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Scale Formation on Ni-based Alloys in Simulated Solid Oxide Fuel Cell Interconnect Environments

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Recent publications suggest that the environment on the fuel side of the bi-polar stainless steel SOFC interconnects changes the oxidation behavior and morphology of the scale formed on the air side. The U.S. Department of Energy Albany Research Center (ARC), has examined the role of such exposure conditions on advanced nickel base alloys. Alloy formulations developed at ARC and commercial alloys were studied using X-ray diffraction (XRD) and Raman spectroscopy. The electrical property of oxide scales formed on selected alloys was determined in terms of area-specific resistance (ASR). The corrosion behavior of ARC nickel-based alloys exposed to a dual environment of air/ H_2 were compared to those of Crofer 22APU and Haynes 230.

Introduction

Significant progress in reducing the operating temperature of a Solid Oxide Fuel Cell (SOFC) stack from ~1000 ºC to 600 ºC [1] allows the use less expensive metallic materials for SOFC interconnects. The interconnects must meet the following requirements[2]: low cost, chemical compatibility and stability, high corrosion stability, good mechanical properties, appropriate coefficient of thermal expansion (CTE), and high electrical conductivity. High corrosion stability and good electrical conductivity in terms of area-specific resistance (ASR) can be achieved by using alloys that form a protective semiconductor scale during SOFC operation. Nickel-based alloys and stainless steels gain their corrosion resistance from the formation of chromium sesquioxide Cr_2O_3, which is protective and relatively conductive (it is a semiconductor). However, Cr_2O_3 is prone to degradation in environments containing water vapor and/or oxygen. In addition, an anomalous corrosion behavior for stainless steels exposed to simulated SOFC environments was found by scientists from both the Pacific Northwest National Laboratory [3] and the U.S. Department of Energy, Albany Research Center (ARC)[4]. Current research efforts, designed to address these problems, focus on modifying alloy surfaces by, for example, depositing coatings or by developing new alloys such as nickel-based alloys with a more conductive and stable native oxide.

This paper describes scale formation of nickel-based alloys, J1[5] and J5. The latter alloy was developed at ARC. The alloys were simultaneously exposed to air on one side and hydrogen on the other side at 700 °C (973 K) and compared to that of Haynes 230 (commercial nickel-based alloy) and Crofer 22APU (commercial ferritic stainless steel) under the same conditions. The area-specific resistance (ASR) of the investigated materials exposed to air is also reported.

Experimental

Chemical composition (wt. %) of the investigated materials is shown in Table 1:

Alloy	Mo	Ni	Fe	Mn	Cr	Al	W	Co	Y
Crofer 22 APU	0.002	0.32	balance	0.45	22.33	0.13	<0.001	<0.001	
Haynes 230	1.32	balance	0.74	0.49	22.32	0.42	14.53	0.20	
J1	17.85	balance	0.040	0	12.07	0.79	0	0	N.D.
J5	22.17	balance	0.027	0.50	12.50	0.038	<0.01	<0.01	0.043

Corrosion experiments were conducted with two sets of flat samples. One set of samples was simultaneously exposed to a dual environment, with air on one side and hydrogen on the other side for 100 h at 700 ^{o}C. The second set of samples was simultaneously exposed to a single environment with air on both sides. The experimental setup used for the flat samples is shown in Figure 1. After the experiment, the topography of the sample surfaces and their cross-sections were observed under SEM. Scale reaction products were determined by XRD and Raman spectroscopy. Elemental microanalysis was performed in different locations of sample cross-sections including bulk metals and their scales.

The ASR measurements were conducted on the samples exposed to a single air/air environment using a 2-point probe method. The resistance of the probe wires was accounted for by making a separate measurement and subtracting the results from the sample measurements.

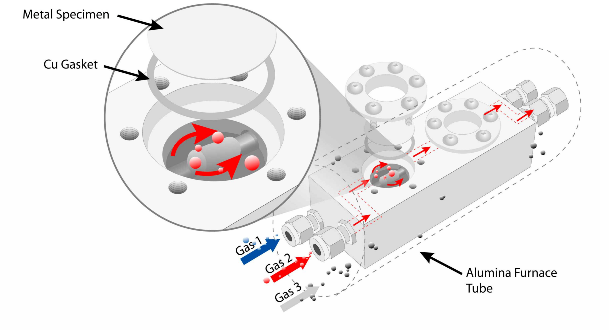
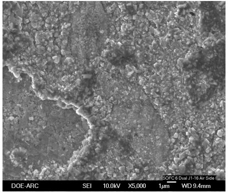


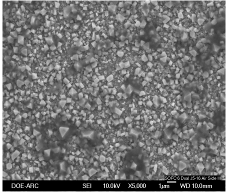
Figure 1. Schematic of 2G fixture for conducting planar samples in SOFC single and dual environments

Results and Discussion

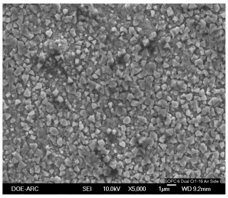
Figure 2 shows the microstructure and topography of the scales formed on the air side of the J1, J5, Haynes 230, and Crofer 22 APU samples in the dual environment.



