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Evaluation of Ferritic Stainless Steel for Use as Metal Interconnects for Solid Oxide Fuel Cells

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Interconnect development for planar solid oxide fuel cells is considered a vital technical area requiring focused research to meet the performance and cost goals. A commercial ferritic stainless steel composition for oxidation resistance properties was investigated by measuring the weight gain due to air exposure at fuel cell operating temperature. A surface treatment process was found to produce a dense, adherent scale and to reduce the oxide scale growth rate significantly. A process was also identified for coating the surface of the alloy to reduce the in-plane resistance and potentially to inhibit chromium oxide evaporation. The combination of treatments provided a very low resistance through the scale. The resistance measured was as low as 10 mΩ-cm^2 at 750 °C in air. The resistance value was stable over several thermal cycles. The treated samples were exposed to a variety of atmospheres that were relevant in fuel cell operation to evaluate changes in scale morphology. Analysis of the scale after such exposure showed the presence of a stable composition. When exposed to a dual atmosphere (air and hydrogen on opposite sides of the metal sheet), however, the scale composition contained a mixture of phases. Additional process modifications are planned to reduce the effect of dual-atmosphere exposure.

Keywords ferritic stainless steel, interconnects, solid oxide fuel cells

1. 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 and solid oxide fuel cells (SOFCs) offer the additional benefits of fuel flexibility and simpler integration of system components. The present thrust of the Solid State Energy Conversion Alliance program by the US Department of Energy is to advance the 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 that must be met 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, and chemical stability over a large oxygen concentration range 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 both materials and processing costs, as well as low electrical and thermal conductivity, and dimensional instability under an oxygen potential gradient. Metal interconnects are, on the other hand, 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. Metals also offer ease of fabrication of gas channels and greater control over dimensions to help improve the conformity as well as the uniform reactant distribution required 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. The high thermal conductivity of metal interconnects helps to distribute the heat generated during the operation of the cell, thereby reducing the cooling air requirement (which has cost implications related to heat exchanger size), as well as eliminating the thermal stress failure of ceramic components caused by sharp thermal gradients.

Critical issues that must be addressed in the development of metal interconnects are given below in Table 1 and can be summarized as follows: a) thermal expansion match with other cell components; b) oxidation resistance in air and fuel at the operating temperature; c) conductive interface (scale) in air and fuel atmospheres; d) limited reactivity with electrode materials

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Table 1 Critical Requirements of Metal Interconnects

Technical Criteria	Approaches Evaluated	Challenges
Thermal expansion match	Use of 95Cr-5Fe (Plansee alloy)	Evaporation of Cr is the major source of degradation
Oxidation resistance in air, maintaining conductive scale	Cr containing alloys that form conductive Cr_2O_3 scale	Cr evaporation, scale growth continues to occur causing high resistance contribution
Conductive scale in fuel atmosphere	Ni coating or cladding	Ni adhesion during thermal cycles
Reactivity with electrode materials to form insulating compound	Surface coating with perovskites such as doped lanthanum chromite, manganite, or cobaltite	Achieving dense layers, spall resistance with thermal cycles
Impurity content reacting with electrodes or forming insulating phases	Custom alloys	Cost/time to develop custom alloys
	Selection of low impurity commercial alloys	Commercial alloys still need to meet other requirements
	Coating of surfaces	Must also address adhesion and reactivity issues
Compatibility with anode and cathode environments	Monolithic alloy with surface treatments	Engineering demonstration is needed to prove technology
	Layered structure engineered for appropriate atmospheres	
Uniformity in contact	Machining or lapping to achieve flatness required for stacking	May be cost prohibitive
	Use of compliant layers	Selection of appropriate layer materials
Thermal cycle capability	No information available	Scale spalling CTE mismatch
Cost	Use of commercial low-alloy stainless steels	Must meet all other requirements

to form insulating compounds; e) limited volatilization and condensation of major or minor constituents that poison electrode activity; f) compatibility with anode and cathode environments; g) uniformity in contact with the cells; h) thermal cycle capability; and i) low cost. Additionally, depending on the stack design, interconnects can also play a role in stack heat removal, partial hydrocarbon reformation, and mechanical support for the cells.

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 available.[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 (CTEs) compared with other cell materials such as zirconia. Even if the alloy thermal expansion is matched to the cell components, the evaporation of Cr species may poison the cathode, resulting in degradation in SOFC performance.[3]To mitigate this problem, the metal interconnect was coated with a perovskite such as lanthanum manganite or chromite to impart oxide scale conductivity and to suppress the Cr evaporation. Scale modification using cerium[4] or another reactive element[5] is known to reduce the scale growth while imparting higher conductivity to the scale. As the equilibrium oxygen partial pressure with Cr-Cr_2O_3 is extremely low, below the partial pressure of typical fuel gas, the oxide is formed even in a humidified hydrogen atmosphere. It has been suggested[6] that at lower temperatures (800 °C) the electronic conductivity in Cr_2O_3 is extrinsic, which explains the low conductivity observed in fuel atmospheres.[7] Thus, it is equally important to explore technical solutions to achieve low resistance in a fuel atmosphere as it is to decrease the scale resistance in air. In prior work at Ceramatec (Salt Lake City, UT), ferritic stainless steel alloys were investigated. Typically, these alloys range from 20-30% Cr and form a Cr_2O_3 scale. These alloys were found to offer good oxidation resistance as well as a CTE that was 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 the current study, 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.

