IV.A.20 Developing Low-Cr Fe-Ni Based Alloys for Intermediate Temperature SOFC Interconnect Application

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Objectives

- Develop a series of new Fe-Ni-based alloys without Cr or with low Cr for intermediate temperature solid oxide fuel cell (SOFC) interconnect application
- Demonstrate suitable oxidation resistance, oxide scale area specific resistance (ASR), and coefficient of thermal expansion (CTE) for these new alloys
- Achieve low Cr evaporation rate and good compatibility with the cathode materials for these alloys without surface coatings

Accomplishments

- The composition of the new low-Cr Fe-Ni-based alloy has been optimized and several promising alloying elements have been identified, which are effective in reducing the oxidation rate of this alloy system. Stable, low oxide scale ASR during thermal oxidation has been demonstrated for the new developmental low-Cr Fe-Ni-based alloy.
- Adequate oxidation performance in the SOFC anode environment has been demonstrated for this new alloy. Furthermore, the alloy surface is conductive even at room temperature after oxidation in such an environment.
- The alloying elements that are effective in improving the oxidation resistance of these new alloys does not negatively affect the thermal expansion behavior of these alloys.

Introduction

With the reduction of the SOFC operating temperatures to 700-800°C, Cr_2O_3-forming ferritic alloys are widely used as interconnect materials in the SOFC stacks being developed by the Solid State Energy Conversion Alliance (SECA) Industrial Teams. These ferritic alloys, including Crofer 22 APU, SS 430, SS 441, Ebrite, etc., posses an overall combination of properties desirable as SOFC interconnect materials such as low cost, excellent manufacturability, adequate match in CTE with other cell components, high electronic conductivity and thermal conductivity. Two of the major concerns (or problems) with these ferritic interconnect alloys are (1) their long-term oxidation resistance and oxide scale electrical conductivity, and (2) Cr evaporation and associated "poisoning" of the cathode under the operating environments of SOFC [1]. This SECA project has focused on the development of new low-Cr Fe-Ni-based interconnect alloys with low CTE and scale ASR, suitable oxidation resistance, and reduced Cr evaporation which is expected to resolve the Cr poisoning issue for SOFC stacks.

Approach

Using alloy-design principles, a series of new low-Cr Fe-Ni-based alloys have been developed. Upon thermal exposure, these low-Cr Fe-Ni-based alloys with 6 wt% Cr maximum develops a double-layer oxide scale consisting of a Cr-free, electrically-conductive $(Fe,Ni,Co)_3O_4$ spinel outer layer that acts as a surface seal for blocking Cr evaporation from the alloy surface atop a protective, electrically-conductive Cr_2O_3 inner layer [2].

The feasibility of thermally growing the double-layer oxide structure on the low-Cr Fe-Ni-based alloys was demonstrated last year and this year we have been focusing on compositional optimization of the new alloys for further fine-tuning and improving their performance for SOFC interconnect application. We have also studied their long-term oxidation resistance in air and oxidation behavior in the SOFC anode environment, the stability of the oxide scale ASR during thermal exposure, and thermal expansion coefficients of these low-Cr Fe-Ni-based alloys.

Results

Through an extensive alloy design effort, a low-Cr Fe-Ni-Co-based alloy with optimal performance as a SOFC interconnect has been developed. Several alloying additions have been found effective in further improving the oxidation resistance of this alloy system. While the detailed alloy compositions will not be disclosed in this report, the effect of one specific element, denoted as X, on the oxidation resistance of this alloy system is given in Figure 1. Obviously, the mass gain of the alloy without X increased significantly with the oxidation time. The second alloy with 0.75% X (all the alloying additions were given in wt.% in this report) exhibited a decreased oxidation rate compared to the alloy without X. However, its weight gains were higher than those of the alloys with 1.5% and 3.5% of X, respectively. For the alloy with 1.5% X, the mass gain increased noticeably during the first week, which remained relatively constant afterwards. The weight gain of the alloy with 3.5% X was the lowest among the four alloys, and increased only slightly with the oxidation time. Clearly, the oxidation resistance of the alloy could be improved by the addition of X.

