OXIDE SCALE FORMATION ON ALLOY INTERCONNECTS IN CH₄ FUELS FOR SOLID OXIDE FUEL CELLS

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ABSTRACT
Oxide scale formations in CH₄-H₂O atmospheres were investigated for different alloys for interconnects in solid oxide fuel cells (Fe-Cr and Ni-Cr alloys). Oxidation with anode gases (CH₄, H₂O, CO, and CO₂) caused a relatively thick oxide scale formation on the alloy surfaces even in the low oxygen partial pressures at 1073 K. The distribution of elements in the oxide scale and the growth rates of oxide scales were compared among the examined alloys by glow discharge optical emission spectrometry (GDOES). Mn-Fe and Mn-Ni spinels were formed on Fe-Cr alloys and Ni-Cr alloy surface, respectively. Oxide scale thickness grew with annealing time by a parabolic relationship, and the growth rates were in the orders of 10⁻⁶⁻¹⁻⁰⁻⁵ μm²s⁻¹ at 1073 K. The electrical conductivity after forming oxide scales was different depending on the oxide scale phases and thickness, and was in the orders of 10 Scm⁻¹ at 973 K.

INTRODUCTION
Alloys are considered candidate materials for interconnects in solid oxide fuel cells (SOFCs) that operate at a medium temperature (773 K-1073 K). Since alloys have the following merits, they are promising materials: (i) achievement of dense and gas-tight barrier between fuel and air gases, (ii) ease of handling, which makes fabrication cost lower, and (iii) high electronic and thermal conductivity, which makes cell performance higher. Several kinds of alloys have been developed as interconnects for SOFCs, such as oxygen dispersion strengthened (ODS) alloys (1-5), ferritic alloys (6-19), and Ni-based alloys (18, 20-21). The main issues for applying the alloy materials are the formation of oxide scales and Cr-vaporization during operation. The oxide scale formation and Cr-vapor will increase the bulk resistance as well as the contact resistance between alloy and electrodes. Therefore, it is important to clarify the oxide scale formation mechanism on alloy surface. The oxidation mechanism and oxide scale formation have been reported by several groups especially in oxidant atmosphere. On the other hand, there still remains uncertainty about oxidation of alloys and oxide scale formation in reducing atmospheres, such as H₂-H₂O or CH₄ containing gases. We have previously reported oxide scale formation on Fe-Cr alloys in H₂-H₂O and CH₄-H₂O atmospheres (22-26). The oxide scale formation mechanism was evaluated by secondary ion mass spectrometry (SIMS) imaging analysis. The aims of the present study are to characterize the oxide scale formation on Fe-Cr and Ni-Cr alloys and its properties at the oxide scale/alloy interfaces under CH₄-H₂O atmospheres. The examined alloys are Fe-Cr alloys (ZMG232 and
SUS430) and Ni-Cr alloy (RA601) in humid methane (CH₄) to simulate steam reforming at 1073 K. Minor and major elements distribution around the oxide scale/alloy interfaces was analyzed by glow discharge optical emission spectrometry (GDOES). Also, we report the oxide scale growth rates and the electrical conductivity for these alloys treated in CH₄-H₂O.

**EXPERIMENTAL**

**Samples**

Three different alloys (Fe-Cr based and Ni-Cr based) are selected because of their relative stability. It has been reported that the formation of Mn-Fe-Ni based spinel and Cr₂O₃ based oxide scales reduce the Cr-vaporization to keep the resistance low as interconnects of SOFCs [4, 11-12, 20-21]. The selected alloys are abbreviated as follows: ZMG232, SUS430, and RA601. The chemical compositions of these alloys are listed in Table I. The samples were cut into pieces in the size of about 1×1 cm², and the surfaces were polished with a diamond paste to obtain a mirror surface (up to 1/4 μm grade).

