydrogen at 750°C, and was stable through multiple thermal cycles. Measurement of interconnect resistance when it is exposed to both air and humidified hydrogen on opposite sides also showed low, stable resistance after additional modification to the pre-treatment process. Resistance stacks, using an interconnect stack with realistic gas flows, also provided favorable results. Chromium evaporation issue however requires testing of fuel stacks and was outside of the scope of this project. Based on results to-date, the alloy selection and the treatment processes appear to be well suited for SOFC interconnect application.

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EXECUTIVE SUMMARY

The U.S. Department Energy's Solid State Energy Conversion Alliance (SECA) initiative has identified the development metal interconnects for the solid oxide fuel cells (SOFC) to be a priority core technology need for the SECA industrial teams, second only to the seal materials development. The interconnect materials make electrical series connection from one cell to the next to form a stack. The importance of metallic interconnects arises from their potential for lowering both the materials and manufacturing costs of a key stack component. Successful development and demonstration of metal interconnects will enable achieving the SECA cost target for the SOFC stack.

The technical challenges in the use of metal interconnect are related primarily to high temperature corrosion in air at the stack operating temperature. Typical corrosion resistant alloys form an oxide phase on their surface at the service temperature, which prevents the alloy from additional corrosion. However, such oxide scales are electrically insulating and thus unsuitable for use as interconnects. Alloys that form a conductive scale are chromium based alloys. At the expected stack operating temperature the chromia scale is expected to continue the growth and add to the interfacial electrical resistance, as well as evaporate and condense on the cathode to deactivate the cathode. Both mechanisms lead to stack performance degradation. In Phase I feasibility study, Ceramatec investigated a low cost commercial ferritic stainless steel alloy for high temperature corrosion and electrical properties and methods of improving such properties to facilitate its use as SOFC interconnects.

The approach evaluated in Phase II consisted of two surface treatment techniques. The first one involved pre-treatment of the alloy surface in order to a) reduce the oxide scale growth rate, b) improve the electronic conductivity of the scale at temperature. A pre-treatment technique was identified that accomplished both objectives. Additionally, the resulting surface oxide scale was dense, well-adhered, and found to contain a stable rare-earth chromium oxide phase that is known to show exceptional stability in SOFC environment. In fact, the oxide scale formed was stable in both dry air and humidified air after 500 hours of exposure at 750°C. The stability of typical chrome oxide scale is known to be unstable in presence of moisture and tended to exhibit poor adhesion. The second treatment consisted of applying a conductive coating on top of the pre-treated surface. The purpose of the coating was two fold: a) to reduce the in-plane resistance of the interconnect-cathode interface, and b) to prevent the evaporation of chrome oxide from the metal oxide surface. In order to meet both the objectives, the conductive coating must be dense and well-adhered to the oxide scale. A coating technique was down-selected to give the desired physical properties. The resistance of metal coupons with the two surface treatments, pre-oxidation and application of conductive coating, was measured. The combination of processes that showed the exceptional stability in terms of slow oxide scale growth, low weight gain in oxidation experiments, also showed the lowest resistance. The measured resistance through a coupon couple, consisting of two oxide scale layers, was 10 milliohm-cm², nearly an order of magnitude lower than target.

A similar pre-treatment on the fuel side was also found to be beneficial in lowering the scale resistance. The coating appropriate for the fuel atmosphere and the application technique were also identified. Resistance values of one milliohm-cm² were measured in humidified hydrogen.

Thermal cycle capability is an important requirement for practical fuel cell applications. The conductivity coupons that showed low resistances were thermal cycled three times. Both in air and in fuel, negligible increase in resistance was observed.

More extensive investigations were conducted to measure the stability of conductivity when the interconnect alloy is exposed to air and fuel conditions on opposite sides to simulate the stack operating environment. With additional modification to the surface treatment, electrically and microstructurally stable oxide layer was obtained. Resistance stacks consisting of interconnects under realistic gas flow conditions also showed reasonable stability of performance. Further evaluation of the treated interconnects in fuel cell stacks however is required in order to fully evaluate chromium evaporation issue. Based on results to-date, the alloy selection and the treatment processes appear to be well suited for application as SOFC interconnects.