2. Experimental

The evaluation of ferritic stainless steel alloys was conducted using 1 × 1 cm coupons having a thickness of approximately 0.2 cm. The experimental evaluation included oxidation properties, conductivity of the oxide scale, and analysis of the effects of exposure to various relevant atmospheres on the scale microstructure.

2.1 Oxidation Study

Coupons of the alloy, 1 × 1 cm, were cut, degreased, and etched with phosphoric acid to clean the surface oxide layer. Various surface treatment conditions were selected to treat the surface of the coupons for oxidation study. Initial tests were conducted at 850 °C and 900 °C. Both the treated and untreated coupons were annealed in a furnace. Samples were pulled at various times and were weighed to monitor the weight gain. As a result of the recent focus on lowering the fuel cell operating temperature to below 800 °C, an annealing temperature of 750 °C was selected for additional study.

2.2 Scale Conductivity Measurements

The conductivity of the oxide scale was measured using a symmetric arrangement (Fig. 1). This arrangement was selected to avoid the use of Pt ink on the scale. If cracks developed with increasing scale thickness, this arrangement would prevent the electromigration of Pt into the cracks, causing artificially lower resistance. In the symmetric arrangement, two coupons were assembled with the treated surfaces against each other. A highly conductive perovskite ink, typically cobaltite-based, was applied over the coupon surfaces to ensure good electrical contact between them.

3. Effect of Humidified Air and Exposure to Dual Atmosphere

The test plan included exposing the metal foil of the alloy to the following conditions: (a) dry ambient air; (b) humidified (3% H_2O) air; and (c) dual atmospheres with dry air and wet air across the sample, and dry air and humidified hydrogen across the sample. To conduct these experiments, ferritic stainless steel foils were used. Based on promising treatment conditions selected from weight gain measurements, the foil surfaces were treated with processes that were appropriate for the atmosphere. The foil was cemented between two zirconia tubes and assembled in a furnace. The test arrangement is shown in Fig. 2. In tests using humidified hydrogen on one side of the foil, the zirconia tube itself was used as an oxygen sensor to monitor the integrity of the cement seal. The air side of the zirconia tube was used as the reference electrode for the sensor. The tests were conducted at 750 °C for 500 h. The samples were then analyzed using x-ray diffraction (XRD) for phase analysis of the oxide scale and a scanning electron microscope (SEM) for scale thickness, morphology, and integrity.

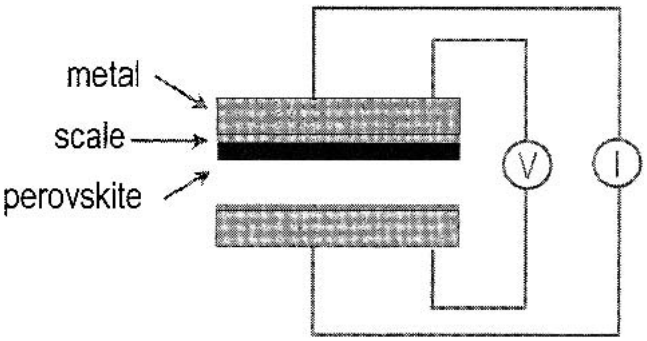


Fig. 1 Coupon conductivity test arrangement

3.1 Conductive Coating Application

The purpose of the conductive coating over the treated surface is 2-fold: on the air side of the interconnect, the coating will prevent Cr evaporation; and on both air and fuel sides, the appropriate coating will reduce the in-plane electrical resistance. Initial coatings, perovskite on the air side and nickel on the fuel side, were applied using screen printable inks. This provided a means to evaluate the nature of the printed layer as well as to provide a means to conduct the electrical conductivity measurements in the coupon tests, which were discussed earlier. In order to achieve a dense coating, a thermal spray technique was evaluated. Treated coupons were

