2011 International Conference on Power Electronics and Engineering Application

Improved oxidation resistance of a nanocrystalline lanthanum-implanted FeCr alloy

Deni S. Khaerudinia,*, M.A. Othmana, S. Mahzan, P. Untoro, D. Sebayang

*Department of Materials and Design Engineering, Universiti Tun Hussein Onn Malaysia, JB 86400, Malaysia
b Indonesian Nuclear Energy Agency, Tangerang 15314, Indonesia

Abstract

The decrease in the solid oxide fuel cell (SOFC) operating temperatures from 1000 to 850 ºC has enabled the use of ferritic alloys, especially FeCr alloy, as interconnects instead of ceramics. However, there are many problems remaining such as the chromia scale growth and chromium evaporation into cells that can cause degradation in the SOFC performance. Therefore, in the SOFC using metallic interconnects the stability of the alloy at the operation temperature is the greatest technical challenge. In this study, the causes of the difference to the oxide scale growth rate was investigate by focusing on the oxide scale, and improve the more protective surface treatment in order to reduce further not only the oxide scale growth but Cr evaporation. The effectiveness of the nanostructure and surface treatment in improving the oxidation resistance of the alloy was demonstrated by oxidation tests at 900 ºC in air corresponding to the cathode environment of SOFC. The surface and cross-sectional morphologies of the alloy after thermal exposure were evaluated and observed using scanning electron microscopy with an energy dispersive X-ray spectroscopy. The phase structures of oxide scale formed on them were identified by X-ray diffraction.

© 2011 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.
Selection and/or peer-review under responsibility of ICSS.

Keywords: Solid oxide fuel cell; Ion implantation; Interconnect; Oxidation resistance

1. Introduction

As the operating temperature of SOFC reduces, metallic alloys can be used as the interconnect material. Metallic interconnect offer many advantages over ceramic interconnect, such as high thermal conductivity, good ductility, and low cost of raw materials and fabrication, etc. Chromia forming alloys are promising
candidates for the interconnect applications because these alloys form a thin, protective layer of Cr$_2$O$_3$ scale on the alloy surface upon thermal exposure. Nevertheless, conventional alloys still cannot endure an operating temperature for a long time [1]. One major concern with these alloys is their long-term stability and compatibility with other fuel cell components [2-5]. Current research on SOFC interconnects is focusing on these issues.

To mitigate these problems, nanostructured alloy development and surface modification (i.e. ion implantation) on the alloy substrate are an attractive approach. The nanostructured alloy is expected to reduce Cr$_2$O$_3$ scale growth increase. Although the FeCr alloys are promising SOFC interconnect material, the exact preparation process has not been elaborated in relevant literatures so far. Different preparation modes have significant effects on material properties. Therefore, the preparation process is optimized by combination of high energy milling and spark plasma sintering (SPS) due to obtain the nanostructured alloy. While the surface modification is expected to act as a seal to the volatile Cr species and provide oxidation protection for the alloy substrate. There are many techniques to conduct surface modification on metallic substrate, such as sputtering, laser ablation, etc. Although many attempts have been made to ‘deposit’ protective layer on metallic substrates by various methods, very few papers focused on the effect of La implantation on mass change of the alloys. It is found that La active element reacts with the thermally grown Cr$_2$O$_3$ to form LaCrO$_3$ upon thermal exposure [6]. The effectiveness of developed nanostructure alloy and La implantation was evaluated by oxidation test at 900 °C in air.

2. Experimental procedures

2.1. Materials preparation

Fe-20%wtCr alloy powder was prepared by ball milling Fe and Cr powder (99.99% purity) in a Retsch PM400 planetary ball mill at 300 rpm milling speed for 60 h under argon atmosphere. The as milled powder was packed in graphite die with an inner diameter of 20 mm and was densified by using SPS system Model 10-3 (Thermal Technology LLC, USA) at a loading pressure of 120 MPa. The resulting compacts were sintered of 800 and 900 °C at a rate of 400 °C/min and maintained for 5 min in a vacuum. The commercially available ferritic alloy (containing 14.5 wt% Cr, 1.07 wt% Si, 0.51 wt% Mn as main alloying elements) was selected as a comparison for this study, because of its ready availability and suitable Cr content. Prior to ion implantation, the samples with the size of surface area of about 8 cm$^2$ were ground using up to #1000 grit SiC sandpapers and polished to 0.05 µm diamond paste. After the samples were ultrasonically cleaned in ethanol over 30 min, they were implanted with La at the nominal dose of 1x10$^{17}$ ions/cm$^2$ using ion implanter of Cockcroft-Walton Type. The ion beam energy was maintained at 100 keV with 10 µA/cm$^2$ beam current density and 200 kV extraction voltages.

