Stability of Fe–Cr Alloys in SOFC Fuel Atmosphere

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Keywords: Fe–Cr Alloy, Interconnects, Solid Oxide Fuel Cells, Oxide Scale

The chemical stability of Fe–Cr alloys (ZMG232 and SUS430) was examined in fuel atmosphere of SOFC, especially in H_2 – H_2O atmosphere. Oxide scales were formed on the alloy surface with a thickness of 3–5 μm at 1073 K for 1000 h by the diffusion of cations through the scale. The microstructures and elemental distribution of oxide scale/alloy interfaces were analyzed by the depth and surface analysis techniques: Mn–Cr–(Fe) spinel, Cr_2O_3 , and internal Si oxides were identified from surface to inner oxides. An anomalous thick oxide scale formation was found on SUS430 surface in H_2 – H_2O atmospheres. A thick oxide scale was composed of Fe, Cr, and Mn oxides. A relatively high concentration of Fe was observed at top surface of oxide scale. The distribution of Si was found inside the oxide scale, suggesting an increase of oxygen potential and fast diffusion of Si inside the oxides. The formation of anomalous thick oxide scale can affect the stability of Fe–Cr alloy interconnects by changing the cell connections at scale/alloy/cell interfaces.

Introduction

Alloy materials are promising candidates for interconnects of Solid Oxide Fuel Cells (SOFCs) operated at 873–1073 K (Anderson and Tietz 2003; Fergus, 2005). Important functions of alloy interconnects are the separation of fuel and air as well as electronic conduction with adjacent cells. During operation of SOFCs, the formation of protective oxide scale is inevitable on the alloy interconnect surface. This oxide scale is necessary to protect the alloys against vaporization of chromium and further oxidation. However, a thick oxide scale formation is not favorable in terms of the electrical conduction and the cell connections in SOFCs. Therefore, the oxide scales should have an optimum thickness and electronic conductivity during long-term operation.

Among several kinds of candidate alloys, Fe–Cr alloys are one of the promising materials because of their cost and a relative stability (For example, Toji *et al.*, 2005). The conventional Fe–Cr alloys are stainless steel based alloys with Cr_2O_3 forming alloys. When Mn is added into Fe–Cr alloy, the oxide scales can have the following phases from surface: Cr–Mn–(Fe) spinel,

Cr_2O_3 based oxide, and internal oxides. The top surface of Cr–Mn spinel can reduce the activity of Cr vapor and have the higher electrical conductivity. The oxide scale formation occurs in an air atmosphere. Even in fuel atmospheres, oxide scales were formed in similar phases and structures due to H_2O (Horita *et al.*, 2003). However, the oxidation rates and the electrical conduction of oxidized alloys were somewhat different from atmospheres and Fe–Cr alloy materials. This can be related to the difference of cation diffusivity in the oxide scale and mass transports of minor elements in the Fe–Cr alloys (such as Si and Al). In some cases under SOFC operation, an “anomalous” thick oxide scale formation was reported by several authors (Yang *et al.*, 2004; Kameda *et al.*, 2005; Sakai *et al.*, 2005). The formation of cation vacancies in the oxide scale can affect the stability of alloys by the formation of thick oxide scales. Also, glass-sealing materials can affect the stability of oxide scales because of the reaction of glass elements with Cr_2O_3 protective oxide scales.

The purpose of the present study is to clarify the stability of Fe–Cr alloy and its oxide scales in fuel atmosphere of SOFC. Especially in this report, the formation of oxide scales is compared between two different Fe–Cr alloys in H_2 – H_2O atmosphere: ZMG232 and SUS430. Also, the formation of an anomalous thick oxide scale formation is discussed based on the mass transports in the oxide scales.

Received on May 15, 2007; accepted on July 12, 2007. Correspondence concerning this article should be addressed to T. Horita (E-mail address: t.horita@aist.go.jp).

Presented at International Symposium on Innovative Materials for Processes in Energy Systems, IMPRES, Kyoto, October, 2007.

