IV.A.1 Evaluation of a Functional Interconnect System for SOFCs

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Objectives

- Identify and/or develop a metal substrate for a low-cost, high-performance mass production interconnect through environmental exposures and electrical property evaluation.
- Optimize methods for solid-state processing of ferritic stainless steels to remove elements which play a role in degrading electrical performance (primarily silicon).

Accomplishments

- An initial set of novel ferritic stainless steel compositions were melted and processed to thin strip. These were tested for oxidation resistance.
- A second set of ferritic stainless steel compositions have been melted, based on the results of the first iteration and a complementary review of the literature. These are currently being processed to thin strip.
- A novel process was developed to remove silicon from commercially available ferritic stainless steel in the solid state. This process was applied to common ferritic stainless steels, which resulted in the desired effect and improved area specific resistance (ASR) by up to 75% in initial testing.
- Cladding was used to produce multi-layered interconnect structures. These were tested in simulated anode gas (hydrogen-base and methane base) and in dual atmosphere exposures.
- Equipment has been installed for long-term ASR testing and evaluation.

Introduction

The interconnect is a critical part of planar solid oxide fuel cells (SOFCs). The interconnect serves to separate the fuel and oxidant gas streams, and also collects the electrical output of the SOFC. A shift from relatively inert ceramic interconnects to metallic structures has been driven primarily by cost and manufacturing considerations. Interconnect alloy selection has been defined as an important issue impeding the commercialization of SOFCs, with the focus being the use of inexpensive substrates in conjunction with special processing and/or coatings [1]. High temperature degradation has been and remains a significant issue in the application of metallic alloys for interconnect substrates. Oxides in general have reduced electrical conductivity, leading to increased contact resistance as they increase in thickness. These oxides can also react with the surrounding ceramic components, resulting in reduced electrical functionality. The cumulative result is degradation of stack performance over time [2].

Successful metallic alloy-based interconnects will have to address these concerns while minimizing the installed component cost. This may be possible through the use of specially formulated alloys, particularly at lower operating temperatures. Higher operating temperatures may be attainable through the use of more heat-resistant alloys, or notably by the application of oxidation-resistant, electrically conductive coatings [3].

Approach

Commercially available, low-cost stainless steels will be evaluated for suitability as SOFC interconnect substrates. Testing will focus on alloys with moderate chromium contents (16-18%) such as Types 430, 439, and 441HP. Testing and evaluation will focus on general oxidation behavior (notably resistance to accelerated oxidation, in simulated anode gas, cathode air, and dual atmosphere environments) and the evolution of ASR with time for both bare and coated metal substrates using controlled laboratory conditions and in button cell test systems. The effect of silicon removal via post-processing will remain a critical area of investigation, as most inexpensive commercially available alloys inevitably contain a moderate amount of residual silicon (typically 0.4% by weight).

Alloy development will proceed in parallel for applications which call for increased resistance to environmental and electrical degradation. Focus areas will be the effect of low-cost reactive element additions, moderate control of residual silicon, and slightly higher chromium contents. Initial testing will be on laboratory-scale heats melted to custom compositions and processed to thin strip via hot and cold rolling.

Results

Clad panels were produced using a variety of alloys which are expected to be inert in the anode environment, notably nickel 201 (UNS N02201), oxygen-free copper (UNS C10100), and a commercially produced Ni-32Cu alloy (UNS N04400). Some panels were also clad on the cathode side with oxidation-resistant nickel-base superalloys.

- Testing of clad samples in both hydrogen- and methane-based simulated anode gas atmospheres at 800°C resulted in a significant reduction in weight gain as compared to a Type 430 stainless steel control sample. This is attributable to the clad face exhibiting only minor surface oxidation. However, some internal attack was noted for both the copper and the copper-nickel alloy-clad samples (Figure 1).
- The sample clad with nickel exhibited considerably less degradation under the same exposure conditions (Figure 2).

Post-process thermal and chemical treatments are being investigated in an attempt to improve the performance of typical ferritic stainless steels in the SOFC environment by mitigating the formation of electrically resistive silica at the scale/alloy interface. Samples of Type 430 stainless steel (Fe-16.5Cr-0.3Si) were exposed in wet hydrogen in an attempt to pre-form a thick silica layer at the surface without oxidizing other elements, notably chromium. The initial results were successful, resulting in the formation of a 0.2 micron thick silica layer during a relatively short-term exposure. The expected effect on a ferritic stainless steel substrate is shown in Figure 3. This treatment can be very efficient in removing silicon, particularly for thin (0.1 mm or less) substrates, but the effect becomes marginal for thicker substrates. This is likely to be counteracted somewhat due to the presence of a silicon depletion gradient, but this is difficult to measure quantitatively.

