Journal of the Korean Ceramic Society
Vol. 45, No. 12, pp. 777~781, 2008.

Research on Performance of LSM Coating on Interconnect Materials for SOFCs

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(Received October 15, 2008; Revised November 30, 2008; Accepted December 2, 2008)

ABSTRACT

Experiments were conducted using SUS430 and Crofer 22 APU steels coated by LSM using plasma spray and slurry spray methods, respectively. High-temperature conductivity and oxidation resistance were investigated. For comparison, SUS430 and Crofer 22 APU without LSM coating were also investigated and coefficient of thermal expansion (CTE) was measured. The results show that the materials without LSM coating exhibit almost the same CTE as YSZ electrolyte in a range of temperatures of 550~850°C. When coated with LSM, the oxidation rate of the steels decreases by 30~40% using slurry spray and by 10~30% using plasma spray whereas the steels using plasma spray have a better high-temperature conductivity than the steels using slurry spray. It is thus concluded that the LSM coating has a limited effect on increasing high-temperature conductivity while it can effectively reduce the oxidation of the steels.

Key words : ***Solid oxide fuel cell, Interconnect, LSM coating, Oxidation, Conductivity***

1. Introduction

Solid oxide fuel cell (SOFC) is an electrochemical power source that directly converts the energy of a chemical reaction into electrical energy with high efficiencies.[1] In practical applications, multiple cells are stacked in series in order to accumulate voltage output. Accordingly, interconnect should be required for connecting the cells. The function of interconnect is two-folded: On one hand, it can provide electrical connection between anodes and cathodes. On the other hand, it acts as a barrier separating air or oxygen (cathode side) from fuel (anode side).[2] Therefore the interconnect materials must be[3] gas tight, highly conductive, and stable in both reducing and oxidizing atmospheres at SOFC operating temperatures, and close match in coefficient of thermal expansion (CTE) with other SOFC components.

Recently significant progress has been made to reduce the operating temperature of SOFC to a range of 600-800 ºC. The reduction in SOFC operating temperature makes it possible to consider metallic alloys with oxidation/corrosion resistance as interconnect materials.[4,5] Increasing attention has been obtained on metallic alloys as the replacement for the ceramic materials in recent years due to their intrinsic advantages such as low cost, good mechanical properties, high thermal conductivity and easy manufacturing process to a large area.[6] Most of previous investigations were focused on Fe-based ferritic alloys[4,11,12] because of their CTE match with other SOFC components.

Alloys that have been exposed to air at operating temperature may lead to drastic change in performance of the stack within its expected service lifetime and formation of volatile Cr (VI) species due to the Cr_2O_3 evaporation. The volatile Cr species may migrate to and thus poison the cathode resulting in the degradation of stack performance over long-term operation.[7,8] The modification of oxide scale can be achieved by addition of rare earth elements such as La, Sr, etc or by the dense ceramic coating layer having high electric conductivity and oxidation resistance.

In this work, the properties of metallic interconnects are investigated using SUS430 steel and Crofer 22 APU with $(La_{0.75}Sr_{0.25})_{0.95}MnO_3$ (LSM) coatings by plasma spraying and slurry spraying, respectively.[9,10]

2. Experimental

Two commercial ferritic stainless-steel of SUS430 and Crofer 22 APU were used for investigation. Rod-shaped samples were prepared with 3 mm in radius and 30 mm in length. The samples were put into the PCY-III apparatus for CTE testing at a rate of 5°C/min in the air atmosphere.

Disks with an area of 10×10 mm^2 and ~3 mm of thickness were cut from the two as-received materials. All the surfaces were grounded using 600-grit SiC paper and cleaned in acetone to remove the oil. Finally, the samples were put into the alcohol to clean the surface and then dried for oxidation test. For isothermal oxidation, the samples were hung in alumina crucibles in a furnace, oxidized at 850°C in air for 96 h. The weight of each sample was measured immediately after furnace cooled to room temperature.