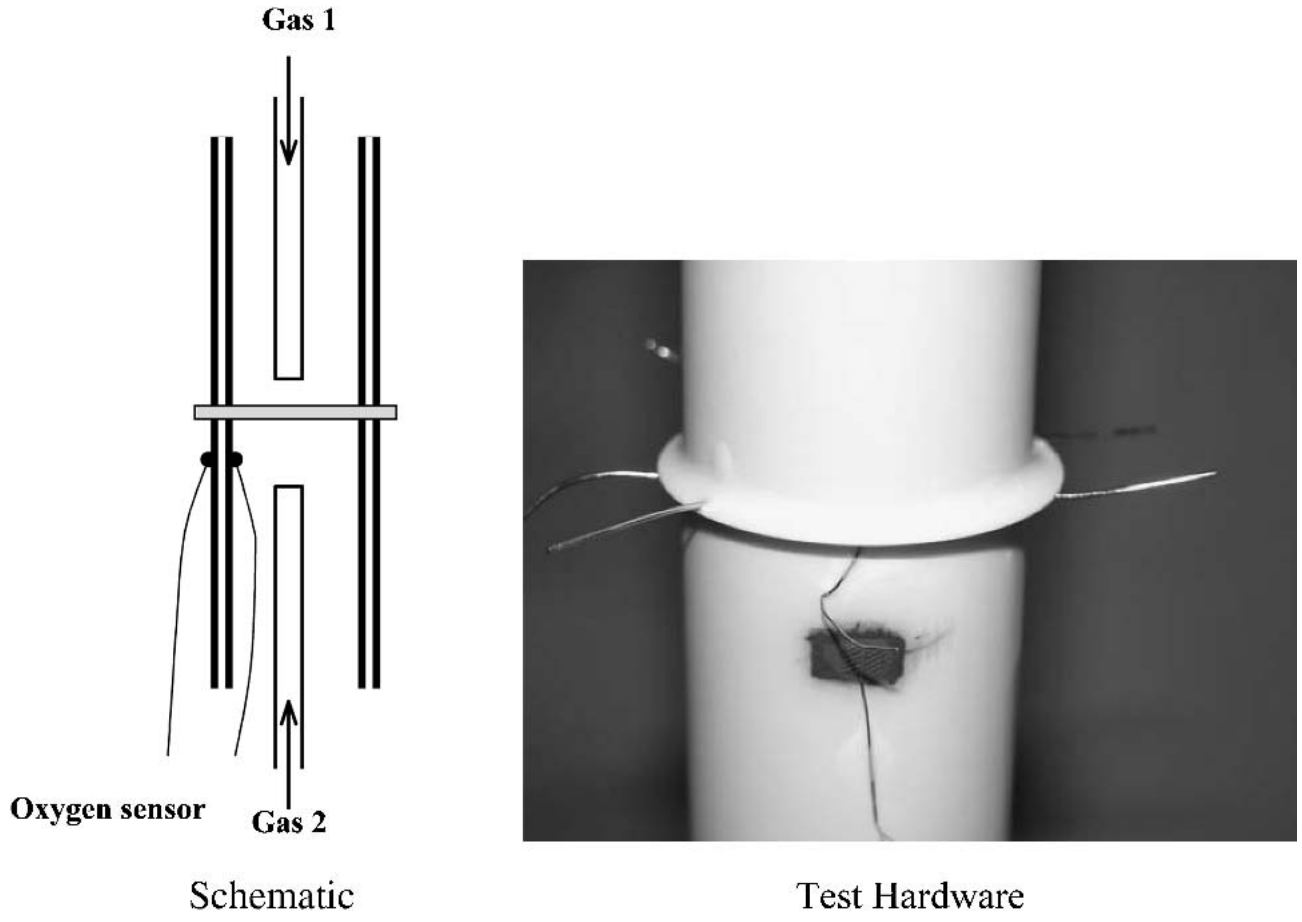


Fig. 2 Test arrangement for dual-atmosphere exposure: (**a**) schematic; (**b**) test hardware

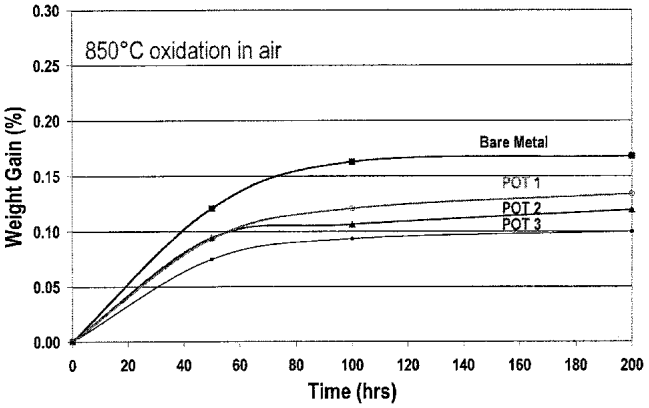


Fig. 3 Weight gain at 850 °C in air as a function of treatment process

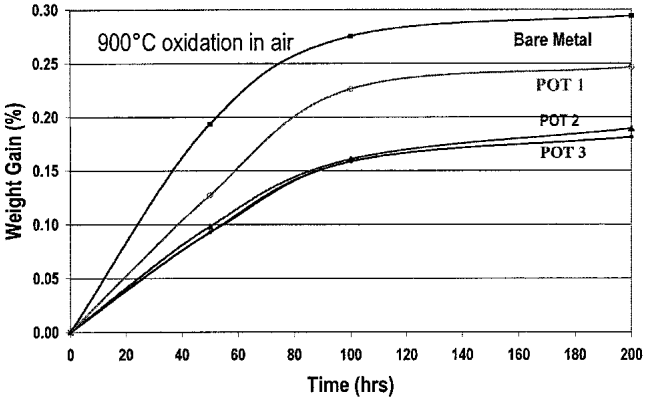


Fig. 4 Weight gain at 900 °C in air as a function of treatment process

sprayed with the appropriate layer and used for conductivity measurements. Selected coupons were also subjected to multiple thermal cycles.

4. Results and Discussion

The primary focus of the work was to study the feasibility of using ferritic stainless steel as the interconnect. Several treatment processes were evaluated to study their effect on the scale conductivity and long-term stability.

4.1 Alloy Selection

A commercial stainless steel 400-series alloy was selected for evaluation. The alloy selection was based on the following general criteria that were 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 Cr vaporization (~20% Cr alloy). The selected alloy has an average CTE of 11.5×10^{-6}/°C (at room temperature to 500 °C) and 12.6×10^{-6}/°C (at 200-700 °C) compared with 11×10^{-6}/°C for 8 mol% yttria-doped zirconia and 13×10^{-6}/°C for the anode. Thus, over the temperature range of interest, the CTE of the alloy fell between the two critical components, the electrolyte and the anode, of the SOFCs.

