MICROSTRUCTURE AND PROPERTIES OF LANTHANUM CHROMITE FILMS PREPARED BY THERMAL SPRAY - SINTERING PROCESS

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ABSTRACT

The thermal spray - sintering process (TSS process) was developed and adopted to prepare lanthanum chromite films. A stoichiometric, single phase and gastight lanthanum chromite film has been prepared by the process. The electrical conductivity at 1000 °C in air and the thermal expansion coefficient of the film were 28.2 S/cm and 10.0 x 10⁻⁶/°C, respectively. Both of these are values suitable for the interconnector of SOFCs. The shrinkage of the film prepared by the TSS process during sintering is so small that the lanthanum chromite interconnector film can be easily formed on the sintered substrate.

INTRODUCTION

Interconnectors are indispensable for stacking SOFCs. Interconnectors, which are generally made of lanthanum chromite ceramic films, are prepared on the electrode material such as lanthanum manganite. For fabricating the interconnector film, many processes such as the thermal spraying, the co-firing, and the vapor deposition have been widely investigated.¹⁻³

Thermal spraying: the process consists of melting lanthanum chromite powder in a plasma and spraying on the sintered electrode substrate. This process has the advantages of easy masking for patterning and the low cost of preparing film. The film shows quite poor gastightness, and low electrical conductivity because of many cracks and chemical heterogeneity.

Co-firing: the process consists of preparing a two-layered green body consisting of a lanthanum chromite layer and an electrode material layer, and sintering them together. This process has the possibility of preparing the film at low cost. But the chemical composition of the interconnector is limited to that which can be densified under normal sintering conditions. Additionally cracks, warp and separation are often observed because the shrinkage of the lanthanum chromite layer is usually larger than that of the electrode material layer.
Vapour deposition: the process consists of depositing lanthanum chromite from chloride vapor on the sintered electrode substrate. This process has the advantage of preparing a pore-free film. But the process limits the chemical composition, and with the limited composition, the thermal expansion of interconnector is different from that of the air electrode substrate. Consequently cracks, warp and separation often occur. Additionally the electrical conductivity is rather low. Moreover, it has the disadvantages of difficult masking for patterning and the high cost of preparing the film.

We have developed a new process, the thermal spray-sintering process (TSS process), combining the thermal spraying and the co-firing to overcome some of above mentioned disadvantages. Through this process the interconnectors of wide chemical composition can be produced at low cost. This paper describes the characteristics both of the TSS process and the prepared films.

EXPERIMENTAL PROCEDURE

Powder preparation

La₂O₃, CaCO₃, and Cr₂O₃ powders were respectively weighed at the compositions shown in Table I. These powders were mixed and fired at 1300°C for 5h in air, and then lanthanum chromite powders were synthesized.

Table I Chemical Composition of Lanthanum Chromite Powders

| Powder | Chemical composition          |
|--------|-------------------------------|
| LC-1   | (La₀.₈Ca₀.₂)Cr₀.₉₅O₃-d      |
| LC-2   | (La₀.₈Ca₀.₂)Cr₀.₁₀₀₃-d      |
| LC-3   | (La₀.₈Ca₀.₂)Cr₀.₁₅₀₃-d      |
| LC-4   | (La₀.₈Ca₀.₂)Cr₁.₀₅₀₃-d      |
| LC-5   | (La₀.₈Ca₀.₂)Cr₁.₁₅₀₃-d      |

Thermal spraying(TS process)

The lanthanum chromite powders, LC - 3, - 4, and - 5 shown in Table I, were thermally sprayed on YSZ plates to form films, TS - 1, - 2, and - 3, respectively. The films were removed from the YSZ plates and were machined into 4mm × 20mm × 0.6mm plates. The chemical composition was measured by the inductively coupled plasma spectrometry (ICP), the microstructure was observed with the scanning electron microscope (SEM), the crystalline phase was identified by X-ray diffraction (XRD), and the electrical conductivity was measured by the direct current 4-probe method in air.
Thermal spray-sintering (TSS process)

TSS-1, -2, and -3 were prepared by sintering TS-1, -2, and -3, respectively. They were sintered at 1000, 1200, 1300, 1400, and 1500°C for 10 min and at 1500°C for 5 h in air. These samples were evaluated by the chemical composition, the shrinkage during sintering, the relative density, the microstructure, the crystalline phase, the thermal expansion, and the electrical conductivity in air.