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Table 1. The Plasma Spray Parameters

Current/A	Voltage/V	Ar flow rate/(L/H)	Powder feed rate/(L/H)
600	55	1500	600

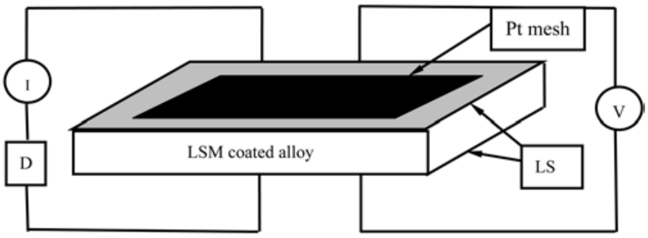

Fig. 1. Schematic illustration of area specific resistance measurements for LSM-coated alloy.

The LSM coating was deposited onto the steels of SUS430 and Crofer 22 APU by plasma spray and slurry spray methods, respectively, in order to enhance the high temperature conductivity and reduce the oxidation. LSM was prepared by solid-state powder reaction process and calcined at 1000°C for 4 h. The compositions of the resultant were confirmed by X-ray diffractometer (XRD). The LSM slurry was made by mixing the calcined powder, organic substances of alcohol as solvent, Polyvinyl Pyrrolidone as dispersant. The alloys were dip-coated in the LSM slurry and sintered at 1200°C for 2 h in N_2 with a heating and cooling rate of 10°C/min. The plasma spray parameters are listed in Table 1.

Area-specific resistance (ASR) of the LSM-coated Fe-Cr alloys was measured as a function of holding time and temperature in air by using a two-point, four-wire probe approach as shown in Fig. 1.[13] Long-term stability of ASR in LSM-coated SUS 430 was examined at 850°C in air. In order to measure the resistance of the specimen, Pt mesh was attached to the sample of coated alloys with small amount of Pt paste. A current of 1 A was passed through Pt probes and the voltage in the sample was measured using a source meter. To ensure adequate contact between the sample and the Pt mesh, constant load was applied. The phase stability and microstructures of the coated and sintered LSM layer were observed using XRD and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS).

3. Results and Discussion

3.1. CTE testing

Coefficient of thermal expansion (CTE) determines if SUS430 and Crofer 22 APU can be applied in anode-supported solid oxide fuel cell stacks or not.[14] Two commercial ferritic stainless of SUS430 and Crofer 22 APU were used as metallic materials because their CTEs match well with other SOFC components. As shown in Fig. 2, the CTE of SUS430 is 12.7×10^{-6} K^{-1} from 400°C to 850°C. The CTE of Crofer 22 APU is 12.5×10^{-6} K^{-1} at the temperature of 400°C, and then the CTE decreases with increasing temperature.

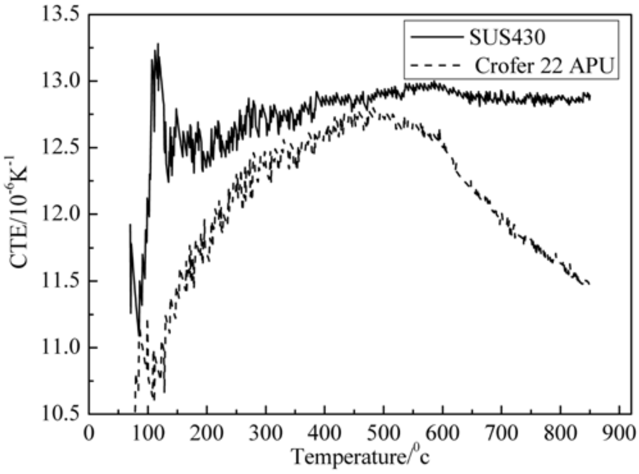

Fig. 2. Coefficients of thermal expansion of Crofer 22 APU and SUS430.

When the temperature reaches 850°C, the CTE of SUS430 is down to 11.5×10^{-6} K^{-1}.Though there is a small change in CTE with temperature, the CTE values of both alloys match well with the SOFC components.

3.2. Oxidation testing

For isothermal oxidation, the unprocessed samples and samples coated with LSM were put in alumina crucibles in a furnace, oxidized at 850°C in air up to 96 h. The weight of each sample was measured immediately after furnace cooling to room temperature and the results are shown in Figs. 3 and 4 for SUS430 and Crofer 22 APU, respectively. The oxidation rate of the interconnect with LSM coating decreases by 30~40% when holding at 850°C for 24 h. It is apparent that LSM coating significantly increases the anti-oxidation ability of the steels. The samples with LSM coating by plamsa spray have less weight gain than that by slurry after 48 h at 850°C.