Table 1 Chemical compositions of Fe–Cr alloys examined for oxidation analysis (Figures are in mass %)

	ZMG232 (Hitachi Metals Ltd.)	SUS430 (Purchased from Nilaco Co.)
C	0.02	0.048
Si	0.40	0.35
Mn	0.50	0.21
Ni	0.26	0.12
Cr	21.97	16.35
Al	0.21	0.05
Zr	0.22	—
La	0.04	—
Fe	76.38	82.87

1. Experimental

1.1 Materials

Test samples examined were Fe–Cr alloys which have about 16–22 mass% of Cr (ZMG232 and SUS430). The chemical composition of the alloy is listed in **Table 1**. There is some minor elements addition into Fe–Cr alloys, which increases the oxidant resistance in ZMG232. The samples surface was polished by a diamond paste to obtain flat and smooth plane to analyze the oxide scale formation at oxide scale/alloy interfaces.

1.2 Oxidation experiments

The oxide scale formation was examined in H_2 – H_2O mixtures at 1073 K for more than 1000 h. The partial pressure of H_2 and Ar was set as $p(H_2)/p(Ar) = 0.09/0.80$ bar with $p(H_2O) = 0.11$ bar. The calculated oxygen partial pressure is estimated to be 1.5×10^{-17} bar. At this oxygen partial pressure, Cr_2O_3 can be formed on Fe–Cr alloy surface from the equilibrium calculation.

1.3 Analysis of oxide scale/alloy interfaces

The microstructures and elemental distribution at oxide scale/alloy interfaces were analyzed by scanning electron microscopy (SEM) (VE-7800, KEYENCE Corp.) with EDX (Kevex). The depth profiles of elements from sample surface were analyzed by Glow Discharge Optical Emission Spectroscopy (GDOES, JY-5000RF, Jobin Yvon/HORIBA). The elemental distribution of minor elements around the oxide scale/alloy interface was analyzed by Secondary Ion Mass Spectrometry (SIMS, CAMECA-ims 5f).

2. Results and Discussion

2.1 Surface microstructures of oxide scales

The surface microstructure of oxide scale was investigated for two different Fe–Cr alloys: ZMG232 and SUS430. **Figure 1** shows surface microstructure of oxidized ZMG232 and SUS430 in H_2 – H_2O at 1073 K for 72 h. Small grains of oxide scales were formed on the oxide scale surface with height difference of sub-

Fig. 1 Surface microstructures of oxidized alloys (annealed at 1073 K for 72 h in H_2 – H_2O). (a) SEM image of oxidized ZMG232; (b) high magnification image of (a); (c) SEM image of oxidized SUS430; (d) high magnification image of (c)

μm level on both alloys. The grain boundaries of alloy parts show relatively the higher heights, and these parts are considered to be the initial oxidation parts on both Fe–Cr alloys. Thus, the oxide scale formation mechanism is considered to be similar at the initial oxidation between ZMG232 and SUS430.

2.2 Cross section of oxide scale/alloy interfaces

The microstructures of cross section were examined at oxide scale/alloy interfaces. **Figure 2** shows microstructures of cross section at oxide scale/alloy interfaces in H_2 – H_2O for ZMG232 (Figure 2(a)) and SUS430 (Figures 2(b) and (c)) after oxidation at 1073 K for about 1050 h. The oxide scales are identified as gray zone on the alloy surface. Black parts at the interfaces are considered to be SiO_2 internal oxides in Figure 2(a). The oxide scale thickness is about 3.8–4.5 μm , which is a little bit different from the alloys (ZMG232 shows the thinner oxide scales). In the case of SUS430 alloy (Figure 2(b)), clean oxide scale/alloy interface is observed. However, black lines were sometimes observed at the interfaces (Figure 2(c)). Since the thickness of the scale is similar between Figure 2(b) and Figure 2(c), the oxide scales were considered to be broken during preparing the samples. This indicates that the mechanical strength or the adhesion of oxide scale is not strong enough in SUS430 alloy.