Moreover, lanthanum chromite powders, LC-3, -4, and -5, were sprayed on the porous air electrode substrates made of lanthanum manganite (2 mm thick). The thickness of the sprayed film was about 150 μm. The two-layered samples were sintered at 1000, 1200, 1300, 1400, and 1500°C for 10 min and at 1500°C for 5 h in air, respectively.

The N₂ gas permeability of the two-layered samples was measured. The effective area was about 70 cm². Furthermore, the total resistance of the two-layered sample made of TSS-2 which was sintered at 1500°C for 5 h was measured at 1000°C in air on the air electrode side and in wet H₂ on the interconnector side with Pt and Ni current collectors, respectively.

Normal sintering (NS process)

To evaluate the interconnectors prepared by the co-firing, the interconnectors prepared by the normal sintering process were examined. The NS process as well as the co-firing process is a method consisting of packing the powder and sintering the compact. Therefore, the NS process can be substituted for the co-firing process to evaluate it.

The lanthanum chromite powders, LC-1, -2, and -3 shown in Table I, were molded and sintered to obtain NS-1, -2, and -3. The molded bodies were sintered at 1000, 1200, 1300, 1400, and 1500°C for 10 min and at 1500°C for 5 h in air, respectively. The sintered bodies were machined into 4 mm × 40 mm × 3 mm rods. These samples were evaluated by the chemical composition, the shrinkage during sintering, the relative density, the microstructure, the crystalline phase, the thermal expansion, and the electrical conductivity.

RESULTS AND DISCUSSION

Chemical composition

The chemical compositions of the prepared samples are shown in Table II. These lanthanum chromite samples, which are chromium deficient (x=0.95), stoichiometric (x=1.00), and chromium rich (x=1.03 ~ 1.07), were obtained through each process. (x is a symbol in (La, Ca)Cr₉O₃₋₄). Cr content of lanthanum chromite did not vary during sintering within the accuracy of the chemical analysis of x (±0.02), while it decreased during thermal spraying. The decrease in Cr content of lanthanum chromite is due to the vaporization of Cr component during thermal spraying. However, the decrease in Cr content could be controlled by the thermal spraying conditions, and the lanthanum chromite films with constant composition were produced.
Table II Chemical Composition of Lanthanum Chromite Samples

| Sample | Powder | Sintering condition | Chemical composition          |
|--------|--------|---------------------|--------------------------------|
| TS-1   | LC-3   | No sintering        | (La0.81Ca0.19)Cr0.95O3-δ      |
| TS-2   | LC-4   | 1500°C × 5 hrs      | (La0.81Ca0.19)Cr1.06O3-δ      |
| TS-3   | LC-5   |                     | (La0.81Ca0.19)Cr1.06O3-δ      |
| TSS-1  | LC-3   |                     | (La0.81Ca0.19)Cr3.95O3-δ      |
| TSS-2  | LC-4   |                     | (La0.81Ca0.19)Cr1.06O3-δ      |
| TSS-3  | LC-5   |                     | (La0.81Ca0.19)Cr1.06O3-δ      |
| NS-1   | LC-1   |                     | (La0.80Ca0.20)Cr1.06O3-δ      |
| NS-2   | LC-2   |                     | (La0.80Ca0.20)Cr1.06O3-δ      |
| NS-3   | LC-3   |                     | (La0.80Ca0.20)Cr1.06O3-δ      |

Shrinkage and relative density

Figs. 1 and 2 show the shrinkage and the relative density as a function of sintering temperature, respectively. As shown in Fig. 2, NS-2 and -3 were not densified but NS-1 was densified. NS-1 was almost fully densified by sintering at 1500°C for 5h with a shrinkage of 15%, while with a shrinkage of less than 1%, TSS-1 and -2 were almost fully densified by sintering at 1400°C. Since the TSS process shows very small shrinkage, the interconnector can be formed on the sintered substrate with little mismatch of shrinkage. Therefore, the interconnector film on the air electrode can be obtained without cracks, warp, or separation.

