La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O protective coatings for solid oxide fuel cell interconnect deposited by screen printing
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Abstract
La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3} (LSCF) is synthesized by a screen printing method as a Crofer22 APU interconnect for solid oxide fuel cells (SOFC). The above (LSCF) coated alloys were first checked for their compositions, morphology and interface conditions. It was then treated in a simulated oxidizing environment, 800°C for 200hrs. The results showed that the LSCF film can change the oxidation behavior of Crofer22 APU. The alloy coated with LSCF sintering at 1100ºC in N\textsubscript{2} atmosphere, the adhesion between the LSCF layer/alloy interface is excellent. After long-term electric resistance measurement, ASR for alloy coated with LSCF was less. The alloy coated with LSCF use for metallic interconnect could reduce working temperature for SOFC.

Keywords: solid oxide fuel cell (SOFC); Interconnect; Screen Printing

1. Introduction
Interconnect is a critical component in solid oxide fuel cell (SOFC) as it functions to bridge structurally and electrically a number of sequentially stacked unit cells. Any favorable candidate alloy for interconnect should be oxidation resistant in order to preserve or even improve the electrical conductive ability of the alloy. The oxide scale formed on the surface of the alloys after exposure in the SOFC environment results in high electrical resistance and causes degradation of stack performance [1-3]. Alloys of high temperature oxidation resistance used as interconnect in SOFC generally contain chromium as an alloying element to form a protective chromium oxide scale (Cr\textsubscript{2}O\textsubscript{3}). At high temperatures volatile Cr species such as CrO\textsubscript{3} and Cr(OH)\textsubscript{2}O\textsubscript{2} are generated over the oxide scale in oxidizing atmospheres [4, 5]. This substance will poison the interface between cathode and electrolyte. Thus, the performance of SOFC will decline rapidly. For this reason, it needs to coat a protective layer on SOFC interconnect in order to increase the anti-oxidative ability of stainless steel. Thereby it will extend the life-time of SOFC. Surface modifications, like protective coatings, are inevitably required to promote oxidation resistance and depress Cr vaporization in the long run. La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3} (LSCF) is probably one of the most common materials
used as cathodes for $O_2$ reduction reactions in SOFC. LSCF is a good electronic conductor, has high stability with electrolyte and high electrochemical activity for the $O_2$ reduction at high temperatures [6]. In this work, the major concerns regarding these metallic interconnect are to investigate protective ceramic layer coating technology with stable electric conductivity by screen printing process. The Crofer22 APU was selected as metallic material and alloy was coated with LSCF film, followed by oxidizing at 800 °C for 200hr in hot air environment. Their compositions, morphology and interface conditions are then checked and analyzed to determine whether the oxidation behavior of their base alloy, Crofer22 APU, is changed in the presence of LSCF coating. Electrical resistance will be measured at elevated temperature to determine how effective the LSM film is when coated on the presently best available metallic interconnect materials.

2. Experimental

One types of metallic material, Crofer22 APU is used as the base of coating of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ (LSCF). Their compositions as determined by induction coupled plasma (ICP)-AES and Spark-OES instruments are listed in Table 1. The alloy was cut in pieces with 2 mm and area of $10 \times 10 \ mm^2$. The surface were ground by using 1200-grit SiC paper and cleaned in acetone. The preparation of LSCF paste for coating film by applying screen printing starts with mixing four kinds of high purity (99.9%) oxide powder, $La_2O_3$, SrCO$_3$, Fe$_2$O$_3$ and Co$_3$O$_4$ at a specific ratio. The LSCF paste was made by mixing the calcined powder, organic substances of polyvinyl butyral as binder, dibutyl phthalate as plasticizer, Triton-X as homogenizer and 2-propanol as solvent. The alloy was coated in the LSCF paste and sintered at 1000 °C for 50 minute in 90%Ar +10% N2 atmospheric environment.