4.2 Surface Treatment and Oxidation Study

The purpose of surface treatment is 2-fold: 1) to achieve a dense oxide scale of uniform thickness; and 2) to selectively form either a conductive chromia based or a Cr-containing oxide 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 could be treated without the complication of process incompatibility. The treated and untreated coupons were aged at different temperatures. Initial measurements were made at 850 °C and 900 °C. The sample weight gain is plotted against time at temperature in Fig. 3 and 4. Results from three different pre-oxidation treatments (POTs) (i.e., POT1-POT3) are shown. It can be seen that the untreated bare sample gained weight at a considerably faster rate than the three treatment processes, at both temperatures.

The tested samples were analyzed using SEM for scale thickness and microstructure. The scale thickness values (Fig. 5) are consistent with weight gain measurements, in that the sample with the thinnest scale also showed the lowest weight gain.

4.3 Conductivity Measurements

In addition, atmosphere-specific conductive coatings were applied to the treated sample. For the air side, different perovskite materials were evaluated. The purpose of the conductive coating, if applied as a dense layer, is to limit the chromia evaporation and to reduce the in-plane resistance of the interconnect. A screen-printing technique was used for the initial study, although the printed layer was expected to be porous and not completely effective in eliminating the potential evaporation of chromium oxide. Some porosity in the coating was not expected to influence the conductivity measurements. The interfacial resistance of the treated/coated alloy was measured using a symmetric couple of the following arrangement: alloy/treated interface/coating||coating/treated interface/alloy, as shown in Fig. 1. Thus, the measured resistance included two interfaces of interest. The lowest resistance was seen with a cobaltite-based conductive layer, while the highest resistance was with a chromite layer (Fig. 6). Again, the initial conductivity measurements were made at the higher temperatures.

4.4 Effect of Various Exposure Conditions at 750 °C

Additional test conditions were included in the evaluation of metal coupons to cover the broad range of exposure conditions that were expected for the interconnects during SOFC operation. The tests were conducted at 750 °C, and compared exposure to dry and wet air, and dual atmospheres. The two treatments that produced scales with promising characteristics were selected. The weight gain at the early time periods was negligible. Figure 7 shows the weight gained after 500 h of exposure

