THE INFLUENCE OF (LaSr)CoO₃ COATINGS ON THE ELECTRICAL RESISTANCE OF Ni-20Cr ALLOYS IN HIGH TEMPERATURE OXIDIZING ATMOSPHERE

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ABSTRACT

Ni-20Cr alloys coated with (LaSr)CoO₃ maintained their electrical resistance as low as 5mΩ cm² for 12000 h at 1273 K in air, and showed their applicability for the separator of solid oxide fuel cell(SOFC). Energy dispersive X-ray analysis of the fracture surface of the coated Ni-20Cr alloys revealed that Sr diffused into the Cr₂O₃ scale and precipitated as oxides in the Sr-Cr-O system. X-ray diffraction profile of the outer portion of the Cr₂O₃ scale adjacent to the coating layer indicated SrCrO₄ and Cr₂O₃. Electron diffraction and Energy dispersive X-ray analysis of the oxide particles inside the scale close to the alloy/scale interface indicated that the oxide is a rhombohedral crystal with the unit-cell dimension of a=11.28, c=36.44 and the atomic ratio of Sr / Cr = 3.165 / 2.

INTRODUCTION

Electrochemical solid oxide fuel cells(SOFCs) offer high efficiency to generate electricity directly from fuel. However, their high operating temperature (1100-1300K) causes difficulties to develop the components. Separator material of electrically connecting single cells should fulfill many requirements: chemical stability, gas-tightness, high electrical conductivity and thermal expansion coefficient close to that of the ceramics composing SOFC. High temperature Ni-based alloys and Sr-doped LaCrO₃ ((LaSr)CrO₃) are distinct candidates for separator material (1-4). To commercialize SOFC, machinability and scaleup feasibility of material are important properties, and high temperature Ni-based alloys have an advantage over (LaSr)CrO₃ in these respects. High temperature Ni-based alloys show high oxidation resistance by forming Al₂O₃ or Cr₂O₃ on their surface as the protective scale. These
scales are stable in a high temperature oxidizing atmosphere and protect the alloys from further oxidation. Nevertheless, for the separator use some surface modification is necessary because of the high electrical resistance of the scales.

In our previous paper, we reported that (LaSr)CoO$_3$ coatings on Ni-20Cr alloys provided a highly conductive Cr$_2$O$_3$ scale in air at 1273K, whereas the coating on Al$_2$O$_3$-forming alloys was not effective at all (5). The electrical resistance of the coated Ni-20Cr alloys was reduced to 1/20 of that of the non-coated Ni-20Cr alloys after 8000h. The Cr$_2$O$_3$ scale formed at the interface between the (LaSr)CoO$_3$ coating layer and Ni-20Cr alloy was as thick as the scale formed on the non-coated alloys which showed high electrical resistance.

In the present paper, details of the microstructure of the highly conductive Cr$_2$O$_3$ scale were determined using scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX). To elucidate the beneficial effect of the (LaSr)CoO$_3$ coatings, which leads to a conductive Cr$_2$O$_3$ scale, the crystal structures and the chemical composition of the oxide particles precipitated in the scale were examined using X-ray diffraction (XRD), transmission electron microscopy (TEM), electron diffraction and EDX.

**EXPERIMENTAL PROCEDURE**

**Electrical resistance change of Ni-20Cr alloys during oxidation**

The composition of the Ni-20Cr alloy is shown in Table 1. The alloy samples (25mm x 25mm x 2mm) were polished by the emery paper (#500) and were washed in acetone using the ultrasonic cleaner before the coating. The coating was carried out by spray-pyrolysis of the solution containing La, Sr and Co. The aqueous solution, of nominal composition La/Sr/Co=0.3/0.2/0.5 in molar ratio, was prepared from La(NO$_3$)$_3$, Sr(NO$_3$)$_3$ and Co(NO$_3$)$_3$. The aqueous solution of 100cm$^3$ was mixed with glycerol (0.2kg). The mixed solution was sprayed on the alloy samples heated at 773 K with a spray gun. The coated alloy samples were heated at 1123 K for 20 min in air. As shown in Fig.1, the electrical resistance was measured by the 4-probe method during oxidation in air at 1273K. The alloy samples were sandwiched between porous LaCoO$_3$ layers which acted as current collector. The LaCoO$_3$ layers were so porous that air was freely supplied to the surface of the alloy sample. The voltage-drop between the two LaCoO$_3$ layers on both sides of the alloy sample was measured.

| Table 1 Chemical composition of the Ni-20Cr alloy (wt%) |
| Ni   | Cr  | Fe  | Al |
|------|-----|-----|----|
| balance | 22.6 | 13.6 | 1.2 |
Characterization of the scale

The crystalline phases present in the scale formed between the \((\text{LaSr})\text{CoO}_3\) coating layer and Ni-20Cr alloy were identified by XRD with CuK\(\alpha\) radiation. The microstructures of the scale were examined using (1) SEM, equipped with EDX, and (2) TEM with EDX. The samples were prepared for TEM by cutting with a diamond saw, grinding and polishing down to a thickness of about 40\(\mu\)m, dimpling both sides of the sample to minimum thickness of 10\(\mu\)m, and ion milling to electron transparency.

RESULTS AND DISCUSSION

Electrical resistance of Ni-20Cr alloy during oxidation

Fig. 2 shows the electrical resistance of the Ni-20Cr alloy during oxidation in air at 1273 K. The electrical resistance of the non-coated Ni-20Cr alloys is small at the initial stage of oxidation up to 100 h. After 100 h, it increases with the slope of 1/2. This means that the electrical resistance increases with the parabolic growth of \(\text{Cr}_2\text{O}_3\) scale. The parabolic low of oxidation is expressed as

\[
X^2 = k_p t
\]

where \(X\) is the oxide thickness, \(k_p\) is the parabolic rate constant and \(t\) is the oxidation time(6-7). The coated Ni-20Cr alloy maintains its electrical resistance as low as 5\(\Omega\) cm\(^2\) for 12000h, and the electrical resistance does not change in a parabolic manner. However, the scale which formed at the interface between the \((\text{LaSr})\text{CoO}_3\) coating layer and Ni-20Cr alloy was as thick as the scale formed on the non-coated alloys.