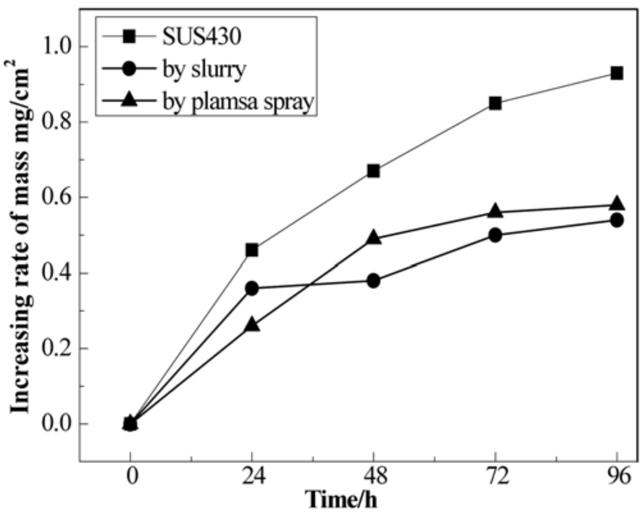

Fig. 3. The mass change of SUS430 with and without LSM coatings at 850°C.

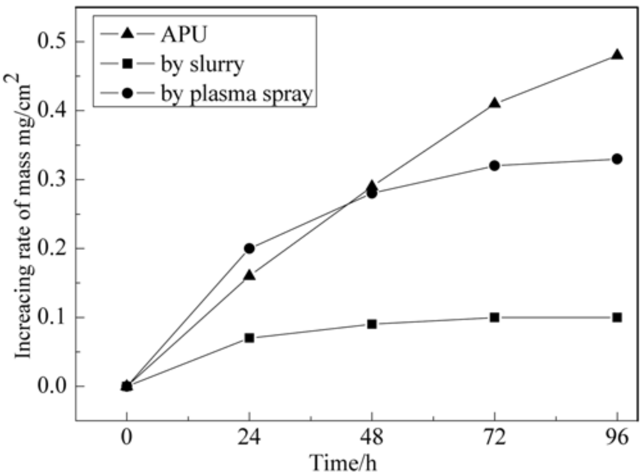

Fig. 4. The mass change of Crofer 22 APU with and without LSM coatings at 850°C.

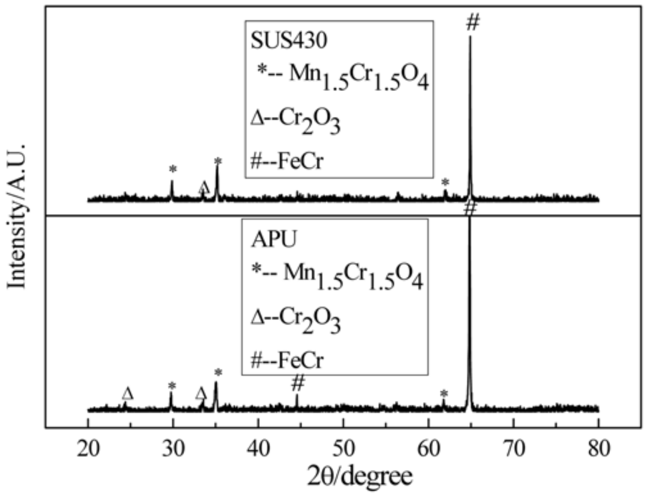

Fig. 5. XRD patterns for SUS430 and Crofer 22 APU after holding at 850°C for 48 h in air.