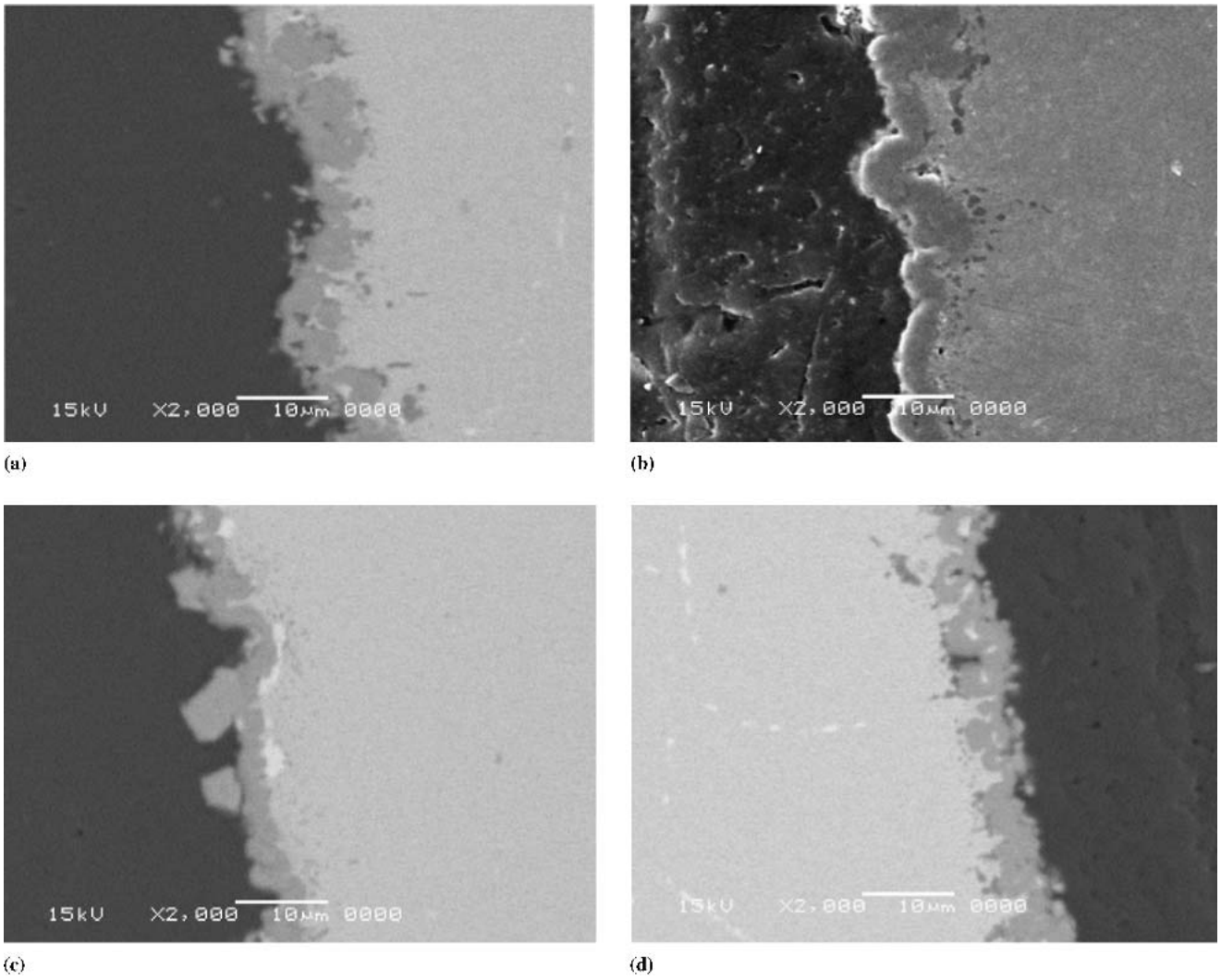


Fig. 5 Micrographs of the scale-metal interface after aging at 900 °C in air for 200 h: (**a**) bare metal, scale thickness 7 μm; (**b**) process 10050H9-4 (POT1), scale thickness 5 μm; (**c**) process 100H9-4 (POT2), scale thickness 5 μm; and (**d**) process 50N9-4 (POT3), scale thickness 3 μm

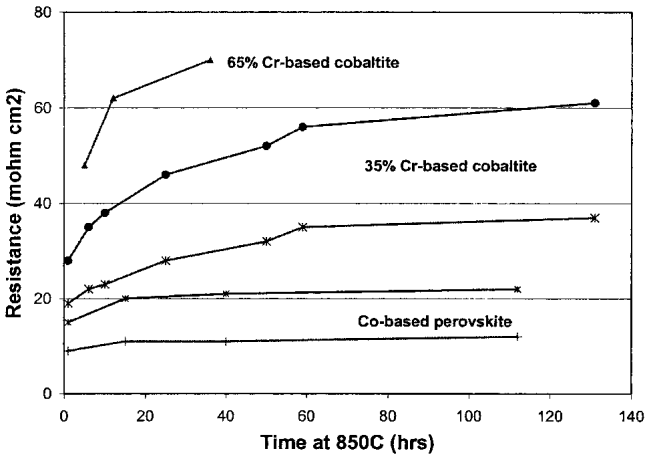


Fig. 6 Conductivity at 850 °C in air as a function of conductive coating materials

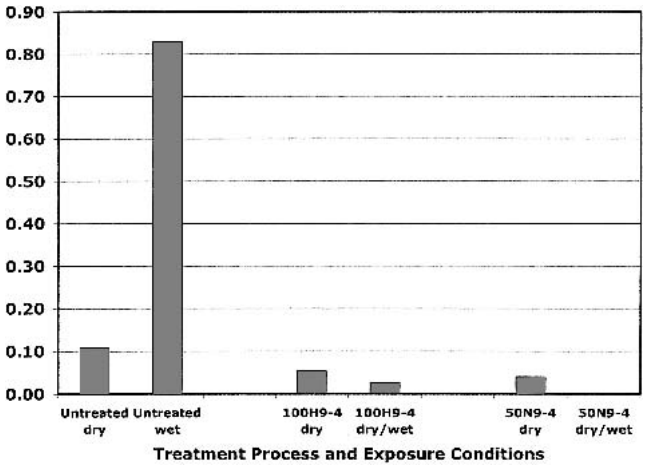


Fig. 7 Weight gain (in %) when exposed to dry and wet air

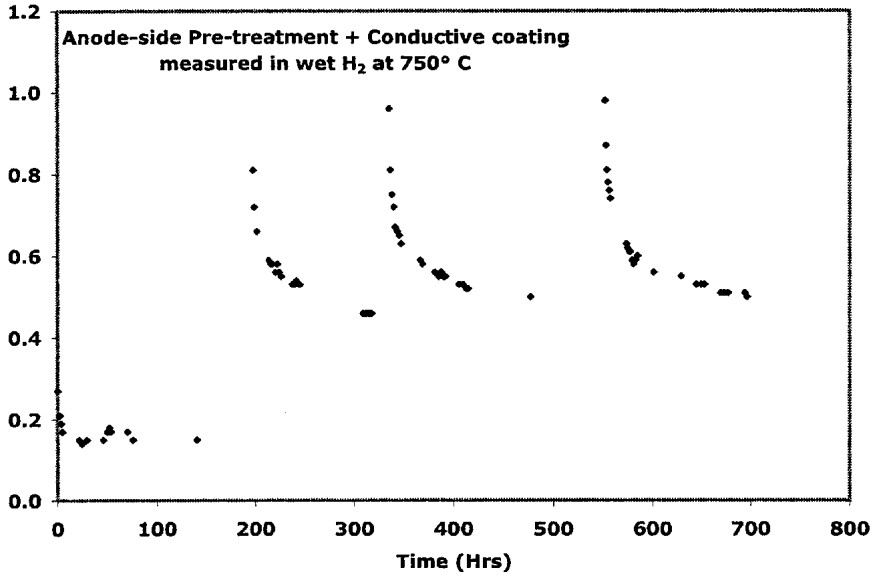


Fig. 8 Resistance (in $m\Omega$-cm^2) of coupon couples in humidified hydrogen at 750 °C