INTRODUCTION

A variety of fuel cell technologies are currently under development, ranging from small portable units for electronic applications to large stationary power plants. The advantages of fuel cells are well known, and they include high efficiency, low emission, reliability, modularity, and vibration-free operation. High temperature fuel cells such as the Molten Carbonate Fuel Cells (MCFC) and Solid Oxide Fuel Cells (SOFC) offer additional benefits of fuel flexibility and simpler integration of system components. Recognizing the potential of fuel cell technologies, several industry-government partnerships, both in the United States and in other countries have promoted and advanced these technologies to various development, technology demonstration, and pre-commercial stages. These partnerships have resulted in commercially available 250 kW Phosphoric Acid Fuel Cells (PAFC) from ONSI Corporation, and a demonstration of 2 MW Molten Carbonate Fuel Cells (MCFC) by Fuel Cell Energy. Megawatt class demonstration of PAFC system has also been conducted in Japan.

The present thrust of the Solid State Energy Conversion Alliance (SECA) program by the US Department of Energy is to advance the Solid Oxide Fuel Cell (SOFC) technology to commercial reality. The primary goal of the program is to develop a low-cost, modular SOFC stack that will form the basic building block for various power output ranges. However, major technical challenges must be overcome to achieve the goals. Critical issues for the stack are low-cost manufacturing and long-term reliability. The interconnect materials and design have remained a challenge to achieve both technical and cost goals.

The SOFC interconnect must simultaneously satisfy several functional requirements. These functions require materials with high electronic conductivity for the series connection of individual single cells, gas impermeability to separate fuel and oxidant gases, chemical stability and conductivity over a large oxygen concentration range in order to maintain integrity in both the fuel and air atmospheres. Thermal expansion match with the rest of the cell elements is desired. Although, doped LaCrO_3 ceramic interconnects have been investigated, and in fact demonstrated in tubular fuel cells, their applicability in planar SOFCs was found to be limited by materials and processing costs, low electrical and thermal conductivity, and dimensional instability under an oxygen potential gradient. Metal interconnects are thus very desirable from the viewpoints of manufacturing cost in addition to other functional requirements, provided that the high conductivity can be maintained at the operating conditions. It also lends itself to ease of fabrication of gas channels and greater control over dimensions to help improve the conformity as well as uniform reactant distribution to ensure uniform current density, high fuel utilization and high fuel efficiency. The use of thin metallic sheets will also reduce overall weight in the fuel cell system. High thermal conductivity of metal interconnects will help distribute the heat generated during the operation of the cell, thereby reducing the cooling air requirement (which has cost implications via heat exchanger size), as well as eliminating thermal stress failure of ceramic components caused by sharp thermal gradients.

The critical issues that must be addressed in the development of metal interconnects are summarized below in Table 1.

Table 1. Critical Requirements of Metal Interconnects

<i>Critical Issue</i>	Approaches tried	Hurdles for success
1. Thermal expansion match	Use of 95Cr-5Fe (Plansee alloy)	Evaporation of Cr is the major source of degradation
2. Oxidation resistance in air, maintaining conductive scale	Cr containing alloys which form conductive Cr ₂ O ₃ scale	Cr evaporation, scale growth continues to occur causing high resistance contribution
3. Conductive scale in fuel atmosphere	Ni coating or cladding	Ni adhesion during thermal cycles
4. Reactivity with electrode materials to form insulating compound	Surface coating with perovskites such as lanthanum based chromite, manganite, or cobaltite	Achieving dense layers, spall resistance to thermal cycles are issues to be resolved
5. Impurity content reacting with electrodes or forming insulating phases	Custom alloys	Cost of custom alloys
	Selection of low impurity commercial alloys	Commercial alloys must still need to meet other requirements
	Coating of surfaces	Must also address issue 3
6. Compatibility with anode and cathode environments	Monolithic alloy with surface treatments	Engineering demonstration is needed to prove technology
	Layered structure engineered for appropriate atmospheres	
7. Uniformity in contact	Machining or lapping to achieve flatness of 10 microns	May be cost prohibitive
	Use of corrugated layers	Selection of appropriate layer materials
8. Thermal cycle capability	No information available	Scale spalling
		CTE mismatch
9. Cost	Use of commercial alloy	Must meet all other requirements