Fig. 2 SEM images of oxide scale/alloy interfaces (in $\text{H}_2\text{-H}_2\text{O}$ at 1073 K for 1050 h): (a) ZMG232; (b) SUS430; (c) SUS430 (detached part)

2.3 Elemental distribution around the oxide scale/alloy interfaces

The elemental distribution was examined at oxide scale/alloy interfaces. **Figure 3** shows depth profiles of elements around the oxide scale/alloy interfaces measured by GDOES. The y-axis indicates the optical intensity for each element, which is proportional to the concentration and sputtering rates. Thus, we assume this parameter for estimating the concentration of elements at a constant sputtering rate. The oxide scale is composed of Mn-rich surface area, Cr-rich part, and Si-rich scale/alloy interface. In the case of ZMG232 (**Figure 3(a)**), high concentration of Fe is identified at the top surface of oxide scale. A relatively high concentration of Si is observed at the oxide scale/alloy interfaces for both alloys (in **Figure 3**). This Si is considered to be SiO_2 precipitated and condensed at the interfaces, not in the oxide scale. Al-internal oxide is observed inside the alloy. The oxide scale thickness

Fig. 3 GDOES depth profiles at oxide scale/alloy interfaces: (a) GDOES profiles of oxidized ZMG232 (at 1073 K for 1050 h); (b) GDOES profiles of oxidized SUS430 (at 1073 K for 1050 h)

is a little bit thinner in ZMG232 from the profiles of O. The difference of elemental distribution can affect the scale stability and adhesion of scale on alloys.

From the GDOES depth profile analysis, the oxide scale thickness was estimated in the flat part of depth profiles of O (also, the thickness of oxide scale was checked in the SEM images). **Figure 4** shows oxide scale thickness of ZMG232 and SUS 430 as a function of annealing time at 1073 K. The scale thickness increases with time in a parabolic relationship. That is, the square of scale thickness increases with time in the following relationship;

$$x^2 = k_p t \quad (1)$$

where x is the thickness of oxide scale from the GDOES depth profiles, t is annealing time, and k_p is the oxide scale growth rate constant. This suggests that the growth of oxide scale is controlled by the diffusion

Fig. 4 Oxide scale thickness for two different alloys as a function of annealing time

process, such as diffusion of cation through the oxide scales. The k_p value was estimated from the slopes of the plots in Figure 4. The obtained k_p values for ZMG232 and SUS430 are $6.2 \times 10^{-6} \mu\text{m}^2 \text{s}^{-1}$ and $1.0 \times 10^{-5} \mu\text{m}^2 \text{s}^{-1}$, respectively. Thus, ZMG232 has the higher oxidant resistance than SUS430. The difference of growth rate constants can come from the diffusivity of cations through the oxide scales. Although some differences were observed on the oxide scale growth rates between ZMG232 and SUS430, the growth mechanism is considered to be diffusion-controlled of cations through the oxide scales. This “normal oxide scales” show the thickness of 3–6 μm after oxidation for 1000 h at 1073 K.

2.4 Anomalous thick oxide scale formation in H_2 – H_2O

A thick oxide scale was occasionally observed on one side of alloy surface annealed in H_2 – H_2O atmosphere. **Figure 5** shows an example of microstructures for anomalous thick oxide scale formed on SUS430 alloy surface. The thickness of oxide scale is about 10–13 μm , which is 2–4 times thicker than the normal oxide scale. The oxide scale has almost no voids but cracks. Therefore, an anomalous oxide scale formation can be related to the fast diffusion of cations through the oxide scale. Some cracks of oxide scale are thought to be formed during sample preparation, such as polishing and cutting. However, the mechanical strength of oxide scale on SUS430 is considered to be smaller than that of normal scale on ZMG232, and this can be related to the stability and scale adhesion on the alloy surface. The formation of anomalous thick oxide scale did not follow the diffusion controlled oxide scale

Fig. 5 SEM images of anomalous thick oxide scale/alloy interface (oxidation at 1073 K for 1050 h)

Fig. 6 GDOES depth profiles at anomalous oxide scale/alloy interfaces (oxidation at 1073 K for 1050 h)

mechanism as was observed in the previous section (Figure 4).