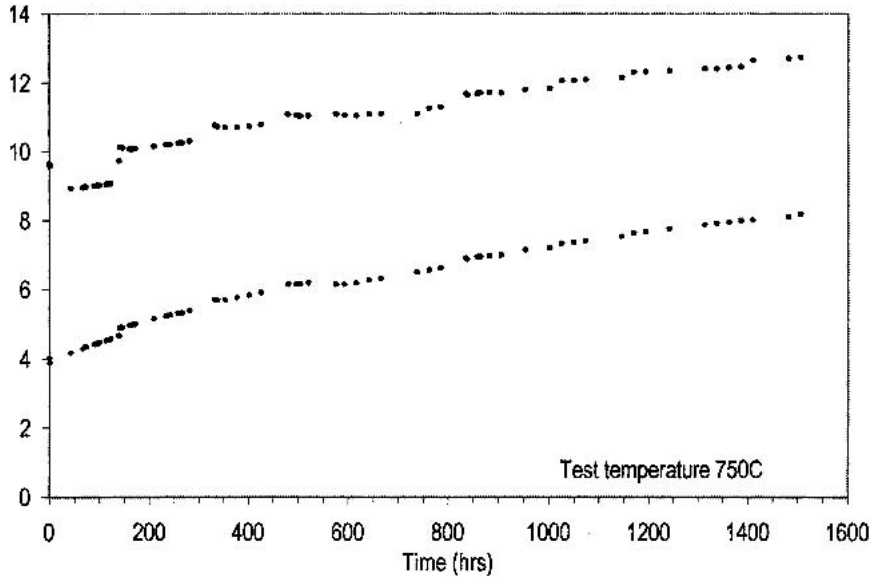


Fig. 9 Resistance (in $m\Omega$-cm^2) of coupon couples in dry air at 750 °C (Data for two treatment processes are shown. Samples were thermal cycles five times at 200 h intervals)

to dry or wet air (~3% H_2O). The treatments caused significant reduction in weight gain relative to the untreated samples. The difference is much more dramatic in wet air exposure conditions.

Using the best combination of treatments and coatings appropriate for the anode and cathode atmospheres, the resistance of coupon couples was measured in humidified hydrogen and in air. The results are shown in Fig. 8 and 9. In humidified hydrogen, the resistance is well below 1 $m\Omega$-cm^2, while in air it is less than 10 $m\Omega$-cm^2. Additionally, the coupon couples have been subjected to several thermal cycles, and they were found to exhibit good stability. Even after numerous thermal cycles, the air side and fuel side resistance values were well below the target values. The thermal cycles were performed using natural furnace cooling (i.e., power turned off) and rapid heat up at the rate of 10 °C/min.

In addition to the proposed evaluations, investigations related to oxide morphology and growth rates in wet air were also conducted.

4.5 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 h are presented (Fig. 10-15). The micrographs shown are for untreated metal and two surface treatments. In general, the

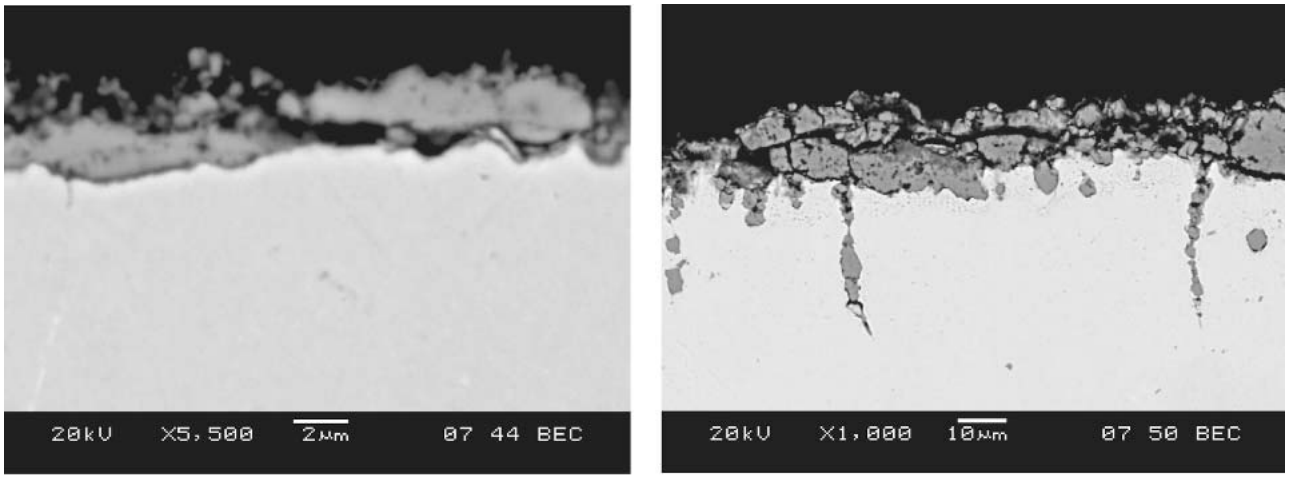


Fig. 10 Micrographs of untreated metal: (**a**) untreated metal, dry air 750 °C for 200 h; and (**b**) untreated metal, wet air 750 °C 500 h. The scale is not well-adhered in dry air and loses integrity in wet air.