3. Results and discussion

Oxidized surface microstructure analysis by SEM and XRD

X-ray diffraction (XRD) patterns of LSCF powders are given in Fig. 2. XRD patterns belong to the perovskite structure, which indicates the formation of a single perovskite phase of the LSCF powders. Fig. 2 (a) shows XRD patterns of the powder can be ascribed by a perovskite structure after heating at 1100 °C for 50 minute in hot air. The XRD patterns show that a crystalline structure has been achieved. Fig. 2 (b) shows the samples oxidized at 800°C for 200hr. From the observation of Fig. 11, it was clear that the oxides were composed of CoFe$_2$O$_4$ spinel in the sample. From this, it was found that reactive element coating could make the $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ change from loose to compact phase structures. So that, subsequently, the
high-temperature oxidation resistance of coating on samples would be greatly improved. Fig. 3 shows the SEM micrographs of surface of Crofer22 APU/LSCF after annealing at 800°C for 200 hour. The nano-sized particles between 200 and 500nm were observed on the surface of the LSCF structure. The smaller LSCF particle size is probably due to its low coarsening and sintering temperatures (1000°C for 50 minute). With oxidation time increase, the LSCF was gradually raised, some fine particles were filled, forming a continuous and porous Crofer22 APU/LSCF network.

Microstructural analysis and discussion of the results

Fig. 3 shows BEI (backscatter electron image) and EPMA (electron probe micro analysis) of Crofer22 APU/LSCF by screen printing. Small particles were not bonded and numerous small pores can be found in this type of coating layer. But densification characteristics of the coating materials directly determine the density of the coating layers, and thus the effectiveness of the chromium vaporization barrier. The EPMA analysis conjectured that the dense layer contains Cr2O3 or CoFe2O4 spinel phase that is comprised of Fe, Cr, La, Sr, Co and O. The innermost layer is in the Fe-Cr matrix phase. The continuous CoFe2O4 spinel layer on the surface of Crofer22 APU leads to a significant reduction of the chromium vaporization. This means that the sintering condition after LSCF coating is important in obtaining a stable coating layer and an interfacial oxide layer.

Electronic resistance

Fig. 4 shows the ASR parameter of oxidized Crofer22 APU at 800°C for 180hr by screen-printing method. The slope in Fig. 4 is somewhat reduced after around 180 hours of the LSCF-coating oxidation by screen-printing, demonstrating a two-stage oxidation characteristic with two slopes in the ASR curve. The first stage (0 ~ 40 hours) is estimated for 0.01375Ω.cm², followed by the second stage (40 ~ 180 hours) with a rate constant of 0.01395Ω.cm². Accordingly, the change in the area-specific electrical resistance as a function of oxidation time can be attributed to an increase in the oxide scale thickness. It is inferred from the above-mentioned preliminary results that the LSCF thin film that is coated on the Crofer22 APU can indeed slow down the high temperature oxidation of metal. This should have something to do with steady production of CoFe2O4 spinels.

4. Summary

Thick film La0.6Sr0.4Co0.8Fe0.2O3 was deposited using screen printing on Crofer22 APU as a protective coating for this candidate SOFC interconnect material. The screen printing coatings improved the oxidation resistance and scale adhesion of the alloy substrate after oxidation in air at 800 °C, and the coated samples show much
lower electrical resistance. So, the preliminary results suggest that the LSCF layer composite coating on interconnect is a good choice for improving the performance of SOFC.

References


Fig. 1. XRD pattern of a LSCF film deposited on substrate. (a) sintering at 900°C for 1.5 hr. (b) oxidized surface as processed at 800°C for 200 hours.
Fig. 2. Micrographs of the oxidized (in 800 °C hot air) surfaces of LSCF/Crofer22 APU displaying small granular portions.

Fig. 3. Micrographs of oxide scale/alloy interface of LSCF-coated Crofer22 APU and; corresponding EPMA indicates that compounds are of Cr, O, Fe, La, Sr and Co at 800°C for 200 hours by screen painting.

Fig. 4. Area-specific resistance of LSCF-coated alloys as a function of holding time 800 °C for 180 hours in hot air.