The phase structures of the oxide scales formed on the alloys were identified using XRD and the results are shown in Fig. 5. The oxides formed in air at 850°C were Cr_2O_3 and $Mn_{1.5}Cr_{1.5}O_4$ spinel, and a large amount of Cr_2O_3 in the oxide scales was observed in Cofer 22 APU by X-ray fluorescence. Table 2 shows the chemical compositions of two steels subjected to oxidation test. It can be seen that the Cr_2O_3 and $Mn_{1.5}Cr_{1.5}O_4$ layer can increase the anti-oxidation ability and enhance the pyro-conductivity.[15,16)]

Table 2. Chemical Compositions of SUS430 Alloy and Crofer 22 APU Alloy

Specification	Fe_2O_3	Cr_2O_3	MnO	SiO_2	TiO_2	Al_2O_3
SUS430	82.4	15.0	0.507	1.56	---	0.108
Crofer 22 APU	68.9	28.5	1.90	0.210	0.223	0.181

The surface morphologies of the oxidized samples were observed using SEM as shown in Fig. 6. Little difference was shown between SUS430 and Cofer 22 APU. Fig. 7 shows the surface morphologies for the alloys with LSM coating by slurry and by plamsa spray. It can be seen that the LSM coating by plamsa spray is more compact than that by slurry spray and thus the LSM coating by plamsa spray is more effective to prevent the oxidation of steels. Figure 8 shows XRD patterns for LSM coating using two different procedures. The LSM coating by slurry and by plamsa spray exhibit the same phases as LSM powder.

3.3. Area specific resistance

Fig. 9 and Fig. 10 show the ASRs of the steels with LSM coating as a function of holding time at 850°C. With the increasing holding time, ASRs of the steels tend to increase. Since the LSM coating by plasma spray is more compact than the LSM coating by slurry spray, the ASRs in Fig. 10 are significantly lower.

4. Conclusions

1) The CTEs of SUS430 and Crofer 22 APU are 12×10^{-6} K^{-1} at the temperature of operation. The CTE values are close to the anode-supported SOFC components.

2) The oxide scale formed on the two steels consists of Cr_2O_3 and $Mn_{1.5}Cr_{1.5}O_4$ spinel. For long-term oxidation test,

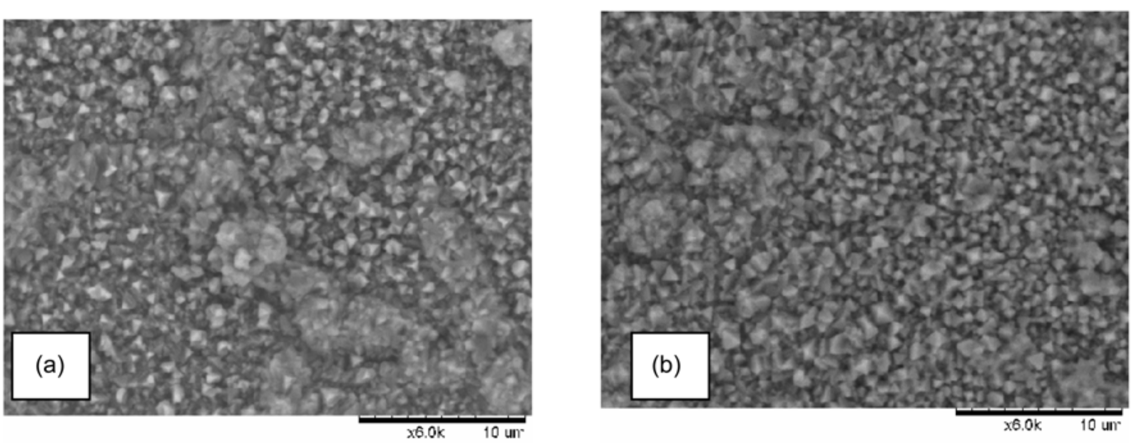

Fig. 6. SEM photographs of the interfaces for (a) SUS430 and (b) Crofer 22 APU after holding at 850°C for 48 h in air.

