THE EFFECTS OF RARE EARTH ELEMENT COATINGS
ON OXIDATION OF ALLOYS
IN SOFC OPERATING ATMOSPHERES

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ABSTRACT

Chromia-forming alloys are one of the best candidates for the interconnecting materials in solid oxide fuel cells (SOFCs). However, low electronic conductivity and volatility of the chromia scale need to be solved to improve performance of planar-type SOFCs. In the field of high temperature oxidation of metals, it is well known that the additions of reactive elements into alloys improve oxidation resistance of alloys at high temperatures. In this paper, La-coating by the vacuum deposition method is applied, and the effects of La-coating on oxidation of the chromia-forming alloy in SOFC operating atmospheres are examined.

INTRODUCTION

In planar-type solid oxide fuel cells (SOFCs), the development of interconnection materials, i.e., separator, is one of the most important subjects to assemble cell stacks. Doped LaCrO₃ oxides show good properties as separator with respect to chemical stability and electrical conductivity under operating atmospheres. However, it is quite difficult to make a large separator with doped LaCrO₃ oxides because of low mechanical strength and thermal expansion mismatch in oxidizing and reducing atmosphere. Cr₂O₃-forming alloys are also a candidate for separator with respect to electrical conductivity, thermal conductivity, mechanical strength and machinability. However, there are still some problems related to the protective oxide layer. The Cr₂O₃ scale formed on alloys is low in electrical conductivity and grows with time, and volatile chromium species such as CrO₂(OH), from the scale are reduced at the electrochemical active sites to lead to polarization losses.

In the field of high temperature oxidation of metals, it is well known that the additions of reactive elements such as Y and Hf into alloys improve oxidation resistance of alloys at high temperatures. However, only a few attempts have so far been made at the rela-
tion between reactive element additives and electrical resistance of the oxide layer grown on alloys(5).

In this study, lanthanum which is one of the reactive elements was added by a coating method, and the effects of La-coating on oxidation of alloys and electrical resistance of oxide layers were investigated.

**EXPERIMENTAL**

Electron-beam physical vapor deposition (EB-PVD) was used for the coating method. The preparation process is as follows: La with a purity of 99.9% was used, and INCONEL600 (main chemical composition, nominally 76%Ni-15.5%Cr-8%Fe-0.5%Mn-0.25%Si in weight per cent) was chosen as the chromia-forming alloy. The alloy sheets were cut into pieces with a dimension of 10 mm x 15 mm x 0.8 mm. The surfaces of the alloy substrates were polished with 1 μm diamond pastes, and then substrates were ultrasonically cleaned in organic solvents. La was deposited onto the substrates to be 3 μm in thickness in a vacuum of 6x10⁻³ Pa at a substrate temperature of 650 °C. The deposition rate was controlled to be approximately 0.1 μm/min.

The La-coated substrates were oxidized at 900 °C in quasi SOFC operating atmospheres for specified periods. Air and H₂/H₂O gas mixtures were prepared for oxidant and fuel gas, respectively. The composition of H₂/H₂O was 94.6/5.4 in volume per cent at room temperature, and the flow rate of these gases was maintained at 30 sccm.

The electrical resistance of the oxide layer formed on the La-coated INCONEL600 was measured at elevated temperatures. As shown in the schematic diagram for the measurement in Figure 1, Pt leads for current and voltage were attached to the substrate after the oxidation. Pt electrode with an area of 0.38 cm² was attached to the surface, and two Pt leads were spot-welded onto the back side of the substrate. A constant current of 80 mA was applied through one of the two leads and the voltage drop between the Pt leads was measured. In this measurement, the voltage drop in the alloy substrate was negligible. For comparison, electrical resistance measurements for the uncoated INCONEL600 substrates were made in the same manner.

The surface layers of the La-coated INCONEL600 were investigated by X-ray diffraction (XRD) with a radiation of Cu-Kα. The surface morphology and the cross section of the substrate were observed with scanning electron microscopy (SEM), and the elemental analysis was carried out with energy dispersive X-ray spectroscopy (EDS) equipped with SEM.

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RESULTS AND DISCUSSION

Figure 2 shows the XRD pattern of the as-deposited specimen. In the XRD pattern, diffraction peaks of \(\text{La}_2\text{O}_3\) are observed, and sharp diffraction peaks are identified as \(\text{LaNi}_3\), \(\text{La}_2\text{Ni}_7\) or \(\text{LaNi}_5\). As the EDS line-analysis shows in Figure 3, nickel and chromium are present in the deposition film of lanthanum. On the other hand, there is a region where lanthanum is present in the alloy, and the depth of the region reaches about 5 \(\mu\text{m}\). Taking into account the chemical composition of INCONEL600 and these observations, it is thought that mainly nickel diffused from the alloy into the film during the deposition, and that lanthanum also diffused simultaneously inward into the alloy.