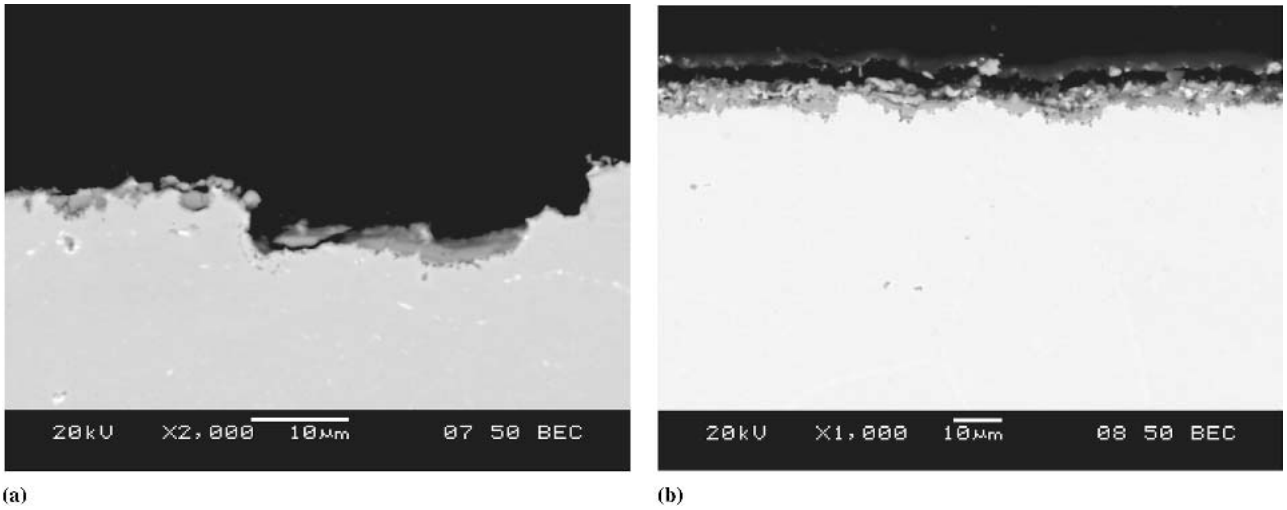


Fig. 11 Micrographs of treated coupons (process 50N9-4). (**a**) 50N9-4 in dry air 750 °C for 500 h; and (**b**) 50N9-4 in wet air 750 °C for 500 h. The scale is well-adhered in both dry and wet air.

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 produced a scale that was well adhered after 72 h of exposure time.

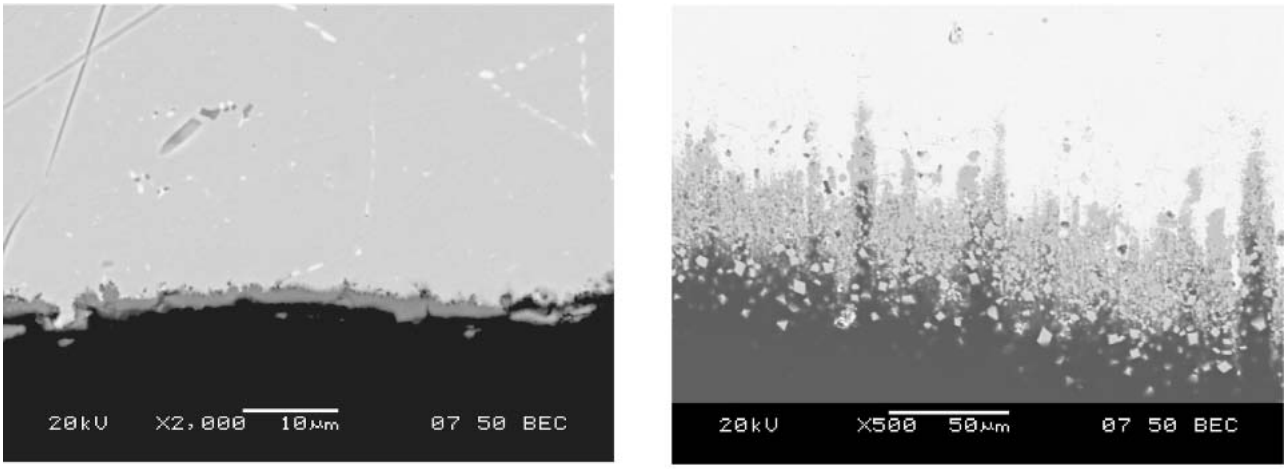
4.6 Summary of Findings

The untreated metal surface exhibits poorly adhered scale in dry air, wet air, as well as in the dry air side of dual-atmosphere exposure. Two proprietary air side surface treatment processes were found to give a low-resistance scale.

- Process 50N9-4 provided scale with good adhesion in dry air, wet air, and on the dry air side of dual-atmosphere exposure.
- Process 100H9-4 provided an oxide scale with good adhesion in both dry and wet air. However, in wet air the outer surface of the scale did not appear well defined.

