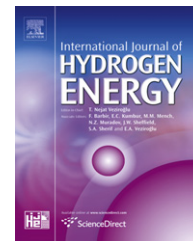


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Effect of Ti addition on the electric and ionic property of the oxide scale formed on the ferritic stainless steel for SOFC interconnect

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ARTICLE INFO

Article history:

Received 23 June 2012

Received in revised form

13 August 2012

Accepted 15 August 2012

Available online 7 September 2012

Keywords:

Titanium

SOFC

Interconnect

Titanium doping

Co-addition

ABSTRACT

Ferritic stainless steels with Ti addition are considered as promising candidates for SOFC interconnect application. In this study, the effect of Ti addition on the electrical conductivity and Cr evaporation resistance was discussed in terms of microstructure and ionic property of the oxide scale by using TEM analysis and asymmetry polarization method. Ti addition induced the generation of ionic defects in the oxide layer and modified the growth kinetics of Cr_2O_3 and MnCr_2O_4 , but in different manner depending on Ti amount. Ti content in a range of 0.05–0.07 wt% was effective for reducing the oxidation rate and electrical resistance. Addition of 1 wt% Ti promoted fast Cr_2O_3 growth due to the excess ionic defect in Cr_2O_3 matrix. However, the formation of the outermost MnCr_2O_4 layer was accelerated by Ti segregation near the scale/alloy interface and it reduced Cr evaporation effectively. Co-addition of a small amount of Ti and La enhanced Ti segregation without generation of excess ionic defect and improved both the electric conductivity and Cr evaporation resistance.

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1. Introduction

The interconnect is one of the most important components in the solid oxide fuel cell (SOFC) stack; it provides an electrical connection between the anode of one unit cell and cathode of the neighboring cell. The interconnect also acts as a physical barrier to separate air and fuel. Hence, the interconnects must have good electrical conductivity, and exhibit good oxidation resistance in the SOFC operating environment [1–3]. Moreover, SOFC interconnect material should have an appropriate coefficient of thermal expansion (CTE) matching to the other stack component and be cost effective [3,4].

Metallic interconnects are easy to fabricate and have higher electronic and thermal conductivity than ceramic

ones. However, the oxide scale formed on the surface of metallic interconnects at high temperature reduces the electric conductivity of the material and SOFC power efficiency [1,2]. The Cr_2O_3 -forming ferritic stainless steels are currently well known as a promising alloy group for SOFC interconnects because an electrically conductive oxide scale is formed at high temperature. They are relatively cost-effective and have similar thermal expansion coefficient to that of other SOFC components [1–3]. Nevertheless, they have low resistance against Cr_2O_3 evaporation in the SOFC operating environment. The volatile chromium (Cr) species such as CrO_3 and $\text{CrO}_2(\text{OH})_2$ can contaminate the cathode and cause rapid degradation of cell performance [5,6].

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The experimental and conventional alloys such as Crofer22 APU and STS441 containing Ti have been suggested for candidates of SOFC interconnect materials [2,7–11]. It was reported that Ti addition to interconnect material was effective to form conductive oxide scale [7,12,13]. Addition of Ti was also effective to reduce Cr evaporation of ferritic stainless steel [7,9]. However, the effect of Ti on the oxidation kinetics is still controversial. Some researchers have reported that Ti addition to Cr₂O₃ forming alloy has no beneficial effect to reduce the oxidation rate or even to increase the oxidation rate due to the excess defect formation by Ti doping [7,9,13,14]. However, Lins et al. have suggested that the addition of Ti can contribute to decrease the oxidation of steel and Geng et al. have observed that steel with a small amount of Ti (0.06 wt%) has lower mass gain than steel without Ti [7,8]. Such controversy comes from obscurity of Ti effect on the oxidation kinetics of ferritic stainless steel.

In this study, the effect of Ti addition to the ferritic stainless steel on the oxidation behavior is investigated in terms of the oxidation kinetics, electric and ionic property in the oxide scale, and Cr-evaporation. The distribution of elements added to the steel and microstructure analysis demonstrate clearly the effect of Ti addition on the feasibility of the ferritic stainless steel for application of the interconnect material for SOFC.