The critical requirements of metal interconnects can be summarized as follows: 1) thermal expansion match with other cell components, 2) oxidation resistance in air and fuel at the operating temperature, 3) conductive interface (scale) in air and fuel atmospheres, 4) prevention of both the reactivity with electrode materials to form insulating compounds, 4) volatilization and condensation of major or minor constituents that poison electrode activity, 5) compatibility with anode and cathode environments, 6) uniformity in contact with the cells, 7) thermal cycle capability, and 8) cost. Additionally, depending on the stack design, the interconnects could also play a role in stack heat removal, partial hydrocarbon reformation, and mechanical support for the cells. When operating on hydrocarbon fuels, it is also vital that the interconnect material is resistant to carburization. Sulfur tolerance is also desired in case of system simplification with low sulfur containing fuels or when sulfur slip occurs from inadequate sulfur clean up. These factors are common to all designs and concepts contemplated by the various SECA industrial teams.

The use of metal interconnects, while well studied, has posed considerable challenges. An extensive report on this topic along with a collection of commercial alloy properties is in the literature.^{1,2} Typical austenitic or ferritic materials undergo rapid corrosion at the temperatures of SOFC operation, leading to large and unacceptable increases in resistance. Thermal cycling is also difficult, since the metals have higher thermal expansion coefficients compared to other cell materials such as zirconia. In work reported by Siemens, Germany that used a powder metallurgical Cr-5 wt%Fe-1 wt%Y alloy, corrosion of the alloy and in particular, the evaporation of Cr species was found to result in degradation in SOFC performance³ even though the alloy had exact thermal expansion match to zirconia. To mitigate this problem, the metal interconnect was coated with a perovskite such as lanthanum manganite or chromite, to impart oxide scale conductivity and suppress the Cr evaporation. Scale modification using cerium⁴ or other reactive element⁵ is known to reduce the scale growth while imparting higher conductivity to the scale. As the equilibrium partial pressure of chrome-chrome oxide is extremely low, below the partial pressure of typical fuel gas, the oxide is formed even in humidified hydrogen atmosphere. It has been suggested,⁶ that at lower temperatures (800°C) the electronic conductivity in Cr₂O₃ is extrinsic (dependent on dopant concentration), which explains the low conductivity observed in fuel atmospheres.⁷ Thus, it is equally important to explore technical solutions to achieve low resistance in fuel atmosphere, as it is to reduce the scale resistance in air. In prior work at Ceramatec ferritic stainless steel alloys were investigated. Typically, these alloys have around 20% Fe and form a Cr₂O₃ scale. These alloys were found to offer good oxidation resistance as well as a thermal expansion coefficient reasonably close to that of zirconia from room temperature to 700°C, permitting their use in SOFC applications. However, additional issues related to long-term stability in air, performance in wet air and wet fuel, and thermal cycles needed to be addressed. In Phase I, the tasks were aimed at addressing the issue of oxide scale growth both in air and fuel atmospheres and the associated increase in electrical resistance by a surface treatment process.

Successful completion of the work will eventually lead to stacks with stable operating characteristics at the target operating temperatures of 750-850°C (nominal) and with the desired low resistance arising from the stable and conductive materials developed. The commercial alloy that is under consideration for the interconnect can be purchased at \$2 per pound in the final use thickness. Featuring the thin sheets, corrugating and welding or brazing to form the final structure is fairly routine and inexpensive in the metal forming industry. The conventional lanthanum chromite ceramic or high chrome alloy interconnects are projected to be \$30 to \$50 per pound in powder form even in large commercial scale and thus form a significant cost element of the SOFC stack. Additionally, both ceramic and conventional high chrome interconnects require expensive fabrication routes. The interconnect alloy selected in Phase I is low cost, is compatible with both SOFC and other high temperature electrochemical ceramic electrochemical devices. In fact, at the current developmental stage, the materials and fabrication costs Ceramatec incurs for the metal interconnect is \$20 per 10x10 cm plate. At the commercial scale the cost is expected to be about \$2 per plate. At a modest stack power density of 500 mW/cm², the final assembly-ready interconnect cost would be less than \$50/kW. Additional cost reduction is expected with stacks of larger footprint and higher power density. Thus the metal interconnect process development will enable fabrication of SOFCs possessing cost competitive performance and endurance characteristics required for commercialization.