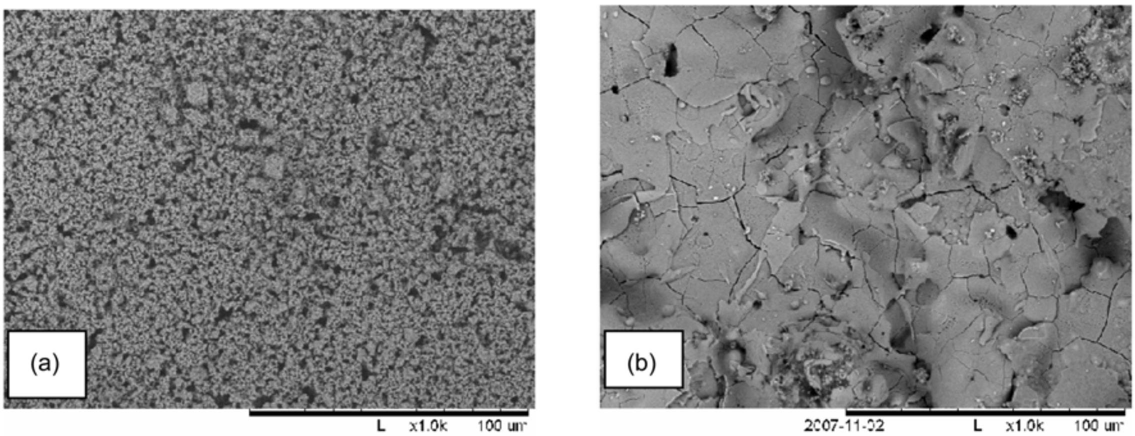

Fig. 7. SEM photographs of the surfaces of SUS430 and Crofer 22 APU with LSM coating LSM coating by slurry spray b) LSM coating by plasma spray.

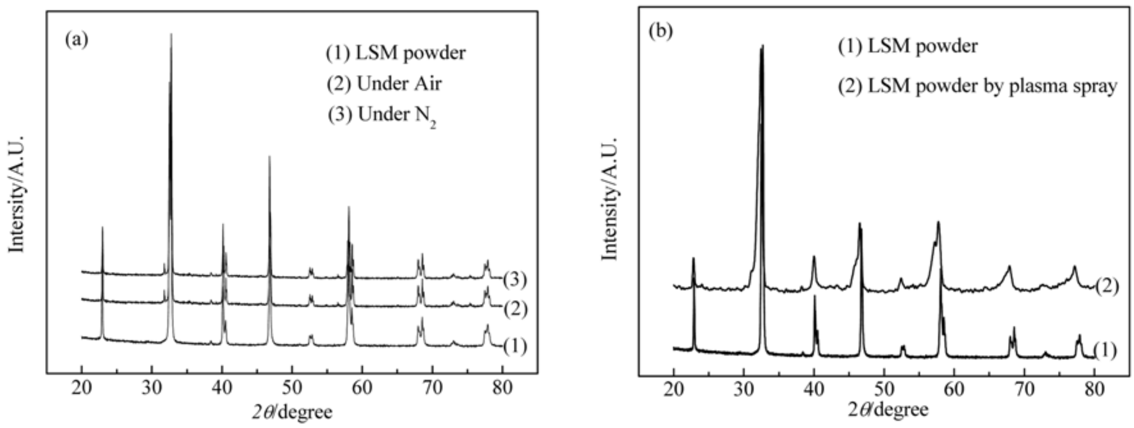

Fig. 8. XRD patterns of LSM power and the LSM coating a) LSM coating by slurry spray b) LSM coating by plasma spray.

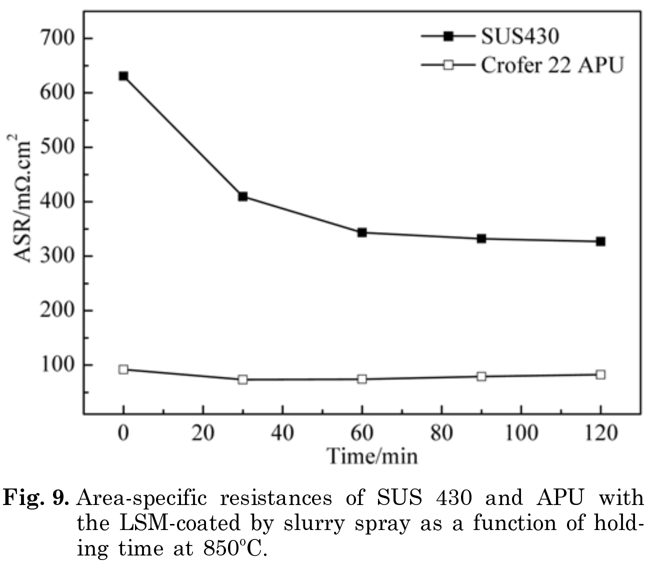

Fig. 9. Area-specific resistances of SUS 430 and APU with the LSM-coated by slurry spray as a function of holding time at 850°C.