**Table I. Chemical composition of examined Fe-Cr alloys and Ni-Cr alloy (in mass%).**

| Elements | ZMG232 (Hitachi Metals Ltd., Japan) | SUS430 (purchased from Nilaco Co., Japan) | RA601 (Rolled Alloys Co., USA) |
|----------|-----------------------------------|------------------------------------------|-------------------------------|
| C        | 0.02                              | 0.048                                    | 0.05                          |
| Si       | 0.40                              | 0.35                                     | 0.2                           |
| Al       | 0.21                              | 0.05                                     | 1.4                           |
| Cr       | 21.97                             | 16.35                                    | 22.5                          |
| Mn       | 0.50                              | 0.21                                     | 0.3                           |
| Fe       | 76.38                             | 82.85                                    | 14.0                          |
| Ni       | 0.26                              | 0.12                                     | 61.5                          |
| Al       | 0.21                              | 0.05                                     | 1.4                           |
| Zr       | 0.22                              | -                                        | -                             |
| La       | 0.04                              | -                                        | -                             |

**Oxidation Experiments (CH₄-H₂O Treatments)**

The alloys were annealed at 1073 K with flowing CH₄-H₂O gases. Dilute CH₄ with Ar was passed through H₂O (at 50°C). The mixed gases had the following partial pressures before being fed to the reactor tube: p(CH₄)=0.05 bar, p(Ar)=0.85 bar and p(H₂O)=0.10 bar. The oxidation treatments were conducted at 1073 K for 72 h-1050 h in an Al₂O₃-tube reactor. When the mixed gases were supplied to the reactor at 1073 K, the CH₄-H₂O gas should be converted to the following composition assuming that the equilibrium is attained in the reactor: p(O₂)=2.58x10⁻² bar, p(H₂)=1.46x10⁻¹ bar, p(H₂O)=1.60x10⁻¹ bar, p(CO)=3.59x10⁻² bar, p(CO₂)=9.56x10⁻³ bar. In this gas composition, the equilibrium calculation suggests no carbon deposition. After the experiments, there was no carbon deposited in the Al₂O₃ reactor tube.
Analysis of Alloys

Microstructures of oxidized surface and cross section of oxide scale were analyzed by scanning electron microscope (SEM, Hitachi S-800) with EDX (Kevex). The reaction phases formed on the alloy surface were identified by X-ray diffraction (Phillips PW 1800). Major and minor elements distributions in depth direction were analyzed by glow discharge optical emission spectrometry (GDOES, Jobin Yvon/ HORIBA, JY-5000RF) with Ar sputtering. The depth profiles were measured in an area of 2 mm in diameter. For RF-generator, the following condition was selected to measure the oxide scales and alloy; Pressure: 600 Pa and Power: 35 W. After the formation of craters, the depths were analyzed by surface profiler system (Dektak, Veeco).

The electrical conductivity of oxidized alloy was measured by 4-probe AC impedance measurements [16]. Pt-paste electrodes were applied to the oxidized alloy surfaces, and the measurements were conducted in an air atmosphere. The measurement time for the conductivity was only 5 h, which was short enough to prevent growth of a new thick oxide scale during the measurements. The AC impedance spectra were measured in the frequency range from 1 mHz to 100 kHz with amplitude of 10 mV.

RESULTS AND DISCUSSION

Surface Oxide Scale Phases and Microstructure of Oxidized Alloy

To confirm the reaction products at the oxidized alloy surface, X-ray diffraction was examined. Figure 1 shows X-ray diffraction patterns of oxidized alloys (oxidized at 1073 K for 288 h in CH4-H2O). In the XRD pattern of ZMG232 (Fig.1(a)), the identified peaks are alloy (“A” in figures), Fe-Mn-Cr spinels (“S”), and Cr2O3 oxides (“C”). Thus the oxide scales mainly composed of spinel and Cr2O3 phases. In Fig. 1(b), similar XRD patterns are observed on the oxidized SUS430. In addition to the spinel phases, several peaks attributed to Cr2O3 are observed in the pattern, and the intensities are stronger than those of ZMG232. In Fig.1(c), the XRD pattern mainly shows Fe-Mn-Cr spinels, Cr2O3, and alloy, which is nearly the same as the other alloys. The oxide phases formed on the Ni-Cr alloy are somewhat different from that on the Fe-Cr alloys. This is due to the difference of crystal structure of alloys.

Figure 2 shows surface microstructure of oxidized ZMG232 and RA601 alloys after exposure to CH4-H2O for 288 h. The CH4-H2O treatments varied the microstructure drastically. Needle-like shape or plate-like shape crystals are observed at the grain boundaries of alloy surface by the reaction with CH4-H2O gases. The oxide phases formed from the grain boundary region of alloys. The chemical composition of needle-like parts was analyzed by EDX, which was close to the composition of Cr2MnO4. On the other hand, the grain parts of the surface are Fe, Ni, and Cr-rich with Mn containing compositions. Thus, the formation of oxide scale starts from the grain boundary region and grows all over the surface. The active parts of oxide scale formations are the grain boundaries for all alloys.

