Development of Low Coefficient of Thermal Expansion (CTE) Nickel Alloys for Potential Use as Interconnect in Solid Oxide Fuel Cells

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This paper deals with the development of low coefficient of thermal expansion (CTE) nickel-base superalloys for potential use as interconnects for SOFC. Ni-Mo-Cr alloys were formulated with CTE on the order of 12.5 to 13.5 x10^{-6}/^{o}C. The alloys were vacuum induction melted and reduced to sheet via a combination of hot and cold working. Dilatometry was used to measure CTE of the alloys. Oxidation behavior of the alloys at 800°C in dry and moist air is reported. The results are compared to results for Haynes 230 (a commercial Ni-base superalloy) and for Crofer 22APU (a commercial ferritic stainless steel designed specifically for use as an SOFC interconnect).

Introduction

Utilization of metallic interconnects can significantly reduce the materials costs of planar Solid Oxide Fuel Cells (SOFC) [1,2]. Interconnects provide electrical connection between individual cells and serve as a gas separation barrier to prevent mixing of the fuel and air [1,2]. The interconnect must be chemically and physically compatible with the other SOFC components, be stable in the both oxidizing and reducing environments, and be electrically conductive. The oxide scale that forms on metallic alloys will affect the conductivity. Cr_2O_3 forming alloys are preferred, since, Cr_2O_3 is an intrinsic semiconductor under SOFC operating conditions; where as, Al_2O_3 and SiO_2 are both insulators [3]. For physical compatibility, the CTE of the interconnect must match that of the ceramic components (CTEs on the order of 12 x 10^{-6}/ ^{o}C). Ferritic stainless steels have CTE values in the range required for application. Hence, there has been considerable effort on developing chromia-forming ferritic alloys for interconnects, culminating with Crofer 22APU (ThyssenKrupp VDM), Hitachi ZMG232 (Hitachi Metals) and E-Brite (Allegheny Ludlum). However, these alloys may not have adequate performance characteristics (oxidation and creep resistance) over the US-DOE SECA target 40,000 hour life span for a SOFC. A preliminary study conducted at Pacific Northwest National Laboratory (PNNL) [4], demonstrated the superior oxidation and corrosion resistance of a nickel base superalloy (Haynes 230) compared to Crofer 22APU. Most superalloys, including Haynes 230, have CTEs too high (15x10^{-6}/ ^{o}C) for most SOFC designs. Thus, a low CTE nickel alloy is desirable. Studies on the CTE of Ni-alloys, revealed that Fe, Co and Cr increase, while Mo, W, C, Al, and Ti decrease the CTE of Ni. Many of these studies have focused on developing alloys with compatible CTE's to ferritic and martensitic ferrous alloys used extensively in fossil fueled power plants. These investigations focused on developing alloys for use at temperatures below 700°C. The present research is aimed at establishing the suitability of low CTE superalloys for use in the SOFC temperature range of 700 to 800°C. This paper reports on the design, microstructure and oxidation resistance of several low CTE (12.5 to 13.5 x10^{-6}/^{o}C) alloys for potential SOFC applications.

Alloy Design

Table I lists the composition of the alloys produced for this study. Alloy J1 is a duplicate of Mitsubishi alloy, LTES700 developed in reference 5. Alloy J5 is a derivate of this composition modified for use as an SOFC interconnect. Mn was added to impart the formation of an outer Cr-Mn spinel, to minimize Cr_2O_3 vaporization in the moist SOFC environment. The reactive element Y, was added to enhance scale adhesion. The Al content was reduced to 0.1% to minimize Al_2O_3

Table I: Alloy composition and coefficient of thermal expansion

Alloy	Nominal Composition (wt%)	CTE (10^{-6}/^{o}C)			
		Predicted 23-700°C	Measured (range ^{o}C)		
			23-700	23-800	23-900
J1	Ni-12Cr-1.1Ti-0.9Al-18Mo	13.1	12.9	13.6	14.4
J5	Ni-12Cr-1Ti-0.1Al-22.5Mo-0.5Mn-0.1Y	12.7	12.6	13.4	14.0
Crofer 22APU	Fe-22Cr-0.5Mn-0.1La	---	11.2	11.9	12.6
Haynes 230	Ni-22Cr-0.3Al-2Mo-14W-3Fe-5C0-0.5Mn-0.02La	---	13.3	14.3	15.4

formation (Al_2O_3 has a high electrical resistivity, and its formation will lower the efficiency of the SOFC). Mo content was increased to lower the CTE. The predicted CTE's listed in Table I were calculated using a formulation derived by Yamamoto et. al.[5] for the CTE of Fe-free Ni alloys from room to 700°C, as follows: CTE = $13.8732 + 7.2764 \times 10^{-2}$ [Cr] $- 1.835 \times 10^{-2}$ [Al] $- 7.9532 \times 10^{-2}$ [W] $- 8.2385 \times 10^{-2}$ [Mo] $- 1.63381 \times 10^{-1}$ [Ti]. The bracketed terms in this equation represent the concentration (in weight percent, wt%) of the specific alloying element.