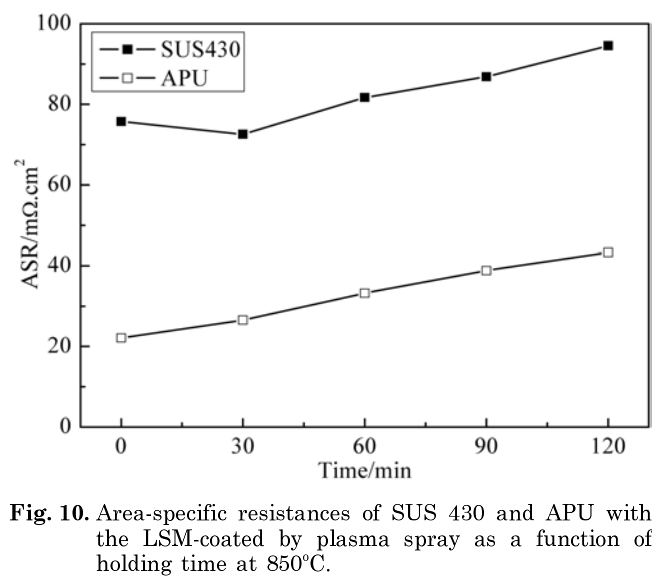

Fig. 10. Area-specific resistances of SUS 430 and APU with the LSM-coated by plasma spray as a function of holding time at 850°C.

the oxidation rate of the steels with LSM coating is lower than that of steels without coating.

3) Comparing the ASRs of the LSM-coated steels, the ASR of the LSM-coated steels by plasma spray is more suitable for the interconnect of SOFC stacks.

Acknowledgment

This work was financial supported by the National High-Tech Research and Development Program of China (863 Program, Grant No. 2007AA05Z140) and the Chinese Academy of Sciences.

REFERENCES

1. M. Mogensen and K. Kammer, *Annu. Rev. Mater. Res.*, 33 321-31 (2003).
2. S.J. Geng, J.H. Zhu, and Z.G. Lu, *Solid State Ionics*, **177** 559-68 (2006).
3. Xiaoxia GUO, Wenjun ZHENG, and Guangyao MENG, *Journal of Function Materials*, **31** [1] 23-5 (2000).
4. S.J. Geng and J.H. Zhu, *Journal of Power Sources*, **160** 1009-16 (2006).
5. Chang-jing FU, Nai-qing ZHANG, Ke-ning SUN, and Derui ZHOU, *Journal of Materials Science & Technology*, **13** [2] 123-6 (2005).
6. Zhongli WANG, Minfang HAN, and Xin CHEN, *Journal of World SCI-THEH R&D*, **29** 30-7 (2007).
7. S. Taniguchi, M. Kadowaki, H. Kawamura et al., *Journal of Power Sources*, **55** 73-9 (1995).
8. S. P. S. Badwal, R. Deller, K. Foger et al., *Solid State Ionics*, **99** [3-4] 297-310 (1997).
9. Z.G. Yang, G.G. Xia, G. D. Maupin et al., *Surface & Coatings Technology*, **201** 4476-83 (2006).
10. C.J.Fu, K.N. Sun, N.Q. Zhang et al., *Rare metal Materials and Engineering*, **35** [7] 1117-20 (2006).
11. S.J. Geng, J.H. Zhu, M.P. Brady et al., *Journal of Power Sources*, **172** [2] 775-81 (2007).
12. Xin CHEN, Minfang HAN, and Zhongli WANG, *Journal of Rare Metal Materials and Engineering*, **36** 642-44 (2007).
13. J.H. Kim, R.H. Song, and S.H. Hyun, *Solid State Ionics*, **174** 185-91 (2004).
14. B.C. Church, T.H. Sanders, R.F. Speyer et al., *Mater. Sci. Eng. A*, [452-453] 334-40 (2007).
15. H. Bin, P. Jian, G. Wei, and LI Jian, *Battery Bimonthly*, **36** [5] 387-89 (2006).
16. P. Jian, H. Bin, Y. Jie, and L. Jian, *J. Iron Steel Res.*, **49** [10] 34-9 (2007).