Based on the oxidation results, 1.5% X is needed to significantly reduce the oxidation rate of this alloy system. On the other hand, if the X content is too high (e.g. 3.5% X), a protective Cr_2O_3 scale was developed upon thermal exposure and the formation of the Cr-retaining spinel outer-layer is suppressed, based on the cross-sectional observation of the oxidized samples. Therefore, it is concluded that the 1.5% X alloy is the most suitable for a SOFC interconnect application with regard to oxidation resistance and Cr evaporation. Furthermore, thermal expansion measurements indicate that the X level in the alloy did not drastically affect the CTE of the alloy. Also, Figure 2 shows ASR values measured at 800°C in air for the alloy with 1.5% X and Crofer 22 APU after oxidation for different times at 800°C in air. While Crofer 22 APU exhibited a continuous increase in ASR as the exposure time increased due to continued oxidation, the ASR of our new alloy was relatively constant, implying that no continuous insulating layer was formed between the oxide scale and alloy substrate.

Figure 3 compared the weight gain of the new alloy in air and the reducing environment of Ar+5%H_2+3%H_2O. The new alloy exhibited lower mass gain in the reducing environment (Ar+5%H_2+3%H_2O)

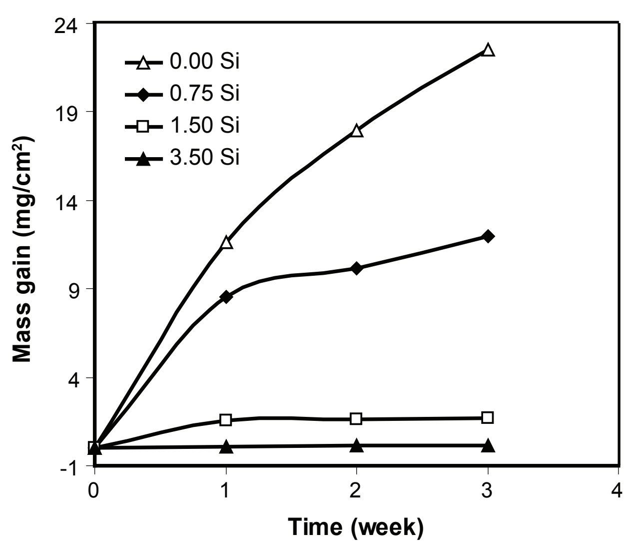

FIGURE 1. Oxidation Kinetics of the Low-Cr Fe-Ni-Co Alloy with Different X Levels in Air at 800°C

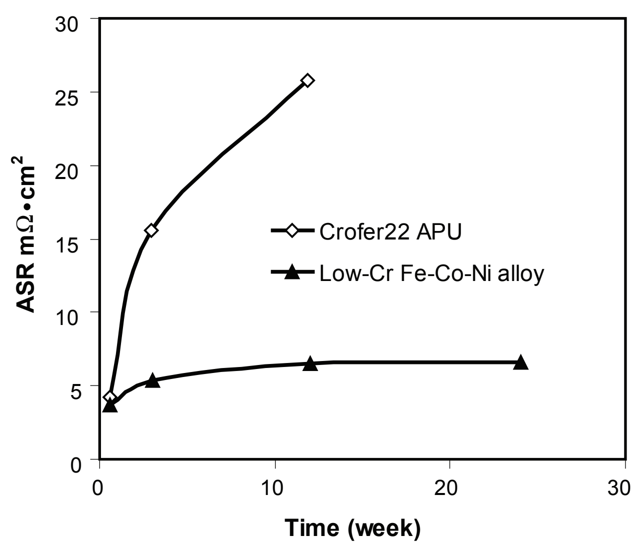

FIGURE 2. ASR Values Measured at 800°C in Air for the New Alloy and Crofer 22 APU as a Function of Oxidation Time at 800°C in Air