2. Experimental

2.1. Sample preparation

The experimental steel specimens were prepared by arc melting in a pure argon (Ar) atmosphere, with the partial pressure controlled to 10⁻⁵ torr and the steels were homogenized by heat treating at 1200 °C for 24 h. Inductively coupled plasma (ICP) analysis and optical emission spectroscopy (OES) were used to determine the chemical composition of the steels. The chemical compositions of Fe–Cr–Mn steel with various amounts of Ti are listed in Table 1.

2.2. Cr evaporation behavior

For Cr-evaporation test, samples with a dimension of 10 mm × 10 mm × 2 mm were ground to a P1200 grit finish and put in the test station. Input air was transported through a bubbler to increase humidity and accelerate evaporation.

The relative humidity (RH) in the test zone was controlled to supply the air saturated with water vapor at room temperature which is equivalent to 91% RH, and the gas flow rate was controlled at 300 ml/min. The sample was oxidized at 800 °C for 24 h and the rate of temperature increase and decrease was less than 5 °C/min. The evaporated Cr species were trapped in the inner surface of the injection tube. After oxidation, the whole silica tube was immersed in 2HCl (35%) + 1HNO₃ (60%) solution at 50 °C for 5 h to dissolve the trapped Cr species. The amount of evaporated Cr was determined by ICP analysis of the test solution.

2.3. Electric conductivity

To measure the electrical resistance of the scale, samples with a dimension of 10 mm × 10 mm × 2 mm were ground to a P1200 grit finish and oxidized at 800 °C in air for 100 h. The electrical resistance of an oxidized specimen is usually measured in terms of the area specific resistance (ASR) since the exact thickness of the oxide formed on the metallic surface is difficult to determine. ASR was measured by a two-probe, four-point DC method and Pt-paste electrodes were applied to the surface of the oxidized steel [15].

2.4. Oxidation behavior

For oxidation test, samples were cut into 20 mm × 10 mm × 2 mm plates, and the surface was polished with grit paper up to P2000 grit. After rinsing with acetone, the samples were oxidized at 800 °C in a box furnace with ambient air. The rate of temperature increase and decrease was controlled to less than 5 °C/min to minimize thermal stress on the oxide scale of samples during operation. The change in sample mass by oxidation was measured at every 100 h interval. For quantitative analysis on the oxidation rate, parabolic rate constant of each steel was evaluated by the following equation.

$$X^2 = k_p t + C$$

where X = mass gain, k_p = parabolic rate constant, t = oxidation time, C = integration constant.

The microstructure of oxide scale formed on the stainless steel was analyzed by focused ion beam (FIB) and tunneling transmission electron microscopy (TEM). The distribution of major and minor alloying elements was analyzed by glow

Table 1 – Chemical composition of Ti-containing ferritic stainless steels (wt%).

	Fe	Cr	Mn	C	S	P	Si	Ti	Nb	La
Base	Bal.	20.7	0.5	<0.01	<0.01	<0.01	0.01			
R–Si	Bal.	21.4	0.4	<0.01	<0.01	<0.01	0.09			
R–Ti	Bal.	20.8	0.4	<0.01	<0.01	<0.01	0.02	0.05		
R–La	Bal.	21.4	0.4	<0.005	<0.005	<0.01	<0.01			0.05
R–TiLa	Bal.	21.1	0.4	<0.01	<0.01	<0.01	0.01	0.06		0.04
H–Ti	Bal.	20.6	0.5	<0.01	<0.01	<0.01	0.01	0.98		
H–Nb	Bal.	21.1	1.0	<0.005	<0.005	<0.01	<0.01		2.3	
H–NbTi	Bal.	22.1	1.2	<0.005	<0.005	<0.01	<0.01	0.06	2.7	
Crofer22 APU	Bal.	22.0	0.4	<0.01	<0.01	<0.01	0.03	0.07		0.08

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