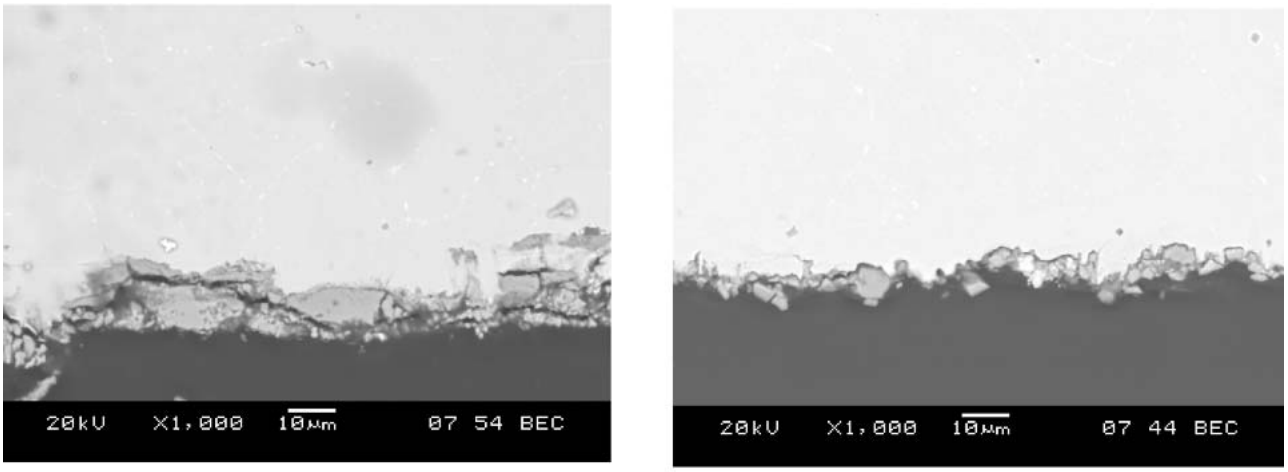
4.7 Future Work

An analysis of the scale composition after surface treatment followed by a 500 h exposure to various atmospheres is under way. Initial results show that the scale contains several oxides of Cr. The focus of current work is to modify the scale composition by the treatment and pre-oxidation processes such that the scale composition contains predominantly oxides that have lower Cr activity than pure Cr_2O_3. This will enable a significant reduction in Cr evaporation during cell operation. Addi-



(a) (b)

Fig. 12 Micrographs of treated coupons (process 100H9-4). (**a**) 100H9-4 in dry air for 500 h; and (**b**) 100H9-4 for 500 h in wet air. The scale is well-adhered in dry air.



(a) (b)

Fig. 13 Micrographs of the dry air side of the dual-atmosphere test: (**a**) untreated metal, dry air side at 750 °C for 500 h, scale cracking seen; (**b**) process 50N9-4, dry air side for 500 h at 750 °C, good adhesion

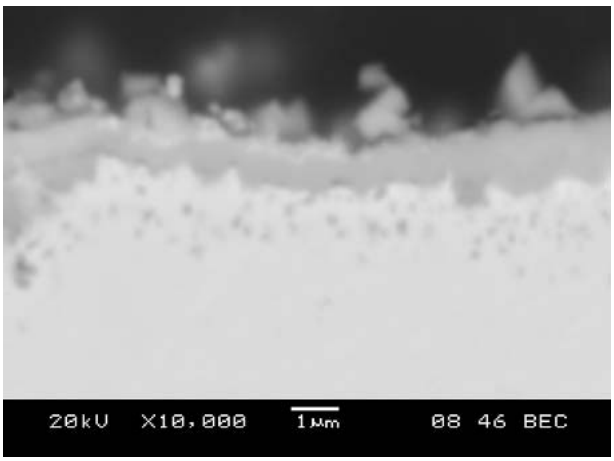


Fig. 14 Micrograph for process 50N9-4 conductivity tested sample in dry air at 750 °C for 500 h

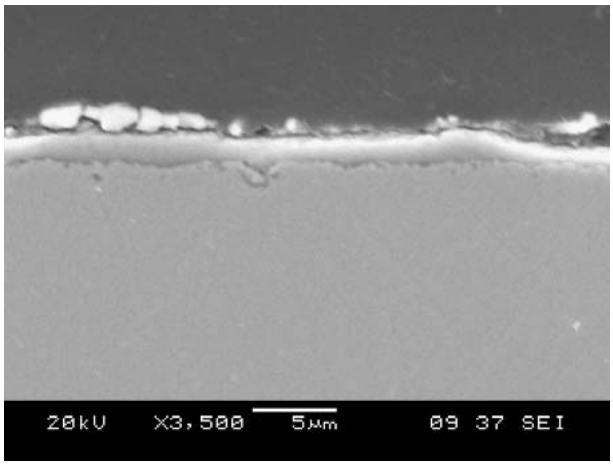


Fig. 15 Micrograph for process NT-0 in wet hydrogen for 72 h at 750 °C

tionally, the improvements observed in coupon tests will be verified in stacks tests.

5. Conclusion

The phase I project resulted in significant advances in the area of SOFC metal interconnect development. Methods to treat and coat the surface of a commercial stainless steel were developed. The treated metal coupons showed exceptional oxide scale stability in SOFC-relevant atmospheres and temperatures. The measured resistance values of 10 $m\Omega\text{-}cm^2$ in air and 1 $m\Omega\text{-}cm^2$ in humidified hydrogen at 750 °C were substantially lower than the target resistance. The resistance values were stable over a limited number of thermal cycles carried out during the project. Additional development work is needed to improve the stable phase content in the scale to enhance the stability further, and to evaluate the alloy when it is exposed to air and fuel conditions on opposite sides. Successful completion of these tasks will play a major role in enabling the SOFC system as a commercial reality.

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