Microstructures of Cross Section

Figure 3 shows typical microstructure of cross section at the oxide scale/alloy interface
after CH4-H2O treatments for above 1000 h at 1073 K. Oxide scale layer is identified as a zone on the alloy surface with dense microstructures. At the oxide scale/alloy interfaces, almost no voids and cracks are observed, which suggests the continuous growth of oxide scale from the alloy surface. The adhesion of oxide scale with alloy is expected to be good from the SEM image. Inside the ZMG232 alloy, many dark spots are observed; these spots are Al2O3 internal oxides that dispersed inside the alloys.

**Elemental Distribution at the Oxide Scale/alloy Interfaces and Growth Rates of Oxide Scale**

Figure 4 shows GDOES depth profiles of elements around the oxide scales/alloy interfaces after the oxidation experiments at 1073 K for 72 h. The x-axis of these profiles indicates the sputtering time (almost equal to the depth from the sample surface) and y-axis indicates the optical emission intensities of each element. In the depth profiles of ZMG232 alloy (Fig. 4a), the thickness of the oxide scale is estimated to be about 0.6 µm because of the constant intensities of O up to the sputtering time of 6 s (this equals to the depth of 0.6 µm). Around the oxide scale/alloy interfaces, the following zones are identified from surface to inner oxides: high concentration zone of Mn and Fe (Mn-Fe spinels), Cr-rich zone (Cr2O3), Si-rich zone, and Al-rich zone. In the RA601 alloy (Fig. 4b), the identified oxide phases are the following oxide phases from surface to inner oxides within 6 s of sputtering time: Ni-Mn rich phase, Cr-rich zone, and Al-rich zone. The difference between ZMG232 and RA601 is the distribution of Si, Al, Ni, and Fe. Since ZMG232 alloy contains Al, the Al2O3 internal oxides were formed in the alloy bulk as were observed in dark spots in Fig. 3(a). Also, for RA601, the Al-based oxides can be formed inside the alloy. A relatively high intensity of Al in RA601 is estimated to be oxide phases existing in the alloy bulk.

From the GDOES depth profiles, we can estimate the thickness of oxide scales for each alloy at different times. The thickness of the oxide scale was estimated from the flat parts of the depth profiles of oxygen (O). Figure 6 shows oxide scale thickness as a function of annealing time. The thickness of oxide scale increases with the following parabolic relationship:

\[ d^2 = k_p \times t \]  

where, \( d \) indicates the thickness of the oxide scale, \( k_p \) is the growth rate constant, and \( t \) is the annealing reaction time. In Fig. 6, the least square fitting lines are also shown. A relatively good agreement is observed between observed and fitted data. This suggests that the growth of oxide scale is controlled by some diffusion process, such as cation diffusion in the alloy. From the slopes of these fitting lines, we can estimate the growth rates, \( k_p \) for each alloy. The calculated values of \( k_p \) are as follows: 6.2x10^6 µm²s⁻¹ for ZMG232, 1.0x10^5 µm²s⁻¹ for SUS430, and 3.0x10^5 µm²s⁻¹ for RA601. Thus, the growth rate of RA601 is smallest among the examined alloys and it is expected to give thinner oxide scale. The diffusivity of Cr can be different between the Fe-Cr alloy and the Ni-Cr alloy. In addition, the growth rate of oxide scale can be controlled by the addition of some minor elements, such as Si, Al, Mn, La, and Zr. Addition of Mn can be effective to reduce the oxide scale growth rates by forming the Mn-based spinel phases on the surface. From these oxide scale growth rates, we can estimate the thickness of oxide scale for a long-term operation. The thickness of oxide scale after 5 years’ operation will be about 14
μm and 10 μm for ZMG232 and RA601, respectively.

Electrical Conductivity of Oxidized Alloys

The electrical conductivity after forming the oxide scale was measured by the 4-probe method. An area specific resistance \( R_{AS} \) was adopted to evaluate the resistance of the samples:

\[
R_{AS} = R \times S \text{ [Ωcm}^2\text{]} \tag{2}
\]

where \( R \) and \( S \) indicate the measured resistance and the surface area of the samples, respectively. The \( R_{AS} \) can contain the resistance from oxide scales and alloy bulk. Since we cannot measure the exact effective oxide thickness of scales, we adopted the \( R_{AS} \) as a resistance of the oxidized alloy. Figure 6 shows electrical conductivity \((\sigma=R_{AS}^{-1})\) as a function of inverse temperature. The electrical conductivity increases with increasing temperature, which is semi-conductor temperature dependence. Thus the electrical conductivity can indicate the contribution from the oxide scales formed on the Fe-Cr and Ni-Cr alloys. The electrical conductivity of ZMG232 shows higher values than the other alloys \((R_{AS}=0.1 \text{ Ωcm}^2 \text{ at } 973 \text{ K})\). High electrical conductivity can come from a relatively thin oxide scale and spinel (Mn-Fe-Cr) formation on the surface.

