DEVELOPMENT OF A CuFe$_2$O$_4$ INTERCONNECT COATING

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ABSTRACT

Use of commercial grade ferritic steel interconnects in solid oxide fuel cells leads to problems of high resistance and chromium poisoning of the cathode during operation between 750-800°C. To avoid this problem, a novel method of applying coatings for interconnect protection has been tried. Copper and iron films have been deposited sequentially on the surface of a ferritic steel (UNS-430), which upon heat treatment in air at 750-775°C form an adherent coating of CuFe$_2$O$_4$ spinel phase. Electrical and microstructural characterization of spinel-coated steel samples have been carried out. The area specific resistivity (ASR) value of a 15 µm CuFe$_2$O$_4$-coated sample was found to be as low as 0.025 Ω.cm$^2$

INTRODUCTION

Of all the cell components, the interconnect constitutes the major part of the materials used in the planar solid oxide fuel cell (SOFC) stack. Doped lanthanum chromite (LaCrO$_3$) used to be the material of choice for the interconnect. Despite several advantages, LaCrO$_3$ also has some drawbacks: a) this perovskite has higher oxygen diffusivity at reduced oxygen activities which results in a decrease of fuel cell efficiency due to oxygen transport through the interconnect, and b) LaCrO$_3$ expands when exposed to decreasing oxygen activities due to the formation of oxygen vacancies, and this may result in warping of the interconnect plate (1). In addition, there are problems of scaling-up ceramic plates to larger dimensions (2).

To overcome the associated problems of the ceramic interconnect, several metallic alloys including commercial ferritic steels (Cr content: 15-25 wt%) such as UNS-430 have been substituted. The anode-supported thin film planar stacks operate at temperatures between 700 and 800°C (3). These metallic interconnects have an advantage in terms of cost, mechanical strength, machinability, weldability, and thermal and electrical conductivities. However, during operation at >700°C, the ferritic steel forms a Cr$_2$O$_3$ surface scale, in both oxidant and humidified fuel atmospheres. The overall stack resistance increases due to the growth of the electrically resistive Cr$_2$O$_3$ scale. Under operating conditions (<800°C), volatile chromium species in equilibrium with the scale impede the cell reaction. Several explanations are available in the literature. According to Peck et al. (4), in atmospheres containing water vapor, the dominant volatile species is chromic acid (H$_3$Cr(VI)O$_4$), which is transported with the oxidant gas through the cathode to the cathode/electrolyte interface and eventually blocks the electrochemically active sites with Cr(III), a phenomenon known as chromium poisoning (4-7).
To eliminate the problem of the cathode poisoning or the suppression of \( \text{Cr}_2\text{O}_3 \) scale formation, two approaches are more or less widely advocated: i) development of new, more oxidation resistant ferritic steel alloys and ii) use of a protective coating on the surface of ferritic steel. Several varieties of protective coatings have been developed and tested \((3,7,8)\). The objective of the present work was to use thin protective films of \( \text{CuFe}_2\text{O}_4 \) on the surface of UNS-430. For this purpose, the electroplating technique was employed.

**EXPERIMENTAL**

Commercial grade ferritic stainless steel (UNS-430) samples of dimension 1 cm x 1 cm x 0.1 cm were used as the substrate onto which \( \text{CuFe}_2\text{O}_4 \) films were deposited. For this purpose, a simple and conventional electroplating technique was employed. Prior to electroplating, the steel substrates were polished and thoroughly cleaned with deionized water and methanol. A special nylon sample holder, which facilitated deposition on both sides, was designed and constructed. A schematic of the sample holder is shown in Figure 1.

![Figure 1. Schematic of the sample holder for depositing coatings on both sides.](image)

Electroplating bath solutions were prepared in ordinary glass beakers. Thin metal films of copper and iron of varying thickness were electroplated. Separate baths were used to deposit copper and iron films, one on the top of the other. Common sulfate baths were used in both cases. It is to be noted that, although both metal salts were sulfates, it was not possible to co-deposit copper and iron using a common plating bath because of the stringent requirements of pH and temperature in each case. While copper was plated at room temperature from a highly acidic (pH ~ 1.2) copper sulphate (\( \text{CuSO}_4 \times 6\text{H}_2\text{O} \)) bath, a neutral (pH ~ 7) ferrous ammonium sulphate [\( \text{Fe(NH}_4\text{)}_2(\text{SO}_4)_x\times\text{H}_2\text{O} \)] bath at 40-45°C was used for plating iron. To avoid reaction between the Fe film and acid (present in the Cu bath), copper plating was done first, followed by iron plating. Current density applied for both Fe and Cu was 60-80 A/cm². The plating time was adjusted to maintain the proper atomic ratio (Fe:Cu = 2:1) and thus the desired mass ratio of ~ 1.73:1. After plating, the coatings underwent a heat treatment within the temperature range 750-800°C for several days in air atmosphere. The total plating time was about half an hour for a thickness of ~ 30 μm.
Oxidation scales were studied using the gravimetric method. Detailed microstructural characterization was carried out using a Philips 515 scanning electron microscope (SEM). Area specific resistance (ASR) values of spinel-coated UNS-430 samples were measured by the four-probe technique using a power supply and multimeter.