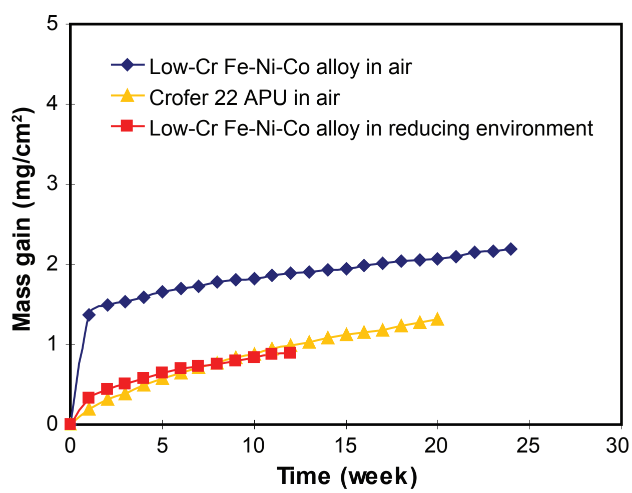

FIGURE 3. Oxidation Kinetics of the Low-Cr Fe-Ni-Co Alloy at 800°C in Air and Ar+5%H_2+3%H_2O

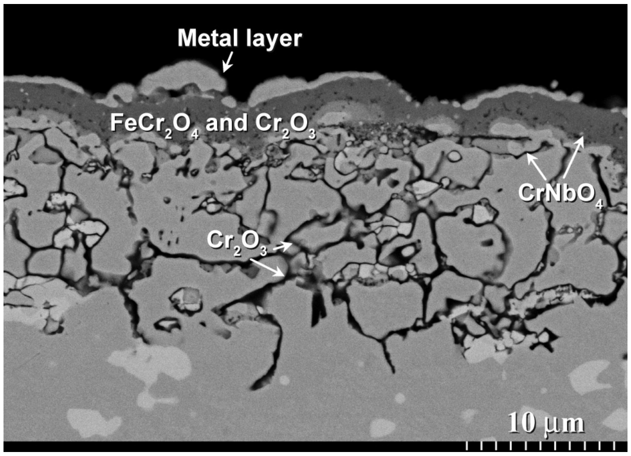

FIGURE 4. Cross-Sectional View of the Low-Cr Fe-Ni-Co Alloy after Thermal Exposure in $Ar+5\%H_2+3\%H_2O$ at 800°C for 12 Weeks

than that in air after similar exposure. The cross-sectional view of the low-Cr alloy after thermal exposure for 12 weeks in the reducing environment is shown in Figure 4. The surface metallic layer consisted mainly of Fe, Co and Ni, which was followed by the oxide layer in contact with an internal oxidation zone. The oxide layer comprised mainly the Fe, Cr and Nb oxides, which according to the X-ray diffraction (XRD) results were $FeCr_2O_4$, Cr_2O_3 and $CrNbO_4$. After thermal exposure in the reducing atmosphere, electrical resistance of the coupon was measured using a multimeter at room temperature, which was similar to that of metal, as the electron passed through the surface metal layer.

The thermal expansion behaviors of the low-Cr Fe-Ni-Co alloys with different levels of Co, Nb and W additions were close to one another, indicating that the effect of the Co, Nb and W additions on the thermal expansion behaviors of this alloy system was insignificant.

Conclusions and Future Directions

The design and development of new alloys, which upon thermal exposure form an electrically conductive Cr-free spinel outer layer atop a protective, electrically conductive oxide inner layer, is highly desirable to mitigate the Cr poisoning problem in the SOFC stack as well as reduce the overall interconnect material cost. Several alloying additions have been identified that effectively improved the oxidation resistance of the alloys without negatively impacting their other properties. The optimized alloys exhibited drastically improved oxidation resistance, low and stable scale ASR, and CTE match with other cell components. Furthermore, this alloy system showed a lower oxidation rate in the reducing environment and the surface remained electrically conductive after thermal exposure in the reducing environment due to the presence of the surface metallic layer. The alloying additions of Co, Nb, W, etc. did not noticeably change the thermal expansion behaviors of this alloy system.