The slope of \( \sigma T = R_{AS}^{-1} T \) versus inverse temperatures was calculated from the following relationship:

\[
\sigma T = R_{AS}^{-1} T = A \cdot \exp(-E_a/kT) \tag{3}
\]

where, \( A \) is pre-exponential constant, \( E_a \) is activation energy, \( k \) is Boltzman constant, and \( T \) is temperature. The activation energy for each oxidized alloy was calculated from least square fitting of the observed data in the temperature range from 689 K to 1081 K. The obtained values are 0.67 eV for ZMG232, 0.57 eV for SUS430, and 0.37 eV for RA601 alloys. The difference in the activation energy of electrical conductivity can be due to the difference from the conduction properties of the Mn spinel on alloys. These values are similar to the reported activation energy for the oxidized Fe-Cr alloys [15]. For the RA601 (Ni-Cr alloy) the activation energy indicates a similar value that of \( \text{Cr}_2\text{O}_3 \) \((=0.18-0.3 \text{ eV})\). The temperature dependence of the electrical conductivity is affected by the formation of Mn-Fe-Cr spinel phases at the surface region.

CONCLUSIONS

The chemical stability of Fe-Cr alloy (ZMG232 and SUS430) and Ni-Cr alloy (RA601) was examined at 1073 K under CH\(_4\)-H\(_2\)O gases to simulate the real fuel gas conditions. Oxide scale layers were formed on the alloy surface by the reaction with CH\(_4\)-H\(_2\)O gases. The surface morphology varied with formation of needle-like or plate-like crystals. The grain boundary parts are active for forming the oxide scales both in the Fe-Cr and Ni-Cr alloys. The depth profiles around the oxide scale/alloy interfaces suggest that the oxide scales have the following layered structure from surface: Fe-Cr-Mn or Ni-Cr-Mn spinels, \( \text{Cr}_2\text{O}_3 \) oxides, Si-condensed part, \( \text{Al}_2\text{O}_3 \) inner oxides, and alloy bulk. High concentration of Mn on the oxide scale surface suggests fast diffusion of Mn in the oxide scale to form
Annealing in CH₄-H₂O made the oxide scale thicker with time. Growth of the oxide scale layer thickness followed the parabolic growth relationship with time. The parabolic growth rate constants were 10⁻⁵-10⁻⁶ μm²s⁻¹ in the order of magnitude for all experimental conditions. The electrical conductivity of the oxidized alloys showed semi-conductor temperature dependences. Thus the electrical conductivity indicates the contribution of oxide spinels.

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Figure 1. X-ray diffraction patterns of oxidized alloys for 288 h at 1073 K in CH$_4$-H$_2$O atmosphere. [(a): ZMG232, (b): SUS430, (c): RA601, A: Alloys, S: spinel, C: Cr$_2$O$_3$].

Figure 2. Scanning electron microscope images of oxidized alloys surface. [(a): ZMG232, (b): RA601, in CH$_4$-H$_2$O, 1073 K for 288 h].
Figure 3. Scanning electron microscope images of oxidized alloys at the oxide scale/alloy interfaces. 
[(a): ZMG232, (b): RA601, in CH₄-H₂O, 1073 K for 1050 h].

Figure 4. Depth profiles of oxidized alloys by glow discharge optical emission spectroscopy (GDOES) as a function of depth from the surface. 
[(a): ZMG232, (b): RA601, in CH₄-H₂O, 1073 K for 72 h].
Figure 5. Oxide scale growth of alloys as a function of treatment time. 
[•: ZMG232, ▲: RA601, ■: SUS430 in CH₄-H₂O at 1073 K].

Figure 6. Temperature dependence of electrical conductivity of oxidized alloys. 
[♦: ZMG232, ▲: RA601, ■: SUS430 in CH₄-H₂O, 1073 K for 1050 h].