EXPERIMENTAL

The work plan for evaluating the ferritic stainless steel involved three types of characterization, and correlation of data. The evaluation process is outlined in Figure 1. The metal coupons are to be monitored for oxidation properties by measuring weight gain as a function of time at temperature and measurement of resistance as a function of time at temperature.

Figure 1. Interconnect Material Characterization Plan

Discussion with various SECA core technology participants and industrial teams identified several additional test conditions that needed to be included in Phase I evaluation. A summary of the discussion is given in Table 2. The test plan was modified to include the suggestions from the team.

Table 2. Additional Tests Recommended by SECA Participants

Test Conditions	Recommendation	By	Modified Plan
Temperature	750, 800, 850 C	Delphi	750 C (more representative target SOFC temperature)
	Higher (900 C)	Pitt	
Test Atmosphere	Ambient and wet air	Pitt, PNNL, LBNL, Delphi	Individual and various combinations
	Wet hydrogen		
	Dual atmosphere		
Duration (hrs)	1000's	Delphi	Plan extended to 500 hrs
	Longer than 200	PNNL and Pitt	
Thermal Cycle	Include in evaluation	Delphi, LBNL and PNNL	On selected coupons after several 100 hours of isothermal tests.

Pitt = University of Pittsburgh, PNNL = Pacific Northwest National Laboratory,
 LBNL = Lawrence Berkeley National Laboratory

Test Configurations

Traditional evaluation of metal coupons consists of applying a contact layer, typically Pt paste, and measuring resistance in air as a function of time. The potential drawback to this approach is the migration of the Pt paste through the pores or cracks in the growing oxide scale and artificially showing low resistance. In addition, the conditions an interconnect will face in an actual stack test is much more complicated than that of a coupon tested in air. A systematic sequence of tests that needed to be conducted is given in Table 3. Instead of a single coupon, A coupon couple arrangement was used with a contact paste in between them. In general, lanthanum cobaltite, a potential contact paste in a stack was used. The dual atmosphere test also used two metal coupons with one of them having air and fuel atmospheres on opposite sides. The arrangements are shown in Figure 2. Finally, using all metal stack in a resistance test that included contact and electrode layers provided a realistic test of the oxide scale behavior. Full stack test was not in the scope of the project.

Table 3. Experimental Configurations

TGA	Coupon Couples	Dual atm. couples	Resistance Stack	Full Stack
<ul style="list-style-type: none"> ○ Single atmosphere ○ No contact / electrode layers ○ No current ○ Isothermal 	<ul style="list-style-type: none"> ○ Single atmosphere ○ Contact layer ○ Intermittent current ○ Isothermal 	<ul style="list-style-type: none"> ○ Dual atmosphere ○ Continuous current ○ Contact layer ○ Isothermal 	<ul style="list-style-type: none"> ○ Dual atmosphere ○ Continuous current ○ Contact/electrode layers 	<ul style="list-style-type: none"> ○ Dual atmosphere ○ Continuous current ○ Contact/electrode layers ○ In-plane thermal, current density gradient ○ Potential chemical species (chromium) interaction with electrochemistry of electrodes

Figure 2. Schematic of Test Configuration

Feasibility / Proof-of-concept Demonstration in Background Work and Phase I

The proposed activities in Phase I included: a) selection of atmosphere-appropriate surface treatment process conditions and conductive coatings for the anode and cathode sides of metal coupons, b) evaluation of interfacial resistance behavior as a function of time in air and humidified hydrogen after appropriate treatments, c) analysis of interfacial microstructure for scale thickness, morphology and chemistry, and d) data analysis to identify and recommend

future work to mature the technology further for industrial team evaluation. Initial evaluations using metal coupons were conducted at 850 and 900°C. After a detailed discussion with the DOE project officer along with several SECA participants (Pacific Northwest National Lab., Delphi, University of Pittsburgh, and Lawrence Berkeley National Lab.), additional tasks that are critical to the project were identified. Those are: evaluation of behavior at a lower temperature (750°C), effect of humidified air, and simultaneous exposure to hydrogen and air on opposite sides. All the added tasks were also completed in Phase I.

