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Short communication

Performance evaluation of several commercial alloys in a reducing environment

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Abstract

Several commercial alloys including Ebrite, Crofer 22 APU, Haynes 230 and Haynes 242, which are candidates for intermediate-temperature solid oxide fuel cell (SOFC) interconnect materials, were isothermally and cyclically oxidized at 900 °C in the reducing atmosphere of Ar + 5 vol.% H_2 + 3 vol.% H_2O corresponding to the SOFC anode environment. Results indicate that these alloys exhibited good scale spallation resistance with the Ni-base alloys possessing better oxidation resistance over the Fe-base alloys. Both Mn–Cr spinel and Cr_2O_3 were formed in the oxide scales of these alloys. For Crofer 22 APU and Haynes 242, a continuous protective MnO and Mn–Cr spinel layer formed outside on the inner layer of Cr_2O_3. The increase in scale ASR after longer-term thermal exposure in the reducing environment was relatively slower for the Ni-base alloys than for the Fe-base alloys.

Keywords: Alloys; SOFC; Interconnect; Cyclic oxidation; Reducing atmosphere

1. Introduction

Solid oxide fuel cell (SOFC) is a solid-state power generation system that directly converts the chemical energy of fossil fuels into electricity without combustion and mechanical processes. It has been extensively studied in the past decades as a promising power generation technology with high efficiency, low emission level and flexibility of fuel choices. Many of the technical challenges in the development of SOFC are materials related [1–3]. Recent progresses in SOFC development has led to the reduction in its operating temperature from about 1000 °C to the range of 600–800 °C [4–5], which widens the materials choice for stack components such as the interconnect. Metallic interconnects attract a great deal of attention due to its low cost, high electronic conductivity, high thermal conductivity, good manufacturability, and improved mechanical strength, etc., compared to traditional ceramic interconnects [6–9]. The metallic interconnects of current interest are the Cr_2O_3-forming alloys such as Ebrite, Crofer 22 APU, Haynes 230 and Haynes 242 due to the electrically conductive nature of Cr_2O_3 compared to other protective scales such as Al_2O_3 and SiO_2 [10–14].

The interconnect in a SOFC stack is exposed simultaneously to both an oxidizing atmosphere (air) on the cathode side and a reducing atmosphere (fuel, such as hydrogen) on the anode side. The stability requirement includes minimizing reactions with the electrode materials and the atmospheres while maintaining good electrical conductivity. Numerous work has been conducted for the investigation of behaviors of metallic interconnect materials exposed to the oxidizing environment [15–17], and some initial effort was also carried out to study the interconnect behaviors in dual atmospheres [18]. However, the understanding of the oxidation behaviors of the interconnect alloys in anode environment is still lacking, especially for the electrical properties of the thermally grown oxide scales on these alloys because of the technical difficulty to measure in the reducing atmosphere. The purpose of this paper is to study the oxidation behaviors of two Fe-based alloys, i.e. Ebrite and Crofer 22 APU, and two Ni-based alloys, i.e. Haynes 230 and Haynes 242 in the reducing atmosphere. Furthermore, a modified 2-probe 4-point method for electrical property measurement of the oxide scale in the reducing atmosphere was proposed and reported in this paper. The suitability of these alloys as intermediate-temperature SOFC interconnects was also discussed.

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Table 1
Alloy compositions (wt.%)

	Ni	Fe	Cr	Mo	W	Mn	Co	Si	Al	Cu	Ti	C	S	B	La
Ebrite		Balance	26	1		0.02		0.025				0.001	0.02		
Crofer		Balance	22			0.45		0.1	0.12		0.08	0.005	0.002		0.06
Haynes 230	Balance	3[a]	22	2	14	0.5	5[a]	0.4	0.3			0.1		0.015[a]	0.02
Haynes 242	Balance	2[a]	8	25		0.8[a]	2.5[a]	0.8[a]	0.5[a]	0.5[a]		0.03[a]		0.006[a]	

[a] Maximum.