RESULTS AND DISCUSSION

The electroplated copper and iron were oxidized at 750-775°C and formed an adherent, crack-free, smooth and continuous oxide coating on UNS-430. The oxide coatings were analyzed by XRD. Figures 2 and 3 show two sets of XRD patterns 750°C (1 and 7 days) and 775°C (1 and 7 days). In each case, the CuFe2O4 spinel was formed in addition to residual oxide phases such as Fe2O3 and CuO. However, samples fired at 775°C for 7 days (Figure 3) exhibited a more phase-pure coating. It is expected that the coatings can be converted to the desired spinel phase after longer periods of exposure, even at 750°C.

![Figure 2. XRD patterns of spinel-coated UNS-430 samples fired at 750°C for (Top) 1 day, and (Bottom) 7 days.](image)
We also attempted to find the degree of alloy oxidation, primarily as a Cr₂O₃ layer on the surface of the steel (6). Weights of UNS-430 samples with and without coating, both before and after firing were recorded. The oxidized scale of uncoated samples seems to have spalled during cooling and the degree of oxidation could not be accurately determined. A thermogravimetric experiment would be required to properly determine the weight gain for the uncoated samples. However, to obtain the CuFe₂O₄ phase, the desired atomic ratio is Fe:Cu = 2:1 and thus the desired mass ratio is ~ 1.73:1. To ensure the proper mass ratio, weight change was systematically recorded after both Cu and Fe deposition. Table 1 lists the weight change results for a few representative coated samples, showing an average value of the mass ratio close to 1.72.

A noticeable change in microstructure can be seen in the surface morphology of the samples fired at 750°C for 1 day and 7 days (Figure 4). Although the grain size remains more or less the same, the texture appears different. Exposure for longer than one week is believed to form a more homogeneous phase, as evident from the XRD data (Figure 2).
Table 1. Estimate of mass ratio of Fe and Cu in the deposited films.

| Sample No. | Change in mass (g) during deposition | Mass Ratio (Fe:Cu) |
|------------|--------------------------------------|-------------------|
|            | Copper | Iron |                  |
| 1          | 0.00530 | 0.00977 | 1.843           |
| 2          | 0.00333 | 0.00591 | 1.775           |
| 3          | 0.00503 | 0.00825 | 1.640           |
| 4          | 0.00474 | 0.00771 | 1.627           |

Figure 4. Surface morphology of spinel coating on UNS-430 after firing at 750°C for (a) 1 day and (b) 7 days.

The advantage of the present deposition procedure is that it is not only a simple and inexpensive process, but also has the potential to produce any thickness. In the present investigation 15-50 µm films was deposited. A typical SEM cross-sectional image of a sample fired at 750°C for 7 days is shown in Figure 5. However, it has been observed that within the thickness of the film, there is a sharp gradient in color when the sample is fired for shorter times (Figure 6). EDX analysis of this sample confirmed that the CuO-phase is predominant adjacent to the steel surface (region 1); next is a mixed phase of Cu

Figure 5. Cross-sectional view of the spinel coating on UNS-430 sample fired at 750°C for 7 days
Figure 6. Cross-sectional view of the spinel coating on UNS-430 showing three distinct morphologies after firing at 750°C for 1 day. EDX study identifies region 1 as CuO, 2 as a mixed oxide phase of Cu and Fe, and 3 as Fe$_2$O$_3$.

and Fe-oxide (region 2) and finally the top surface consists of Fe$_2$O$_3$ (region 3). From this observation, it is clear that more time is necessary to achieve equilibrium, namely the homogeneous CuFe$_2$O$_4$ phase. Moreover, it is expected that any volatile chromium oxide phases would react with the Cu and Fe spinel before attacking the electrolyte interface.

