

## Effect of Slurry-Coated LaSrMnO<sub>3</sub> on the Electrical Property of Fe-Cr Alloy for Metallic Interconnect of SOFC

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### 1. Introduction

A common objective of SOFC work is to lower the operating temperature to below 800°C because the commercial materials can be used. The reduction of operating temperature of solid oxide fuel cell allows the use of metallic interconnect instead of the ceramic interconnect of LaCrO<sub>3</sub>-based ceramic material. The metallic interconnect has many advantages of low material cost, good mechanical properties, high thermal conductivity, and easy manufacturing process to large area, etc.

The Fe-based ferritic stainless steel has many advantages of similar thermal expansion coefficients with other cell component, good workability, and low cost. Since the Fe alloy has also the chromia scale with low conductivity, the oxide formation with high electric conductivity is required. The modification of the oxide scale by addition of rare earth elements or the dense ceramic coating with electric conductivity and oxidation resistance is required. A few of researchers reported the effect of the ceramic coating by expensive vacuum plasma spray process but effect of its coating is not clearly in the oxidation behavior and the electric conductivity of the coated metallic interconnect.

In this work, the major concerns regarding these metallic interconnect are to investigate protective ceramic layer coating technology with stable electric conductivity by cheap wet process such as slurry dipping process. Two ferritic Fe-Cr alloy of Fe-16Cr alloy (SUS 430) and Fe-20Cr-5Al alloy (Fecralloy) were selected as metallic materials and this alloys were dip-coated with LaSrMnO<sub>3</sub> slurry, followed by sintering at 1200°C in various atmosphere. The influence of oxide scale on the electric conductivity behavior of the LSM-coated Fe alloy was examined and the experimental results were discussed as related to the elemental distribution of the oxide scale and its electric conductivity.

## 2. Experimental

Two commercial ferritic stainless of Fe-16Cr (composition: 0.10 %C, 16.40 %Cr, 0.24 %Si, 1.09 %Mn, 0.37 %Ni, 81.8 %Fe in weight, SUS 430, POSCO, Korea) and Fecralloy (composition: 0.05 %C, 20.50 %Cr, 0.26 %Si, 0.20 %Mn, 5.77 %Al, 0.26 %Nb, 72.96 %Fe in weight, Changwon Special Steel Co., Korea) were used as metallic materials. These were prepared with thickness of 3mm and area of 10 x 10 mm<sup>2</sup>, and then grinded using 600-grit SiC paper and cleaned in acetone. The LSM slurry was made by mixing the calcined powder, organic binder, some additives, and solvents. The alloys were dip-coated in the LSM slurry and sintered at 1200°C for 2hr in air, Ar gas with 10 vol.% H<sub>2</sub> or N<sub>2</sub> gas with a heating and cooling rate of 100°C/h.

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. Long-term stability of ASR in LSM-coated SUS 430 was examined at 750 °C in air for 2600 hr. For measuring the resistance of the specimen, the coated alloy sample was attached with Pt mesh and small amount of Pt paste. The current in the range of fifty to several hundred mA is flowed through Pt probes and the voltage across the sample is measured by using a multimeter [HP 3457A]. To ensure the adequate contact between sample and Pt mesh, some constant load is applied in the through-thickness direction. Interfacial resistance of the LSM-coated alloys were analyzed by ac impedance technique using a Solartron 1260 frequency response analyzer coupled with a Solartron 1287 electrochemical interface in the range of 0.01 to 105 Hz. Phase stability and microstructure of the coated and sintered LSM layer was analyzed by X-ray diffractometer (RINT 2000, Rigagu Co.) and scanning electron microscopy (Philips model SEM515, USA) equipped with EDS and WDS.

## 3. Results and Discussion

The microstructure and elemental distribution at the interface of LSM-coated SUS 430 sintered at 1200°C for 2 h in Ar gas with 10 vol.% H<sub>2</sub>, which corresponds to oxygen partial pressure of PO<sub>2</sub> = 7 x 10<sup>-6</sup>atm. The LSM layer was coated uniformly on the metal surface and its thickness was found to be about 20µm. The coating layer is relatively dense and strongly bonded to metal substrate. The oxide layer with thickness of 5 µm exists in the interfacial region and the oxide layer is considered to consist of Cr<sub>2</sub>O<sub>3</sub> oxide, small amounts of Cr-Mn complex oxide, and few Si oxide.