Alloy Selection

A commercial stainless steel alloy selected for evaluation. The alloy selection was based on the following general criteria set forth earlier: conductive oxide scale (chromia former), thermal expansion compatibility (for thermal cycles), impurity content (low Si and Al that form insulating phases), and low propensity for chrome vaporization (~20 % Cr alloy). The selected alloy has a thermal expansion coefficient (CTE) of 11.5 ppm/°C (room temp. – 500°C) and 12.6 ppm/°C (200 – 700°C) compared to 11 ppm/°C for 8 mole% yttria doped zirconia (YSZ) and 13 ppm/°C for the anode. Thus the CTE over the temperature of interest the alloy falls between the two critical components of SOFCs.

Surface treatment and Oxidation Study

The purpose of surface treatment is two fold: a) it results in a dense oxide scale of uniform thickness and b) it selectively forms a conductive chromia based scale. After evaluating a variety of surface treatment processes, separate process steps were found to be optimal for the anode and cathode environments. The conditions for treatment to grow the initial oxide scale was however kept identical so that a full interconnect that would face both atmospheres can be treated without the complication of process incompatibility. The treated and untreated coupons were aged at different temperatures. Initial measurements were done at 850 and 900°C. The sample weight gain is plotted against time at temperature in Figure 3 and Figure 4. It can be seen that the untreated bare sample gained weight at a considerably faster rate than the three pre-treatment processes, at both temperatures. The tested samples were analyzed using the scanning electron microscopy for scale thickness and microstructure. The scale thickness values (Figure 5) are consistent with weight gain measurements, in that the sample with the thinnest scale also showed the lowest weight gain.

Figure 3. Weight Gain at 850°C in Air as a Function of Pre-treatment Process

Figure 4. Weight Gain at 900°C in Air as a Function of Pre-treatment Process

Bare Metal
Scale thickness 7 microns

Process: 10050H9-4 (POT1)
Scale thickness 5 microns

Process: 100H0-4 (POT2)
Scale thickness 5 microns

Process: 50N9-4 (POT3)
Scale thickness 3 microns

Figure 5. Micrographs of Scale-Metal Interface after aging at 900°C in air for 200 Hours

Weight Gain Measurements (750°C)

For 750°C test, coupons were tested using a Thermogravimetry Analyzer. As shown in Figure 6 below, the treated coupons show a significant reduction in weight gain over untreated coupons.

Figure 6. TGA of Coupons at 750°C

In addition to exposure to dry and wet air conditions, separate experiments were conducted for weight gain under both exposure conditions. Samples were periodically pulled out of the furnace and weighed. The test was started with sufficient number of samples such that the samples pulled out for weight measurements were not re-inserted into the furnace to avoid the effect of thermal cycles to confound the static weight change measurements.

The weight gain after 300-hour exposure is shown in Figure 7 for the as-received (no pre-oxidation) and different pre-oxidation treatments. Significant additional weight gain was observed when exposed to wet air for both as received and several treatment conditions. Combination of half the duration in dry and the rest in wet air also showed some weight gain. However, some of the pre-oxidation conditions showed negligible weight gains.

Conductivity Measurements

Using the best combination of treatments and coatings appropriate for the anode and cathode atmospheres, the resistance of coupon couples was measured in air and in humidified hydrogen. The conductivity rig arrangement is shown in Figure 8. The results are shown in Figure 9 and Figure 10. In humidified hydrogen, the resistance is well below 1 milliohm-cm² while in air it is less than 10 milliohm-cm². Additionally, the coupon couples have been subjected to several thermal cycles and they were found to exhibit good stability. The thermal cycles were done using natural furnace cooling (power turned off) and rapid heat up at the rate of 10°C per minute.

Figure 8. Conductivity Rig

Figure 9. Resistance of Coupon Couples in Humidified Hydrogen at 750°C

Figure 10. Resistance of Coupon Couples in Dry Air at 750°C

Scale Morphology

Several treatment processes were evaluated. For simplicity, only a few of those exposed to dry and wet air at 750°C for 500 hours are presented in Figure 11 Figure 16. The micrographs shown are for untreated metal and two surface treatments. In general, the untreated samples show poor scale adhesion both in dry and wet air exposures. Both treatments show well adhered scale in dry air and wet air exposures. The treatment process 100H9-4 shows some instability in the scale structure, while the process 50N9-4 shows much more stable scale microstructure. Treatment NT-0 for the fuel side produces a scale that is well-adhered after 72 hour exposure time.