2. Experimental

The materials used in our investigation are Ebrite, Crofer 22 APU, Haynes 230 and Haynes 242, the chemical compositions of these alloys are listed in Table 1. Rectangular samples (about 12 mm × 11 mm × 1 mm) were cut from the alloy sheets by electric discharge machining (EDM). Each sample was drilled a hole with a diameter of 1 mm on the upper center and then polished to 800 grits using SiC sand paper, ultrasonically cleaned in acetone and dried immediately before the oxidation test. A Cahn thermobalance was employed to investigate the initial oxidation kinetics of these alloys by recording the mass gain as a function of time. The samples were oxidized at 900 °C (900 °C was selected in order to expedite the oxidation process) for 100 h in the reducing atmosphere of Ar + 4 vol.% H_2 + 3 vol.% H_2O with a flowing rate of 45 ml min^{-1}. Longer-term cyclic oxidation test was also conducted to evaluate the oxidation performance and scale spallation resistance. Each cycle consisted of isothermal holding at 900 °C in the reducing atmosphere for 20 h and followed by quenching to room temperature, with a total of 50 cycles. The cumulative oxidation time for cyclic oxidation test was, therefore, 1000 h. The phase structures of the oxide scales thermally grown on the alloys were identified with X-ray diffraction (XRD). The surface morphologies and cross-sections of the oxidized samples were observed using scanning electron microscopy (SEM) with an energy-dispersive X-ray analysis attachment (EDX).

Electrical resistance of the oxidized samples was measured using a modified 2-probe 4-point method in the reducing atmosphere from 500 °C to 800 °C with a step size of 50 °C. Fig. 1 shows the schematic of the experimental setup for electrical resistance measurement. The upper and lower oxide surfaces were covered with Au paste and Au meshes with four Au leads for current supply and voltage drop measurement. Pt paste, which was widely used for corresponding measurement in the oxidizing atmosphere, was found not suitable for the reducing atmosphere because the paste was observed to penetrate into the metal substrate during the test at high temperature in the reducing environment. In our work, Au paste here was chosen in place of Pt paste for the measurement in the reducing environment to prevent such a problem. It is critical that Au paste was fired separately with the Au mesh in order to decrease or eliminate the strain in it during the firing and cooling process. The variation of voltage across the samples under different currents ranging from 1 mA to 10 mA was verified to obey the Ohm's law exactly, which indicated that the interfacial polarization was negligible within the applied current range. A constant current of 10 mA was used in all the measurement. A widely accepted parameter for scaling the electrical resistance of the oxide scales, area specific resistance (ASR), was reported here. ASR reflected both the electrical conductivity and the thickness of the oxide scale. At each temperature, the resistance (R) was calculated according to the Ohm's law, $R = V/I$. The ASR was then equal to R multiplied by the area that the Au paste covered.

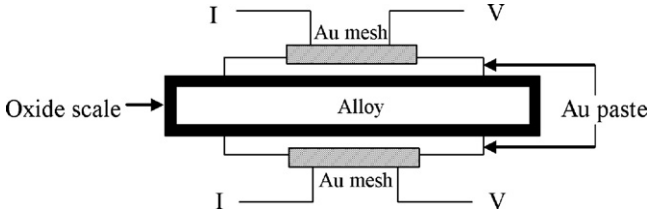

Fig. 1. Schematic of the ASR measurement setup.

3. Results and discussion

3.1. Surface morphologies and structure of the oxide scales

The XRD results of the alloys oxidized in the reducing atmosphere at 900 °C for 1000 h are given in Fig. 2, while the surface morphologies and element line scanning results of the cross-sections of these alloys are shown in Figs. 3 and 4, respectively. For the oxide scale thermally grown on Ebrite, peaks from Cr_2O_3 and $MnCr_2O_4$ were detected, as shown in Fig. 2. According to the element line scanning results, Mn element was mostly concentrated on the top surface of the oxide scale. Combining

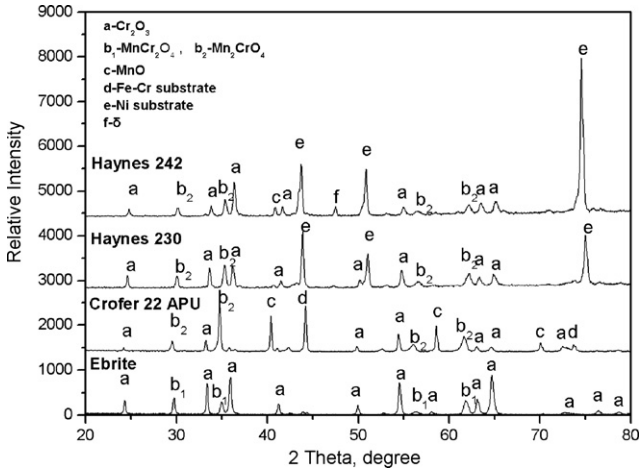

Fig. 2. XRD results of the alloys cyclically oxidized in the reducing atmosphere at 900 °C.