Fig.1. shows ASR of the SUS430 coated with LSM layer as a function of holding time at 750 °C in air after sintering at 1200 °C in Ar with 10 vol.% H<sub>2</sub>. Its ASR was 148 mΩcm<sup>2</sup> at initial stage and lowered to 43 mΩcm<sup>2</sup> after 450 hr, and then maintained

almost constant. The ASR of the metal with the protective oxide layer was affected by the conductivity of the coating layer and the interfacial oxide layer. The interfacial oxide layer is known to be formed between the metal and the coating layer during sintering process or cell operation, which is consistent with the results of Fig.1. Thus, the ASR is described as follows;

$$ASR = \rho_m \ell_m + 2 \rho_i \ell_i + 2 \rho_c \ell_c \quad (1)$$

where  $\rho$  and  $\ell$  are resistivity and thickness of subscripts m, i, c (m = metal, i = interfacial oxide layer between metal and coating layer, c = coating layer), respectively. Since the ASR of the metal is negligible in the measured temperature due to its low value, the equation (1) is expressed as the following;

$$ASR = 2 \rho_i \ell_i + 2 \rho_c \ell_c \quad (2)$$

From equation (2), the reason for lowering the ASR as a function of holding time in Fig. 1 is related to the coated LSM layer and the interfacial oxide formation. Therefore, high ASR of the SUS 430 with the coating layer during initial holding time is attributed to unstable phase formation of the LSM coating layer and thus the interfacial oxide layer. However, after holding time of 450 hr, the ASR of the LSM-coated SUS 430 is considered to be due to only interfacial oxide layer because a stable LSM perovskite phase has good electronic conductivity of 150 S/cm that produces a negligible low ASR.

To examine the dissociation condition at the present sintering process, the LSM-coated SUS 430 alloy was sintered at 1200°C for 2hr in lower oxygen partial pressure condition below 10–6 ppm that is Ar atmosphere with 20 vol. % H<sub>2</sub>, followed by ageing for 100 hr in air at room temperature, and the XRD patterns of the resulting LSM coating layer is represented in Fig. 2. The XRD peaks of La(OH)<sub>3</sub> and MnO phases were observed. The La(OH)<sub>3</sub> phase is due to reaction of a dissociated La<sub>2</sub>O<sub>3</sub> with water in air during ageing. Thus the sintering condition of the LSM coating layer is limited to a range of low oxygen partial pressure where the LSM phase is not dissociated and also should suppress a formation and a growth of the oxide scale to lower its electric resistance. Therefore, it is concluded that the sintering condition after LSM slurry coating is of importance to obtain a stable coating layer and an interfacial oxide layer with low resistivity.

Fig.3 shows ASR of the LSM-coated SUS 430 sintered in N<sub>2</sub> and heat-treated in air atmosphere as a function of holding time and of temperature. In contrast with the results of Fig.1, an initial drop of the ASR was not observed, and the ASR kept a constant value of 74mΩcm<sup>2</sup> with increasing holding time in the range of 2600 hr. Although one thermal cycle with cooling and heating rate of 100 °C/hr was applied for the specimen at the holding time of 800hr, there was no variation of ASR. These results are attributed to formation of the stable LSM phase on the surface of SUS 430 after heat-treatment in air, which results in the prevention of growth of the interfacial oxide

layer.

Fig. 4 shows Arrhenius plot of the ASR for two different holding times. The  $\log(\text{ASR}/T)$  vs.  $(1/T)$  plot shows good linear dependence and the activation energies,  $E_a$  for each holding time of 24hr and 1393hr are found to be 0.799 and 0.810 eV, respectively. The difference of the  $E_a$  values for each holding times is small, which means the interfacial oxide layer is stable for a long time without change of the oxide scale. The activation energy is known to result from the contribution of both oxidation ( $E_{ox}$ ) and electrical conduction ( $E_{co}$ ) processes in the oxide layer and is described by  $E_a = -E_{ox}/2 + E_{co}$  on the assumption of parabolic oxidation reaction. Thus the conduction process is considered to dominate the ASR of the LSM-coated SUS430 on the base of positive  $E_a$ .

To examine the contribution of interfacial resistance to the ASR, the impedance of the LSM-coated SUS 430 was measured and the result is represented in Fig.8. The impedance curve of the LSM-coated SUS 430 did not show some circle shape at 750 °C due to a very low interfacial capacitance but the clear circle shape was obtained from the measured impedance only at low temperature of 400 °C. In the equivalent circuit of Fig.4,  $R_1$  is the resistance of LSM coated layer with negligible resistance of the metal,  $R_2$  and  $Q_2$  are the interfacial resistance and capacitance, respectively. The value of  $R_1$ ,  $R_2$ , and  $Q_2$  are calculated by Z-View analysis software. The interfacial resistance measured at 400 °C showed high value as compared with that of the LSM coating layer. This implies that the contribution of the interfacial oxide to the total resistance is dominant, which is consistent with the result of the ASR.

#### 4. Conclusions

The LSM layer on the SUS430 and FeCrAlloy were coated by slurry dip-coating process for metallic interconnect of SOFC and then the LSM-coated alloys were sintered at 1200 °C. The area specific resistance of the LSM-coated alloys depends on the interfacial oxide layer formed at the interface between the metal alloy and the LSM coating layer during sintering and at operation temperature. Especially, the LSM-coated SUS 430, prepared by sintering at 1200 °C in inert gas and by heat-treatment at 1000 °C in air, showed a low area specific resistance and long term stability in the electric property probably due to formation of the interfacial oxide layer with low resistivity and to prevention of its growth, caused by the stable LSM phase coated on the SUS 430. Also the LSM coating layer sintered only in Ar with  $H_2$  did not form a stable phase and the unstable phase is dissociated into La hydroxide by reaction with water. This means that the sintering condition after LSM slurry coating is of importance to obtain a stable coating layer and an interfacial oxide layer with low resistivity.