Current work is focused on optimizing this treatment and extending its applicability. Test panels of various commercially available stainless steels (Types 430, 439HP and 441) have been processed and are being characterized using surface science and ASR measurements to determine the effect of processing variables. Larger panels (200 mm on a side) have been prepared and have been sent to researchers at the National Energy Technology Laboratory (NETL) for in-cell testing.

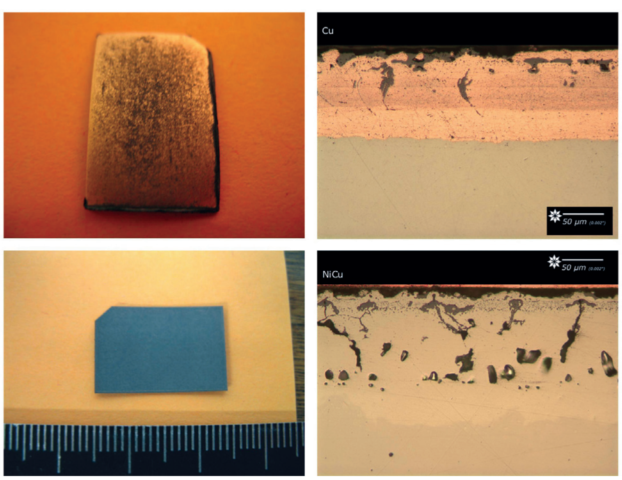

FIGURE 1. Post-exposure images of samples exposed in Ar-4% H_2-3%H_2O at 800°C for 1,371 hrs. (top left) macrophotograph of the Cu-clad surface; (top right) light optical micrograph of the Cu-clad sample cross-section; (bottom left) macrophotograph of the Ni-32Cu-clad surface; (bottom right) light optical micrograph of the Ni-32Cu-clad sample cross-section.

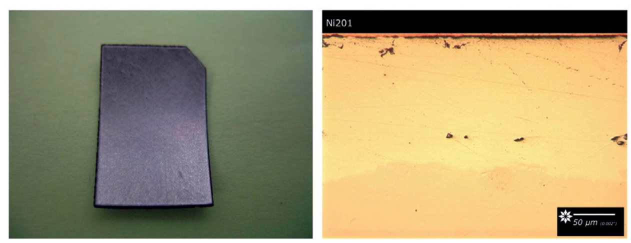

FIGURE 2. Post-exposure images of samples exposed in Ar-4% H_2-10%H_2O at 800°C for 1,221 hrs (left) macrophotograph of the Ni-clad surface; (right) light optical micrograph of the Ni-clad sample cross-section.

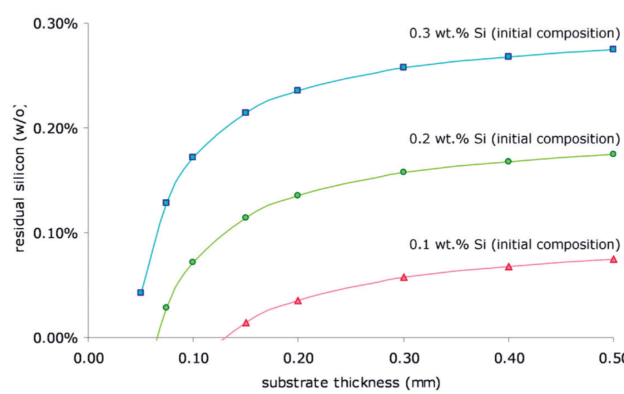

FIGURE 3. Calculated Effect of Silicon Removal Treatment on Ferritic Stainless Steels (Nominally Fe-18Cr) with Different Starting Silicon Levels as a Function of Substrate Thickness