Experimental

Vacuum induction melting was used to produce 5 kg (10 lb) ingots. The ingots were reduced to plate by hot working and cold rolling, with the ultimate aim of producing strip material for application. Complete details on the fabrication and microstructure of these alloys can be found elsewhere [6].

Linear variable differential transducer (LVDT) based dilatometer measurements were used to determine the thermal expansion of the alloys in accordance with ASTM standard E-228-85. Samples were 25.4x12.5x6.3 mm^3 in size. Length changes were recorded every minute as the specimen was cycled between the temperatures of 900 to 23°C at an average of 5°C/min. The CTE value was calculated as the secant CTE.

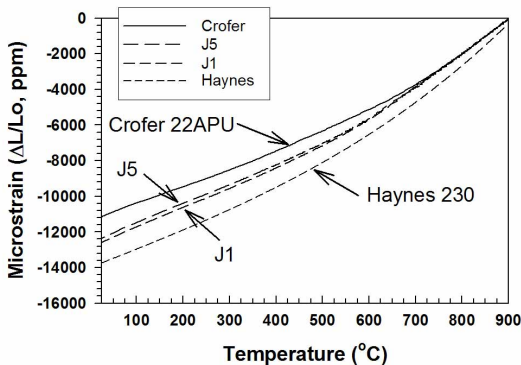Oxidation coupons were machined from sheet/strip to dimensions of 25.4 mm x 12.5 mm x thickness. A 3.175 mm diameter hole was drilled into the upper portion of each sample to allow hanging on a quartz rack. Oxidation tests were conducted at 800°C in flowing dry or moist air. The moist air consisted of 3% H_2O and was generated by bubbling dry air through water. Prior to testing, the surfaces of the coupons were polished through a 600-grit finish. After ultrasonically cleaning in alcohol, the dimensions and weight of each coupon were measured and recorded. Samples were placed on a quartz rack, which was placed inside a pre-heated furnace. After an appropriate time interval, the coupons were removed from

Figure 1 Dilatometry curves for the alloys.

the furnace and the weight of the coupons were measured and recorded. The samples were then replaced into the furnace for the next cycle.

Results and Discussion

Alloys J1 and J5 proved readily workable and were reduced to strip with a thickness on the order of 1 mm by a combination of hot- and cold-working. Complete details on the processing of these alloys can be found in reference 6. Dilatometry curves are shown in Figure 1 and the predicted and measured CTE for the alloys are also listed in Table I. The

Figure 2. Oxidation behavior at 800°C in moist air.

results show that the CTEs of the experimental alloys are between that of Crofer 22APU and Haynes 230. The results indicate that the CTE formulation derived by Yamamoto et al, [5] is reliable for predicting values for Ni-alloys from room to 700°C.

At 800°C in moist air (Figure 2), Haynes 230 is the most oxidation resistant alloy tested, as it has the lowest specific mass gain. Initially Crofer 22APU appears more oxidation resistance than alloys J1 and J5. However, after about 500 hours at temperature, Alloy J5 becomes more oxidation resistant than Crofer 22APU. Alloy J1 behaves quite interestingly. After about 200 hours there is a mass loss followed by a slight but steady increase in mass. The rationale for this "break-in" behavior is unclear at this time. A prediction of the behavior of the alloys over 40,000 hrs, the SECA target life span, is shown in Figure 3. The extrapolations were generated by curve fitting the data to an r^2 of 0.999. After 40,000 hrs, Alloy J5 is predicted to be 60% more resistant to this environment than Crofer22APU.