ASR measurements were carried out for some selected samples (Table 2). It appears from the data that the initial values were relatively high (110 mΩ.cm$^2$) for samples fired at 750°C for 1 day, which decreased by a factor of four when the soaking was extended to 7 days. This result once again is consistent with our XRD, SEM and EDX data. In general, a normal trend of reduction of ASR values for longer soaking time was observed. Therefore, ASR values may give more insight about the homogeneity of the spinel phase.

Table 2. Area specific resistance (ASR) values of 15 µm thick films.

| Firing Temperature (°C) | Soaking Time (Day) | ASR (mΩ.cm$^2$) |
|-------------------------|--------------------|-----------------|
| 750°C                   | 1                  | 110             |
|                         | 7                  | 25              |
| 775°C                   | 1                  | 150             |
|                         | 7                  | 90              |

We have not examined the long-term stability of the spinel coating. Although CuFe$_2$O$_4$ is quickly formed on the surface, the subsurface reaction of Cr in the alloy will result in a chromium oxide phase. The Gibbs energy of formation of CuCr$_2$O$_4$ at 800°C is -13.3 kJ/mol relative to its component oxides (9), which is more stable than CuFe$_2$O$_4$ (-8.9 kJ/mol). Therefore, the CuCr$_2$O$_4$ phase is expected to form by exchange with CuFe$_2$O$_4$ resulting in the formation of a spinel solid solution at equilibrium. Furthermore, within the oxide scale, the partial pressure of O$_2$ may be sufficiently low to enable Fe to exist in both divalent and trivalent states, which adds to the complexity of the spinel solid solution.

Given sufficient time, the equilibrium phases will be a combination of spinel solid solution and corundum solid solution. The rate and sequence of formation of different phases of different composition is critical to the use of a Cu+Fe oxide layer for protection.
of the SOFC interconnect. Long term experiments or calculations using thermodynamic software would be required to determine the applicability of this material.

CONCLUSIONS

The dual-stage deposition process (electroplating) of copper and iron on UNS-430 ferritic steel and post firing at 750-775°C gave a crack-free, adherent oxide coating on the surface. XRD revealed CuFe₂O₄ as the major phase with certain amount of other phases such as CuO and Fe₂O₃, when the sample was fired at 750°C. A distinct change in surface morphology is attributed to more homogeneous phase. It has been observed from SEM that a change in surface morphology occurs when the sample was equilibrated at longer times. However, an indication of greater homogeneity was revealed when samples were kept at 775°C for 7 days. The area specific resistance (ASR) value of a 15 μm CuFe₂O₄-coated sample was found to be as low as 25 mΩ.cm².

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REFERENCES

1. P. Kofstad, in Second European Solid Oxide Fuel Cell Forum Proceedings, B. Thorstensen, Editor, p. 479, European SOFC Forum, Oberrohrdorf, Switzerland, (1996).
2. N. Oishi and Y. Yamazaki, in SOFC-VI, S. C. Singhal and M. Dokiya, Editors, PV99 -19, p. 759, The Electrochemical Society Proceedings Series, Pennington, NJ, (1999).
3. T. J. Armstrong, M. A. Homel and A. V. Virkar, in SOFC-VIII, S. C. Singhal and M. Dokiya, Editors, PV2003-07, p. 841, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).
4. D. H. Peck, M. Miller, H. Nickel, D. Das and K. Hilpert, in SOFC-IV, M. Dokiya, O. Yamamoto, H. Tagawa and S. C. Singhal, Editors, PV95-1, p. 585, The Electrochemical Society Proceedings Series, Pennington, NJ, (1995).
5. K. Hilpert, D. Das, M. Miller, D. H. Peck and R. Weiß, J. Electrochem. Soc., 143, 3642 (1996).
6. C. Gindorf, K. Hilpert and L. Singheiser, in SOFC-VII, H. Yokokawa and S. C. Singhal, Editors, PV2001-16, p. 793, The Electrochemical Society Proceedings Series, Pennington, NJ, (2001).
7. H. U. Anderson and F. Tietz, in High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, S. C. Singhal and K. Kendall, Editors, p. 173, Elsevier Advanced Technology, Kidlington, UK, (2003).
8. R. N. Basu, F. Tietz, O. Teller, E. Wessel, H. P. Buchkremer and D. Stöver, J. Solid State Electrochem., 7, 416 (2003).
9. K. T. Jacob, G. M. Kale and G. N. K. Iyengar, J. Mater. Sci., 21, 2753 (1986).