The XRD pattern of the La-coated INCONEL600 after oxidation in air at 900 °C for 600 h is shown with the uncoated INCONEL600 in Figure 4. The surface oxide layer grown on the uncoated INCONEL600 substrate consists of chiefly \(\text{Cr}_2\text{O}_3\) and spinel oxides. From the cross-sectional SEM observation, the oxide layer was about 10 \(\mu\text{m}\)-thick. On the other hand, it is found that the surface oxide layer of the La-coated INCONEL600 consists of perovskite oxides, NiO and spinel oxides. Figure 5 shows the cross-sectional elemental mapping results of the oxide layer. The oxide layer can be divided into two regions: the top region where lanthanum is abundantly present, and the bottom region where the concentration of nickel is low and the concentration of chromium is high. The thickness of the former is close to the sum of the thickness of the deposition film and the depth of the La-diffusing region. The latter, Cr-rich region, is thought to be formed by chromium being oxidized internally.

Figure 6 shows the XRD patterns of the La-coated and the uncoated INCONEL600 after oxidation in \(\text{H}_2/\text{H}_2\text{O}\) at 900 °C for 200 h. The diffraction peaks of the uncoated INCONEL600 related to oxides are identified as \(\text{Cr}_2\text{O}_3\) and spinel oxides. The oxide layer was about 4 \(\mu\text{m}\) in thickness from the cross-sectional SEM observation. On the other hand, for the La-coated specimen, any phases related to oxides remain unidentified. The elemental mapping results of the cross-section are shown in Figure 7. The mapping result of nickel indicates that nickel is present on the surface of the specimen. Taking into account the oxygen partial pressure (10\(^{-19}\) atm) under the \(\text{H}_2/\text{H}_2\text{O}\) gas mixture at 900 °C, nickel is not oxidized. Therefore, the sharp diffraction patterns observed which are similar to the diffraction patterns of INCONEL600 are thought to be derived from the metallic phase of nickel. The segregation of nickel on the surface is thought to be as follows: in a low oxygen partial pressure, nickel in the deposition film is not oxidized, so lanthanum which has a high affinity for oxygen reacts with other elements in the alloy like chromium to be oxidized. In the mapping result of chromium, there is a similar tendency that chromium is enriched under the La-containing region, and it is thought that this region is formed by oxidation of chromium in the alloy.

Figure 8 shows Arrhenius plots of electrical conductance of the oxide layer grown on
the La-coated and the uncoated INCONEL600 under each atmosphere. It is found that the electrical resistance of the La-coated specimen is lower than that of the uncoated specimen by one order of magnitude. In addition, the activation energy for electrical conduction of the La-coated specimen is lower than that of the uncoated specimen in both atmospheres. In the oxides identified, Cr₂O₃ has a low conductivity, therefore taking into account the structure of the oxide layer grown on the alloy, it is thought that Cr₂O₃ in the oxide layer determines the overall electrical resistance of the oxide layer, and that the magnitude of the electrical conductance can be attributed to the thickness of the Cr₂O₃ layer. However, since there is a difference observed in the activation energy, the electrical conduction mechanism in the Cr₂O₃ is thought to be changed by the La-coating.

SUMMARY

Lanthanum was added to the chromia-forming alloy INCONEL600 by a coating method, and the effects of La-coating on oxidation of the alloy and electrical resistance of oxide layers were investigated. The elemental analysis results of La-coated specimen indicate that chromium in the alloy is oxidized internally under the La-containing region. From electrical resistance measurements, it is found that the electrical resistance of the La-coated specimen is lower than that of the uncoated specimen by one order of magnitude. Furthermore the activation energy for electrical conduction of the La-coated specimen is lower than that of the uncoated specimen in both atmospheres. Since there is a difference observed in the activation energy, the electrical conduction mechanism in the Cr₂O₃ is thought to be changed by the La-coating.

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Figure 1. Experimental set up for the electrical resistance measurement.

Figure 2. XRD pattern of the as-deposited sample.

Figure 3. EDS line analysis results of the cross-section of the La-coated INCONEL600.
Figure 4. XRD patterns of the La-coated INCONEL600 (top) and the uncoated INCONEL600 (bottom) after oxidation in air at 900 °C for 600 h.

Figure 5. Elemental mapping results of the cross-section of the La-coated INCONEL600 substrate after oxidation in air at 900 °C for 600 h.
Figure 6. XRD patterns of the La-coated INCONEL600 (top) and the uncoated INCONEL600 (bottom) after oxidation in $H_2/H_2O$ at 900 °C for 200 h.

Figure 7. Elemental mapping results of the cross-section of the La-coated INCONEL600 after oxidation in $H_2/H_2O$ at 900 °C for 200 h.
Figure 8. Arrhenius plots of electrical resistance of oxide layers grown on the La-coated INCONEL600 and the uncoated INCONEL600 in each atmosphere. top: in air, bottom: in H₂/H₂O.