The chemical composition of TSS-2, x=1.00, was the same as that of NS-2. Almost fully densified films of the chemical composition of (La,Ca)Cr1.06O3-δ were obtained by the TSS process, but not by the NS process.

Microstructure

Fig. 3 shows the polished surface of the samples. TS-2 had many cracks and showed a laminar structure corresponding to chemical heterogeneity. The black portions are pores or cracks and the white and gray portions are lanthanum chromite material, where the white portion contains more La ions than the gray portion. Cracks in TS-1, -2, and -3 were transformed into isolated spheres by sintering, which resulted in a dense microstructure. Furthermore, the chemical heterogeneity was healed.

The black portions of TSS-1 and NS-1 are not only pores formed during sintering but also voids formed by removal of CaO during polishing. The CaO phase was observed on the fracture surface. Because the chemical composition of TSS-1 and NS-1 is x=0.95, excess CaO should precipitate. On the other hand, the Cr2O3 phase was observed on the fracture surface of TSS-3 which had a Cr rich chemical composition.
Crystalline phase

The crystalline phases in the samples are shown in Table III. The XRD patterns of TS-1, -2, and -3 samples were broad, while TSS-1, -2, and -3 samples showed sharp XRD patterns. This may be due to the improvement of chemical heterogeneity.

The CaO phase in NS-1, and the Cr2O3 phase in NS-3 were detected by XRD. As described above, TSS-1 and -3 samples also contained the CaO phase and the Cr2O3 phase, respectively. Therefore, the chemical compositions of x=0.95 and x=1.05 may be out of the solid solution range of the lanthanum chromite phase. Since CaO precipitation often makes the stability of lanthanum chromite poor under SOFC operating conditions, the chemical composition of x=1.00 is preferable. Dense lanthanum chromite films having this chemical composition can be obtained by the TSS process.

Table III Crystalline Phase

| Sample | Sintering condition | Crystalline phase          |
|--------|---------------------|---------------------------|
| TS-1   | No sintering        | perovskite (broad)        |
| TS-2   | ↑                   | perovskite (broad)        |
| TS-3   | ↑                   | perovskite (broad)        |
| TSS-1  | 1500°C×5 hrs        | perovskite, (CaO)         |
| TSS-2  | ↑                   | perovskite                |
| TSS-3  | ↑                   | perovskite, (Cr2O3)       |
| NS-1   | ↑                   | perovskite, CaO           |
| NS-2   | ↑                   | perovskite                |
| NS-3   | ↑                   | perovskite, Cr2O3         |

N2 gas permeability

Fig. 4 shows the N2 gas permeability of the two-layered samples consisting of the sintered air electrode substrate and the interconnector film prepared by the TSS process. TS-1, -2, and -3 showed a N2 gas permeability near 2×10⁻⁶ cm²g⁻¹sec⁻¹, which was decreased significantly by sintering. TSS-1 and -2 sintered at 1500°C for 5h showed very low N2 gas permeability, 1×10⁻⁸ and 5×10⁻⁸ cm²g⁻¹sec⁻¹, respectively. These values satisfy the gastightness which is required for SOFCs' interconnectors. TSS-3 showed a higher N2 gas permeability. As shown in Fig. 3 it included channel pores, which may cause higher gas permeation.

Based on the relative density measurement, sintering at 1400°C was sufficient to densify, but sintering at 1500°C for 5h was necessary for the decrease in N2 gas permeability.