Untreated metal dry air 750°C 200 hours

Untreated metal: wet air 750°C 500 hours

Figure 11. Micrographs of Untreated Metal
The scale is not well-adhered in dry air; scale loses integrity in wet air

Figure 12. Micrographs of Treated Coupons (Process 50N9-4)
Scale is well-adhered in both dry and wet air

Figure 13. Micrographs of Treated Coupons (Process 100H9-4)
Well-adhered scale in dry air

Figure 14. Micrographs of Dry Air Side of Dual Atmosphere Test

**Figure 15. Micrograph for Process 50N9-4
Conductivity Tested Sample
Dry air 750°C 500 hours**

**Figure 16. Micrograph for Process NT-0
in Wet Hydrogen
72 hours in at 750°C**

Exposure to Dual Atmosphere - Untreated Coupons

A schematic of the test set-up is shown in Figure 17. A metal coupon (with or without preoxidation) is sealed to a zirconia tube. The inside of the tube maintained at the desired wet atmosphere while the outside is exposed to dry air to obtain dual atmosphere exposure. Additional coupons inside and outside are placed so that they are exposed to a single atmosphere on both sides of the coupons. In the case of wet hydrogen the seal quality is monitored by using the zirconia tube as a sensor.

**Figure 17. Schematic of a Dual
Atmosphere Test Rig**

Results (Figure 18)

Sample - no pre-oxidation: Exposed to dual atmosphere for 120 hours

- Very thin scale is present at some areas of metal surface on both sides.
- Scale is not continuous.
- Some areas of scale are not well-bonded to metal.
- On air side, the scale shows poor adhesion.

Hydrogen side

(SE)

(BSE)

air side (SE)

(BSE)

(SE)

Scale cracks (BSE)

Figure 18. Micrographs of Untreated Metal Coupons Exposed to Dual Atmosphere Dual Atmosphere Couples with Treated Coupons

In order to test surface treated coupons under various test conditions, a set up shown in Figure 19 is used. This arrangement allows for microstructural analysis of three distinct exposure zones: 1) air/air, 2) air/fuel with no current, and 3) air/fuel with current. The rig arrangement was initially validated using air on both sides and measuring the coupon resistance to compare with earlier coupon couple measurement. The results shown in Figure 20 confirm that the new

arrangement provides reliable resistance values. The microstructure shown in Figure 21 after test also confirms that the surface treatment significantly enhances scale adhesion.

Figure 19. Dual Atmosphere Test Arrangement

Figure 20. Comparison of Resistance Values of Treated Metal using Two Test Techniques

Figure 21. Scale Microstructure of Treated Coupons After Exposure To Air / Air at 750°C for 300 hours

In dual atmosphere tests with modified surface treatment to provide an outer layer of lanthanum chromite, the resistance was fairly low at 15 milliohm-cm² after 400 hours (Figure 22). However, the microstructure showed nodules of chromium oxides instead of well adhered scale (Figure 23).

Figure 22. Coupon Resistance in Dual Atmosphere

Figure 23. Air-side Microstructure After Dual Atmosphere Test

Modification to the pretreatment process to achieve a dense scale layer showed an improvement in both the resistance value and microstructure, as shown in Figure 24Figure 25. The resistance was less than 10 milliohm-cm² initially and increased somewhat after a thermal

cycle. Even after 1,000 hr exposure to dual atmosphere, the oxide scale was thin and well adhered.

Figure 24. Air-side Resistance of Coupons in Dual Atmosphere Testing with Improved Treatment Process

- **Coupon sandwich area (current flow)**
- **1000 hrs in dual atm.**
- **Away from sandwich area**
- **1000 hrs in dual atm.**

Figure 25. Microstructure of Air-side Scale after 1,000 hrs Exposure to Dual Atmosphere

Conductive Layer / interconnect interaction

Our stack test results (from the gallate SBIR program) and reports from other developers indicate the formation of Sr-Cr-O species in the contact layer. This phase is formed by the interaction between Cr diffusion from the interconnect (presumably via vapor phase transport) and the conductive layer (typically cobaltite) that is between the cathode and interconnect. The formation of the new phase is suspected in part to cause stack degradation by depositing in the triple phase region to reduce the cathode catalytic activity and by forming at the interface to introduce additional ohmic resistance.