Figure 4 shows the cross-section of the oxide scale that formed on Alloy J5 after 300 hours exposure to dry air at 800°C. Semi-quantitative Energy Dispersive X-Ray (EDX) chemical analyses at various points are also shown. The outer surface of the oxide is mostly Cr, but contains a
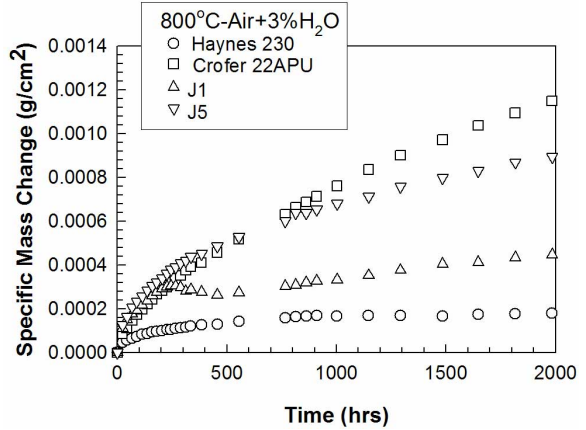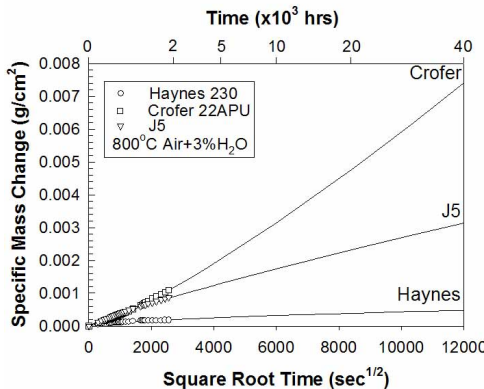

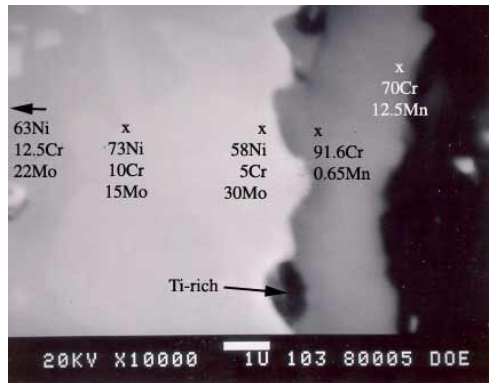Figure 3. Oxidation behavior extrapolated to 40,000 hours.

Figure 4. Oxide scale that formed on J5 after 300 hours at 800°C in dry air.

significant amount of Mn. The inner region of the oxide, near the metal-oxide interface contains little Mn. A discrete Ti-rich phase is found at the metal-oxide interface. As is expected, there is a Cr-depletion zone in the metal adjacent to the oxide-metal interface. There is a corresponding buildup of Ni and Mo in this zone. These results correlate quite well with an X-Ray diffraction analysis of this surface, which detected Cr_2O_3, TiO_2 and a spinel (Cr-Mn-oxide) phase. The formation of an outer Mn-containing spinel over the Cr_2O_3 is desirable, as the spinel protects the Cr_2O_3 from evaporation during oxidation in the presence of moist air. Cr-evaporation may lead to poisoning of the SOFC. Details on the oxide that form on the other alloys can be found in reference 6.

The oxidation resistance of Alloy J5 can further be improved through the utilization of a proprietary treatment. Figure 5 shows relatively short term (~800 hrs) oxidation results for Alloy J5, Haynes 230 and Crofer 22APU that have been subjected to the treatment. The treatment has a greater effect on the low-Cr alloy (alloy J5) than the higher-Cr alloys (Haynes 230 and Crofer 22APU). Treated Alloy J5 has comparable oxidation resistance to both treated and untreated Haynes 230. Longer term tests are presently underway.
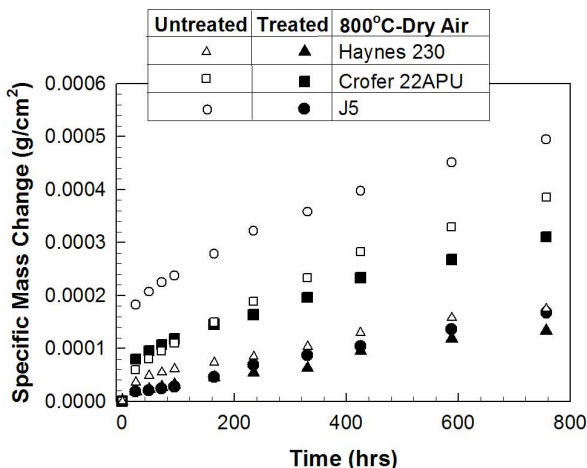

Untreated	Treated	800°C-Dry Air
△	▲	Haynes 230
□	■	Crofer 22APU
○	●	J5

Figure 5. Oxidation behavior at 800°C in dry air

Summary and Conclusion

A low-CTE Ni-alloy based on the composition Ni-22Mo-12Cr has been produced an evaluated. The CTE of the alloy is between that of Haynes 230 and Crofer 22APU. The oxidation resistance of the alloy is between Haynes 230 and Crofer 22APU. The oxidation resistance this alloy could further be improved through the application of a proprietary treatment. The oxidation resistance of the treated low CTE-alloy is significantly better than Crofer 22APU and is comparable to Haynes 230. Work is continuing at the Albany Research Center to evaluate the performance this alloy in a simulated SOFC environment.

References

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