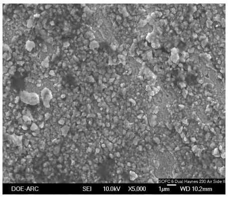
J1



J5



Crofer 22 APU



Haynes 230

Figure 2. SEM Micrographs of air side of J1, J5, Crofer 22 APU, and Haynes 230 after exposure to air in air/H_2 for 100 h at 700ºC

The surfaces of J5 and Crofer 22 APU were covered uniformly with cubic-shape grains. J1 and the Haynes 230 included both cubic-shape grains and fine structure scale. This difference in scale morphology could be associated with a different mechanism of scale initiation. The phases formed on the investigated materials in single air/air and dual air/hydrogen environments identified by XRD are shown in Table 2a and 2b, respectively.

Table 2a. XRD Results of the oxide phases present in scales on J1, J5, Haynes 230, and Crofer 22 APU formed in single environment (Note: Spinel-type structures are underline)

Material	**Air Side (Gas 2)**	**Air Side (Gas 3)**
J1	Cr_2O_3;	Cr_2O_3; $\underline{Fe_3O_4;}$; NiO; $NiMoO_4$
J5	Cr_2O_3; $\underline{Mn_3O_4}$	$\underline{Mn_3O_4}$; Cr_2O_3
Haynes 230	Cr_2O_3	Cr_2O_3
Crofer 22 APU,	Cr_2O_3, $\underline{Fe_3O_4}$	Cr_2O_3, $\underline{Fe_3O_4}$

Table 2b. XRD Results of the phases present in scales on J1, J5, Haynes 230, and Crofer 22 APU formed in Dual Environment (Note: Spinel-type structures are underline)

Material	**Hydrogen Side (Gas 1)**	**Air Side (Gas 3)**
J1	Ni_3Mo; Cr_2O_3;	Ni_3Mo; Cr_2O_3; $\underline{Fe_3O_4}$
J5	Ni_3Mo; Cr_2O_3;	Ni_3Mo; $\underline{Fe_3O_4}$; Cr_2O_3
Haynes 230	M_6C like Co_3W_3C; Cr_2O_3	M_6C like Co_3W_3C; Cr_2O_3
Crofer 22 APU	Cr_2O_3, $\underline{Fe_3O_4}$	Cr_2O_3, $\underline{Fe_3O_4;Fe_2O_3}$

Chromia was found in the scales of all the materials. Magnetite spinel-type structure was found in the scales formed on the J5, Crofer 22APU, and Haynes 230. Hematite was identified in the scale formed on the air side of the Crofer 22 APU sample in the dual environment. Raman spectroscopy confirmed the presence of Cr_2O_3 in the scales and determined the presence of spinel structures.

The results of the ASR investigations for J1, J5, and Crofer 22 APU as a function of reciprocal temperature are shown in Figure 3. The lowest electrical conductivity was found for J5 and the highest for Crofer 22APU.

Conclusions

SEM investigations of the J5, J1, Crofer 22 APU, and Haynes 230 surfaces exposed to air in dual environment show formation of cubic- shaped grains. The scale was uniformly distributed on the surfaces of J5 and Crofer 22 APU after 100 h of exposure.

Cr_2O_3 was present in the scales formed in dual and single environments. Hematite was found in the scale formed on the air side of Crofer 22 APU in dual environment.

Nickel-based alloys oxidized in the single environment have lower electrical conductivity then Crofer 22APU.

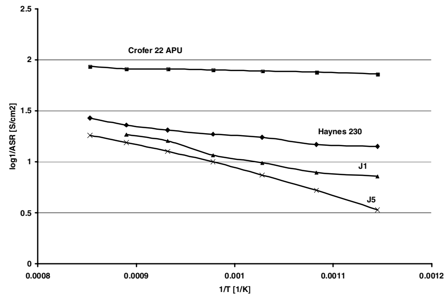


Figure 3. Electrical conductivity of the scale formed on J1, J5, Haynes 230, and Crofer exposed to single air environment at 700 °C for 100 h

Future Research

Plans are in progress to study the corrosion behavior of ARC novel and commercial nickel-based in dual environments simulating sulfur-containing and sulfur-free interconnect atmospheres as a function of time. The electrical property of the corroded materials will be studied using ASR measurements. Also, the corrosion behavior of selected nickel-based alloys and stainless steels will be studied for balance-of-plant applications.

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