The following contact layer compositions were synthesized for interaction study with the stainless steel powder (with and without the surface treatment). The rationale for selection of the above compositions is (a) Lower or no Sr content will reduce tendency to form a Sr-based reaction product and (b) Effect of Ca vs Sr as A-site dopant.

- $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_{3-x}$
- LaCoO_3
- $\text{La}_{0.95}\text{Ca}_{0.05}\text{CoO}_{3-x}$
- $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_{3-x}$

We received a custom batch of stainless steel composition in powder form from Hoeganaes Corporation, Riverton, New Jersey. This powder was used for the metal/conductive layer interaction study by annealing a mixture of the powders. With untreated stainless steel powder, the mixture formed Fe-Cr spinel while the treated stainless steel powder did not show any reaction product with the perovskite powder after calcinations at 750°C (Figure 26).

Dual Atmosphere Exposure Tests of Baseline La(Sr)CoO₃ Contact Layer

A schematic of the test set up is shown below in Figure 27. On treated coupon, a strip of LSCo was fired on at 900°C for two hours. Another strip of wet LSCo ink was applied on top of the pre-fired strip and separate LSCo strip was applied on the treated metal surface. The sample was exposed to dual atmosphere for 300 hours. SEM analysis was done on three different areas of the air-side interface (Figure 30). While the resistance in dual atmosphere test (Figure 33) was low in one case, in general the thermal spray process disrupted previous surface treatment resulting in uneven oxidation scale.

Figure 27. Schematic of a dual atmosphere exposure test rig for contact paste reactivity

Figure 28. SEM No LSCo area

Comment: A thin, dense, well adherent oxide scale is formed on the air side in dual atmosphere exposure condition, as is typical of treated samples.

Figure 29. Wet LSCo area

Comment: Good interface between the oxide scale and the painted cobaltite. Some Cr migration into the cobaltite layer is seen.

Figure 30. Fired (900C, 2 hours)+wet LSCo

Comment: No difference between the two layers of cobaltite.

Thermal Sprayed LSCo (at Idaho National Lab.):

Figure 31. Surface Image of thermal sprayed LSCo

Figure 32. Surface X-ray map from different areas show identical elemental composition

Figure 33. Conductivity of LSCo thermal sprayed coupon in dual atmosphere

Chromium Evaporation Test

Experimental Set-up

The chromia evaporation was quantified using a getter technique. The metal coupon of interest was placed at a distance of approximately 0.2 cm from a bed of a known quantity of high purity alumina powder. The powder chamber was constructed (Figure 1) using a zirconia disk (approx. 4 cm diameter) sealed to ring of zirconia, which in turn was sealed to a long zirconia tube. The metal coupon was cemented on to the zirconia ring in four places such that a small air gap was maintained between the metal and the ring. The arrangement was maintained at 800°C for 500 hours. The exposed alumina powder was dry milled using zirconia media to homogenize the powder. The powder was analyzed for Cr and Mn content using the ICP technique.

Three coupon types were tested. The first one was a baseline stainless steel 400-series coupon, the second one was a surface treated coupon, and the third one was surface treated and thermal sprayed with Lanthanum Strontium Cobaltite (LSCo).

Figure 34. Schematic of Cr evaporation test rig

Chromium evaporation Measurement

The Cr and Mn contents of the alumina powder batches are shown in Table 4. A baseline alumina powder and the powder batches exposed to untreated and surface treated metal coupons are compared. The treatment reduces the Cr evaporation by nearly 50%. It is likely that when complete surface coverage with LaCrO_3 phase is achieved further reduction in Cr evaporation can be expected. More significantly, when the treated surface was thermal sprayed with LSCo the chromium evaporation is substantially reduced from a baseline of more than 200 ppm to less than 5 ppm.