## References

- [1] J. Q. Li, P. Xiao, *J. of European Ceramic Society*, 21 (2001) 659.
- [2] K. Huang, P. Y. Hou, J. B. Goodenough, *Solid State Ionics*, 129 (2000) 237.
- [3] T. Horita, Y. Xiong, K. Yamaji, N. Sakai, H. Yokokawa, *J. of Power Source*, 118 (2003) 35.
- [4] W. Z. Zhu, S.C. Deevi, *Materials Research Bulletin*, 38 (2003) 957.
- [5] T. Brylewski, M. Nanko, T. Maruyama, K. Przybylski, *Solid State Ionics*, 143 (2001) 131.
- [6] K. Huang, P. Y. Hou, J. B. Goodenough, , *Materials Research Bulletin*, 36 (2001) 81.

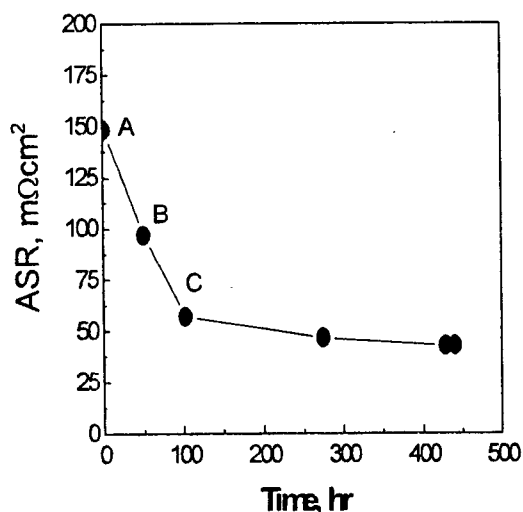


Fig.1 Area specific resistance of LSM-coated SUS 430 as a function of holding time at 750 °C in air. The coated LSM layer was sintered at 1200 °C in Ar with 10 vol.% H<sub>2</sub>

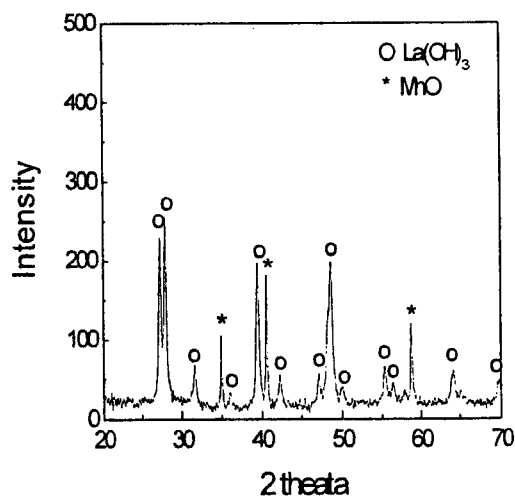


Fig.2 XRD pattern of the LSM coating layer on the surface of SUS 430 alloy sintered in Ar with 20 vol.% H<sub>2</sub> and aged for 100 hr at room temperature.

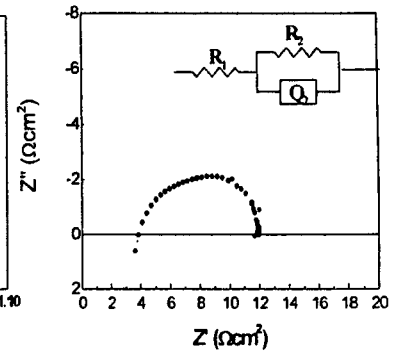
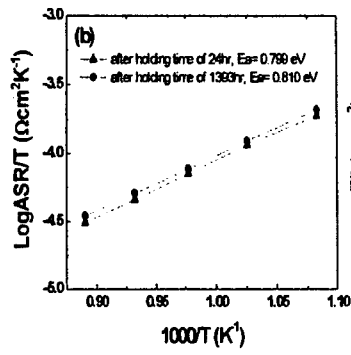
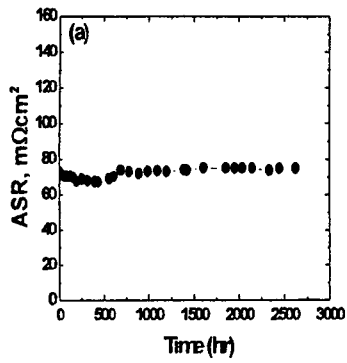


Fig. 3 Area specific resistance of the LSM-coated SUS 430, (a) as a function of holding time at 750 °C and (b) of temperature at each holding time.

Fig. 4 Impedance curve and equivalent circuit of the LSM-coated SUS430 measured at 400°C.