The elemental distribution of this part was investigated by GDOES depth profiles (**Figure 6**). The oxide scale is composed of Fe-rich surface, Mn and Cr rich intermediate part, and Si rich oxide scale/alloy interface. Relatively high signal counts of Si are observed at the oxide scale part, suggesting high diffusivity and reaction of Si inside the oxide scale. A relatively high signal count of Fe is observed at the top surface of oxide scale, suggesting a fast diffusion of Fe through the scale. From XRD analysis, Fe_2O_3 phase was also identified at the top surface, which confirms the anomalous diffusion of Fe. The elemental distribution of anomalous thick oxide scale is completely different from that of normal oxide scale: the existence

Fig. 7 SIMS images of each secondary ion at anomalous oxide scale/alloy interfaces (Oxidation at 1073 K for 1050 h)

of Si and Fe in the oxide scales can be related to the formation of anomalous thick oxide scales.

To investigate the elemental distribution of anomalous oxide more precisely, SIMS imaging analysis was examined at the anomalous oxide scale/alloy interfaces (Figure 7). The SIMS images show that the oxide scale is composed of Cr, Mn, and Fe, which is considered to be Fe_2O_3 , Fe–Cr–Mn-spinel and Cr_2O_3 from the X-ray diffraction analysis. The most surprising thing is the distribution of Si, as indicated in GDOES depth profiles: relatively high signal counts of Si are observed inside the oxide scale as well as the oxide scale/alloy interface. This distribution of Si is completely different from the normal oxide scale. The concentration of Si is not homogeneously distributed inside the oxide scale, which suggests the difference of diffusivity and reactivity of Si from the positions of the oxide scale. The grain boundaries of oxide scale can be related to this phenomenon.

In terms of oxide scale stability, a thick oxide scale formation is not favorable because of the break down of protective oxides layers. The break down of protective oxide scale can increase the thickness of oxide scale, which deteriorates the electrical conductivity. The Fe–Cr–Mn spinel oxide is replaced by Fe_2O_3 based oxide at the top surface of oxide scale. The formation mechanism of such a thick anomalous oxide scale is under consideration. One possibility is the reaction of MnFe_2O_4 spinel with SiO_2 (from impurity in the gas phase, such as from Al_2O_3 tube); this reaction altered the diffusivity of cations inside the oxide scales since the cation diffusivity is significantly changed by the substitution of cations in M_3O_4 (M: metals) as follows:

The formation of Fe_3O_4 increases the diffusion coefficient of Fe in the oxide more than 100 times that in MnFe_2O_4 . The higher diffusivity of Fe generates the thicker oxide scales than the normal one. We will report further results in the future. In any reasons for the formation of anomalous thick oxide scales, they affect the stability of Fe–Cr alloy in terms of connections at oxide scale/alloy/cell interfaces.

Conclusions

The chemical stability of Fe–Cr alloys was examined in H_2 – H_2O atmosphere for SOFCs. The oxide scales were formed on the alloy surface with a thickness of 3–6 μm at 1073 K for more than 1000 h. The diffusion controlled mechanism was assumed for the normal oxide scales, in which the cation diffusion through the scale is rate-determining for oxide scale growth. The microstructures and elemental distribution of oxide scale/alloy interfaces were analyzed by depth analysis and surface analysis techniques: Mn–Cr–(Fe) spinel, Cr_2O_3 , and internal Si oxides were formed from surface to inner oxides. An anomalous thick oxide scale formation was found on SUS430 surface in H_2 – H_2O atmospheres. A thick oxide scale was composed of Fe, Cr, Mn oxides. Relatively high concentration of Fe and Si were observed at surface and inside the oxide scale, suggesting a fast diffusivity of cations inside the oxides. The formation of anomalous thick oxide scale can affect the stability of Fe–Cr alloy interconnects by changing the cell connections at scale/alloy/cell interfaces.

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