Distribution of the elements in the \(\text{Cr}_2\text{O}_3\) scale

Fig. 3 shows an SEM image and EDX element-mapping of the cross-section of the Ni-20Cr alloy coated with \((\text{LaSr})\text{CoO}_3\) after 1500 h oxidation at 1273 K in air. Between the coating layer and the Ni-20Cr alloy, the scale of 15\(\mu\)m thickness formed. The main component of the scale is \(\text{Cr}_2\text{O}_3\). The diffusion of Sr into the \(\text{Cr}_2\text{O}_3\) scale was observed.

Crystal structure and chemical composition of the oxide particles in the scale

Several phases are reported in Sr-Cr-O system. Their crystallographic data are summarized in Table 2(8-13). \(\text{SrCrO}_3\) and \(\text{Sr}_3\text{Cr}_2\text{O}_7\) shown in Table 2 are the high pressure phases.

Fig. 4 shows the XRD profile of the scale. The profile was taken from the outer portion of the scale adjacent to the coating layer, and consists of lines from \(\text{SrCrO}_4\) as well as \(\text{Cr}_2\text{O}_3\). Fig. 5 shows TEM image (A), electron diffraction pattern (B) and corresponding EDX spectra (C) for the oxide particle in the scale close to the
alloy/scale interface. In the electron diffraction pattern taken for a beam direction along (362), the reflections of a rhombohedral symmetry ((026), (223), (420) and (203)) are observed (Fig. 5(B)). The lattice spacings of the reflections are 3.808 Å for (026), 4.517 Å for (223), 2.775 Å for (420), and 4.517 Å for (203). The EDX spectra showed that the oxide particle contained Cr and Sr in the atomic ratio of Sr/Cr=3.165/2. The obtained atomic ratio of Sr/Cr is close to Sr$_3$Cr$_2$O$_7$ and Sr$_2$Cr$_2$O$_8$, but the unit-cell dimensions in rhombohedral do not agree with the reported phases (Table 3).

These results showed that Sr-Cr-O phases formed in the scale. (1) In the outer portion of the scale exposed to relatively high O$_2$ partial pressure, SrCr$_6$O$_4$ formed. (2) In the inner portion close to the alloy of low O$_2$ partial pressure rhombohedral phase formed. The formation of the Sr-Cr-O phases in the Cr$_2$O$_3$ scale probably leads to the low electrical resistance of Ni-20Cr alloy coated with (LaSr)CoO$_3$.

**Table 2** Crystallographic data of Sr$_x$Cr$_y$O$_z$

| Phase       | SrCrO$_3$ | Sr$_2$CrO$_4$ | Sr$_3$Cr$_2$O$_7$ | Sr$_3$Cr$_2$O$_8$ | SrCrO$_4$ | SrCr$_2$O$_7$ |
|-------------|-----------|---------------|------------------|------------------|-----------|--------------|
| Crystal system | cubic     | orthorhombic  | tetragonal       | rhombohedral     | monoclinic| tetragonal   |
| Unit-cell dimensions | a=3.8180  | a=10.01       | a=3.820          | a=11.16          | a=7.083   | a=11.19      |
|              | b=14.19   |               |                  |                  | b=7.388   |              |
|              | c=5.809   | c=20.10       | c=40.37          | c=6.771          | c=9.483   |              |

**Table 3** Crystallographic data calculated from electron diffraction pattern and EDX chemical composition of Sr$_x$Cr$_y$O$_z$ particle.

| Crystal system | rhombohedral |
|----------------|--------------|
| Unit cell dimension | a=11.28, c=36.44 |
| Chemical composition | Sr$_{3.165}$Cr$_{2.0}$O$_z$ |

**CONCLUSION**

The Ni-20Cr alloy coated with (LaSr)CoO$_3$ maintained its electrical resistance as low as 5 m$\Omega$ cm$^2$ for 12000 h at 1273 K in air. Sr contained in the coating layer diffused into the Cr$_2$O$_3$ scale formed at the interface between the coating layer and the alloy. The XRD profile showed that SrCrO$_4$ formed in the outer portion of the scale. Electron diffraction of the oxide particle in the scale close to the alloy/scale interface indicated a rhombohedral crystal with unit-cell dimension of a=11.28 Å and c=36.44 Å.
A. EDX analysis showed that the particle contained Sr and Cr with the ratio of \( \text{Sr}/\text{Cr} = 3.165/2 \).

ACKNOWLEDGEMENTS

We are pleased to acknowledge the TEM work of Mr. Eiji Okunishi of KOKAN KEISOKU Corp. A part of this work was performed as a R&D program of NEDO under the Moonlight project of Agency of Industrial Science and Technology, MITI.

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Fig. 1 Experimental setup for electrical conductivity measurement of coated and non-coated alloys.

Fig. 2 Electrical resistance change of Ni-20Cr alloy during oxidation at 1273K in air.
Fig. 3 Cross-sectional SEM image (A) and EDX element-mapping (B, C) of the Ni-20Cr alloy coated with LaSrCoO$_3$ after oxidation at 1273K for 1500h.

Fig. 4 XRD profile for the outer surface of the scale adjacent to the coating layer.
Fig. 5 TEM image (A), electron diffraction pattern (B) and corresponding EDX spectra for the particle in the scale formed on the Ni-20Cr alloy.