Future directions for this project are listed below:

- **Compatibility and in-cell performance evaluation.** The interaction and compatibility of the new interconnect alloys with the contact and cathode materials are being conducted using screen-printed interconnect/contact/cathode couples. After thermal exposure of the couple, ASR measurement will be conducted to get the overall resistance of the couple. The effect of the new interconnect alloys on the cell performance will be conducted with a SOFC test stand, which will be compared with that of the ferritic interconnect steels.
- **Characterization of the mechanical properties of the new interconnect alloys.** The mechanical properties of the optimized alloy sheets will be determined, including hardness test for the annealed alloy sheets, as well the alloy sheets aged at 800°C for various durations. Additionally, tensile testing in air at different temperatures to determine the effect of test temperature as well as the aging treatment on the yield strength, tensile strength, and ductility of the alloys will be determined.
- **Electroplating of the new Fe-Ni-Co alloy on low-cost ferritic steels.** By combining the attributes of the new Fe-Ni-Co alloy and the ferritic steels, a new interconnect material with superior performance may be achieved. The Fe-Ni-Co alloys will be codeposited onto the ferritic steels using electroplating techniques; upon thermal oxidation, the deposited alloy layer will be converted into a Cr-free, electrically-conductive $(Fe,Ni,Co)_3O_4$ spinel layer that blocks the Cr evaporation as well as reduces the oxygen penetration into the steel substrate.

Special Recognitions & Awards/Patents Issued

1. An invention disclosure on the new low-Cr Fe-Ni alloys has been completed.

FY 2007 Publications/Presentations

1. "Evaluation of Several Low Thermal Expansion Fe-Co-Ni Alloys as Interconnect for Reduced-Temperature Solid Oxide Fuel Cell", *International Journal of Hydrogen Energy*, in press, 2007.

2. "A low-Cr Metallic Interconnect for Intermediate-Temperature Solid Oxide Fuel Cells", *Journal of Power Sources*, in press, 2007.

3. "Evaluation of Binary Fe-Ni Alloys as Intermediate-Temperature SOFC Interconnect", manuscript under internal review, to be submitted to *Journal of the Electrochemical Society*, 2007.

4. "Evaluation of Several Commercial Alloys as SOFC Interconnect in the Reducing Environment", presented at the Symposium "Fuel Cells and Energy Storage Systems: Materials, Processing, Manufacturing and Power Management Technologies" as part of MS&T 06, Cincinnati, OH (October 15–19, 2006).

5. "Evaluation of Several Low Thermal Expansion Alloys as Interconnect for IT SOFC", presented at the symposium "Fuel Cells and Energy Storage Systems: Materials, Processing, Manufacturing and Power Management Technologies" as part of MS&T 06, Cincinnati, OH (October 15-19, 2006).

6. "Some Issues Related to the Measurement of Area Specific Resistance of Interconnect Alloys", Presented at the Symposium Materials in Clean Power Systems II: Fuel Cells, Solar, and Hydrogen-Based Technologies, TMS Annual Meeting, Orlando, FL (February 26 - March 1, 2007).

References

1. Gindorf, C., Singheiser, L & Hilpert, K., Chromium vaporisation from Fe,Cr base alloys used as interconnect in fuel cells. Steel Research 72 (11-12), 528-533 (2001).

2. Geng, S.J., Zhu, J.H., Brady, M.P., Anderson H.U., Zhou X.D. & Yang, Z.G., "A low-Cr Metallic Interconnect for Intermediate-Temperature Solid Oxide Fuel Cells", *Journal of Power Sources*, in press, 2007.