Table 1. Table 4. ICP analysis of alumina getter for Chromium content (ppm by weight)

	Baseline powder	Powder exposed to untreated coupon	Powder exposed to treated coupon	Powder exposed to treated and LSCo thermal sprayed coupon
Cr	< 0.5	250	140	4.1
Mn	< 0.25	3.4	< 2.5	0.74
Sr				1.8
Co				<10
Fe				<2.0

Fuel-side Evaluation

Resistance with Ni sprayed coupon

Figure 35 shows the resistance values of the stainless steel coupon couple that was thermal sprayed with a nickel layer. The initial resistance was about 0.2 milli ohm.cm² and was stable for 150 hour test duration. Subsequently, the coupon couple was thermal cycled to room temperature three times at an interval of 150 hours at 750°C. Each time immediately following the thermal cycle, the resistance increased to about one milli-ohm.cm², still a significantly low value, and returned to a value of 0.5 milli-ohm.cm² within a few hours. The thermal cycles were done at a slow heating and cooling rate of a few degrees per minute.

Figure 35. Stability of Ni thermal sprayed coupons over three thermal cycles

Exposure to Syngas and H₂S

SEM analysis of bare metal exposed to Syn gas. Exposure time-250 hours.

Untreated coupon exposed to syngas at 750°C for 250 hours was analyzed and the results are shown below. The analysis shows that the exposure forms a Cr oxide scale with Ti oxide particles. Nb segregation in the scale is also noted.

Figure 36. Micrograph of syngas exposed metal coupon

EDS of metal/scale interface

EDS of scale

(Note: Nb mislabeled as Hg)

Figure 37. Elemental analysis of syngas exposed interface

SEM analysis of metal exposed to ~ 1,000 ppm H₂S + Syn gas. Exposure time-250 hours.

Stainless coupon exposed to syngas with ~ 1,000 ppm H₂S at 750°C for 250 hours was analyzed and the results are shown below. Analysis shows that the scale is predominantly Cr oxide and segregation of Ti at the interface is also seen. The base metal develops considerable porosity.

Figure 38. Microstructure of coupon exposed to syngas with H₂S

- Effect of sulfur in fuel on the scale formation was studied (Figure 1 – 5). The tests were done at 750°C with about 50 ppm H₂S
 - When the coupon is exposed to hydrogen or hydrogen followed by H₂+H₂S the scale was predominantly chromia
 - When the coupon is exposed directly to H₂S, syngas, or syngas followed by syngas + H₂S, then Fe-oxide is also noted in addition to chromia scale.

Resistance Stack

A three-cell stack equivalent of a resistance stack was built. Three set of full interconnects and three separator plates functioning as pseudo-cells comprise the stack. Three different contact treatments were using LSCo material, namely, thermal sprayed with screen printed green LSCo on top, screen printed and fired, and finally screen printed, fired, with a green LSCo bond layer (Figure 39).

The resistance stack was initially operated at a low current of 1.3 Amps for about 150 hours and then increased to 12 Amps for another 350 hours. Comparison different segments were made by measuring voltage drops across various segments. From this test, it appears that the plasma sprayed + screen printed green layer LSCo shows the lowest resistance and good stability. The other two variations show higher resistance, but reasonable stability in this short term test.

Figure 39. Schematic of Resistance Stack

Figure 40. Performance Stability of Resistance Stack

Summary

This project focused on metal interconnect development for SOFC power systems. Commercial stainless steel (Fe – 22%Cr) was evaluated under different test conditions to simulate SOFC operation in order to characterize its performance behavior. A surface treatment process was identified that simultaneously reduces oxidation scale growth rate on the air side, provides stable microstructure in dual atmosphere conditions, and reduces chromium evaporation and reactivity with common perovskites. Further evaluation in actual stack tests are needed to understand additional technical issues that need to be addressed. The highlights of the project are listed below.

Commercial stainless steel with graded coating shows:

- Low, stable interface resistance through several thermal cycles
- Low air-side resistance in dual atmosphere
- Modified treatment process provides stable microstructure on the air-side in dual atmosphere exposure
- Powder mixture heat treatment shows no observable reactivity with potential contact materials (perovskites)
- Limits chromium evaporation – additional stack tests are needed to evaluate the effect
- Sulfur tolerance needs further investigation to understand morphology changes
- Resistance stack provides resistance information in a stack arrangement

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