Thermal expansion

Thermal expansion coefficients of the samples measured from 40°C to 1000°C in air are shown in Table IV. All samples had thermal expansion...
coefficients from $9.7 \sim 10.0 \times 10^{-6}/\degree C$. These values are similar to those of YSZ, $10.2 \sim 10.5 \times 10^{-6}/\degree C$. TSS-1, -2, and -3 should therefore be candidates for SOFCs' interconnectors.

### Table IV Thermal Expansion Coefficients

| Sample | Sintering condition | Thermal expansion coefficient ($\times 10^{-6}/\degree C$) |
|--------|---------------------|---------------------------------------------------------|
| TSS-1  | $1500^\circ C \times 5$ hrs | 9.7                                                      |
| TSS-2  | $10.0$                                                               |
| TSS-3  | $10.8$                                                               |
| NS-1   | $9.9$                                                               |
| NS-2   | $9.9$                                                               |
| NS-3   | $9.7$                                                               |

Electrical conductivity

The electrical conductivities of the samples at R.T. and 1000°C in air are shown in Table V. TSS-1, -2, and -3 showed higher conductivities than TS-1, -2, and -3, which should be due to the elimination of cracks and chemical heterogeneity by sintering.

The electrical conductivity at R.T. increased nearly 10 times by sintering, while those at 1000°C increased only 20 to 50%. This is because the microstructure improved even during measurement at 1000°C. The electrical conductivities of the samples were as high as that presented by Sakai et al. and sufficient for the interconnectors of SOFCs.

### Table V Electrical Conductivities

| Sample | Sintering condition | Electrical conductivity ($Scm^{-1}$) |
|--------|---------------------|-------------------------------------|
|        |                     | R.T.  | 1000°C                      |
| TS-1   | No sintering        | 0.4   | 30.6                         |
| TS-2   | $19.3$              |      |                              |
| TS-3   | $28.8$              |      |                              |
| TSS-1  | $1500^\circ C \times 5$ hrs | 5.3   | 42.4                         |
| TSS-2  | $28.2$              |      |                              |
| TSS-3  | $34.2$              |      |                              |
| NS-1   | $31.2$              |      |                              |

The electrical resistance of the two-layered sample under SOFC operating conditions at 1000°C is shown in Table VI. The resistance was quite low, which consisted of the resistance of interconnector, air electrode, current collectors and their interfaces. The interface between two layers showed low resistance and no second phase was observed.
Table VI Electrical Resistance of the Two-layered Sample

| Sample            | Sintering condition | Electrical resistance (Ωcm²) |
|-------------------|---------------------|-----------------------------|
| TSS-2 on the Air Electrode | 1500°C x 5 hrs | 4.1 x 10⁻³ |

CONCLUSIONS

Interconnectors prepared by the thermal spray-sintering process (TSS process) have been investigated. Compared with other processes, the TSS process shows the following advantages.

1. Comparison with the thermal spraying process:
   1. High gastightness.
   2. High conductivity due to the fine microstructure without cracks and chemical heterogeneity.

2. Comparison with the co-firing process:
   1. Small shrinkage (less than 1%) of the interconnector film during sintering, which prevents cracks, warp and separation of the cell caused by the mismatch with that of the substrate.
   2. Availability of stoichiometric lanthanum chromite dense films without other phases which have high stability.

3. Comparison with the vapor deposition process:
   1. Easy masking for patterning.
   2. Easy doping with additional elements to match the thermal expansion with other cell components, and to increase the electrical conductivity.

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Fig. 1. The shrinkage during sintering

Fig. 2. The relative density after sintering
Fig. 3. Microstructures of the films prepared by TS, TSS, and NS process.
Fig. 4. $N_2$ gas permeability

$N_2$ gas permeability (cm$^2$/g·sec)

Sintering Temperature (°C)

- TSS-1
- TSS-2
- TSS-3

Fig. 4. $N_2$ gas permeability