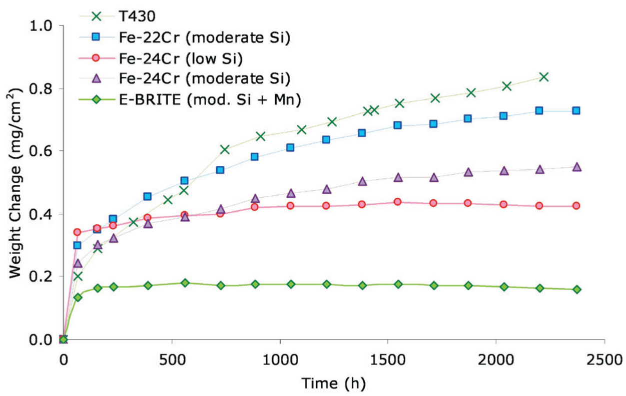

FIGURE 4. Oxidation Test Results for Various Ferritic Stainless Steels Exposed in Air Containing 10 Percent (by Volume) Water Vapor at 800°C

Substrate alloy development continues, based on the results obtained from an initial set of laboratory-scale vacuum induction melting (VIM) heats. Initial heats results of novel and modified stainless steels have been produced and tested in simulated cathode environments (humidified air). Selected results are presented in Figure 4 and are summarized below.

- A heat of T430 with a relatively low silicon content (nominally 0.1%) exhibited good oxidation resistance, but a heat with very low silicon content (nominally 0.03%) exhibited rapid breakaway oxidation.
- A series of alloys with increasing chromium content (18-24%) with relatively low silicon content exhibited a general trend towards decreasing oxidation rate with increasing chromium content.
- Modified E-BRITE®-type alloys containing low silicon and small (0.1%) to moderate (0.4%) manganese additions exhibited low oxidation rates and increased resistance to oxide scale evaporation.

A set of five refined compositions have been melted, cast, and are being processed to light-gauge strip. Two primary alloy families are being investigated, based on the test results from the first set of compositions.

- A superferritic stainless steel based on a modified E-BRITE® composition. The goal is to produce an alloy with the beneficial qualities of E-BRITE® alloy (e.g. very low oxidation rate), while improving the resistance to oxide scale evaporation, resistive oxide formation, and intermetallic phase evolution.
- A specialty ferritic stainless steel, resembling commercially available 16-18Cr alloys but with significant modifications to improve SOFC-specific properties.

Conclusions and Future Directions

- Cladding has been identified as a potential method for improving the performance of the anode-side of a solid oxide fuel cell by eliminating the resistive oxide layer entirely. Commercially pure nickel (Ni201 alloy) in particular appears to be resistant to degradation and also appears to be relatively mechanically and chemically compatible with a ferritic stainless steel substrate when applied as a thin surface layer. No further work is planned for clad structures in the future.
- A post-process, solid-state method for removing silicon from the surface of a ferritic stainless steel has been identified. Process parameters will be refined and the long-term efficacy of the technique will be tested using ASR evaluation.
- Two general compositional ranges for ferritic stainless steel substrates have been identified based on the initial work for this project. A set of five heats has been melted and is currently being processed. The resulting strip material will be extensively tested for oxidation resistance in both anode and cathode environments and for ASR evolution with time. Electrically conductive oxidation-resistant coatings will also be explored as a means for enhancing performance.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent Application filed March 6, 2007 for *Method For Reducing Formation Of Electrically Resistive Layer On Ferritic Stainless Steels*, Serial No. 60/905,219.

FY 2007 Publications/Presentations

1. Quarterly Report for 1st calendar quarter 2007, April 26, 2007.

2. Quarterly Report for 4th calendar quarter 2006, February 27, 2007.

3. Quarterly Report for 3rd calendar quarter 2006, October 31, 2006.

4. Quarterly Report for 2nd calendar quarter 2006, July 27, 2006.

5. *Metallic SOFC Interconnect Systems*, presented at the 7th Annual SECA Workshop and Peer Review, Philadelphia, PA, September 12-14, 2006.

6. Project Fact Sheet Update, August 31, 2006.

References

1. *U.S. DOE Fossil Energy Fuel Cell Program*, W. Surdoval, presented at the 7th Annual SECA Workshop and Peer Review, Philadelphia, PA, September 12-14, 2006.

2. Fuel Cell Handbook, 7th Edition, EG&G Technical Services, Inc. p. 7-6.

3. *SOFC Interconnects and Coatings*, J.W. Stevenson et. al., presented at the 7th Annual SECA Workshop and Peer Review, Philadelphia, PA, September 12-14, 2006.