2.2. Oxidation test

Oxidation test of the unimplanted and implanted samples were carried out in stagnant air using a box furnace at 900 °C for 100 h. The samples were taken out of the furnace at the interval of 20 h to check the mass gain using an analytical balance with an accuracy of ± 0.01 mg.

2.3. Microstructural characterization

The surface structure and morphologies of the unimplanted and implanted samples after oxidation were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with an energy
dispersive X-ray spectroscopy (EDS). The thickness of the thermally grown oxide scale was estimated by SEM cross-sectional observation.

3. Results and discussion

The results of crystallite size, density, and parabolic rate constant calculation are shown in Table 1. It showed that as SPS sintered resulted in finer crystallite size than the commercial alloy. The beneficial effect of SPS in the densification of alloy was on its capability to pin the grain boundaries which will limit the grain growth of the alloy. Table 1 also shows the parabolic rate constant which calculated according to the parabolic law after plots the mass gain of the substrates at 900 °C in air for 100 h. All the implanted samples exhibited smaller mass gain (lower \( k_p \) value) than the unimplanted samples. The SPS-800 sample shows the lowest \( k_p \) values, interestingly, the SPS samples have a relatively lower density than the commercial alloy. This means that the samples itself decrease the mass gain (\( k_p \) value), not by increasing the density but perhaps by the decreasing the crystallite size. The oxidation resistance of some materials is also reported [7] to be superior in nanocrystalline form when compared with that in microcrystalline state. In this study, the interesting phenomenon is also distinguished which increased remarkably with finer of the nanocrystalline structure. It is noted that the improved oxidation resistance in nanocrystalline alloys arises mainly because of the faster diffusion of elements that can form passive oxide film (Cr\(_2\)O\(_3\)) and/or because of improved adhesion of passive film formed over nanocrystalline structure. Meanwhile, the lanthanum ion implantation is primarily contributed to the adherence of oxide scale/substrate, as evidenced by surface and cross sectional SEM analysis (Figs. 2 and 3).

Table 1. Crystallite size, density, and parabolic rate constant (\( k_p \)) of as sintered and received alloy

| Specimens            | Crystallite size* (nm) | Density (g/cm\(^3\)) | \( k_p \) (g\(^2\) cm\(^{-4}\) s\(^{-1}\)) |
|----------------------|------------------------|-----------------------|---------------------------------------------|
|                      |                        |                       | Unimplanted  | Implanted |
| SPS-800              | 17.94                  | 6.95                  | 1.43 \times 10\(^{-10}\)   | 8.83 \times 10\(^{-11}\) |
| SPS-900              | 23.32                  | 6.90                  | 1.73 \times 10\(^{-10}\)   | 1.26 \times 10\(^{-10}\) |
| As received commercial alloy | 77.03                  | 6.97                  | 1.04 \times 10\(^{-10}\)   | 8.17 \times 10\(^{-09}\) |

* calculated using the Williamson-Hall technique.

Fig. 1. XRD patterns of (a) unimplanted; and (b) La-implanted samples after oxidation test at 900 °C for 100 h in air
The phase structure of the samples after oxidation tests were characterized by XRD, as shown in Fig. 1. After the oxidation test, Cr₂O₃ and (Fe,Cr)₂O₃ were the major oxidation product and very weak peaks of Fe₂O₃ formed on all unimplanted and implanted substrates. For the lanthanum ion implantation, the diffraction peaks observed the existence of La₂O₃ or LaCrO₃. The FeCr phase was easily observed only on the SPS samples which could be associated due to the layered thinness scale formed on substrate surface, as evidenced by SEM cross-section in Fig. 3.

The surface morphologies of the La-implanted samples after the oxidation test were different from that of the unimplanted samples, as shown in Fig. 2. The SPS-800 surface was composed of very fine particles (Fig. 2(d)); meanwhile the SPS-900 shows relatively similar fine particles with isolated large particles on top (Fig. 2(e)). The commercial alloy surface exhibited another features, as shown in Fig. 2(f) which composed very large nodule-like grains. Meanwhile, the unimplanted samples (Figs. 2(a-c)) exhibited relatively similar features with the respective implanted samples except coarser particles and cracking are observed. EDS results indicated that the particles were mainly Cr₂O₃ which were embedded in a layer of (Fe,Cr)₂O₃ spinel structure. The thickness of the oxide scale is consistent with the mass gain ($k_p$ values) after oxidation test for all samples. Fig. 3 shows only for selected samples which considered due to the significant different of oxide scale and sample type. It can be clearly seen that the SPS-800 shows better scale thickness, dense, and adherence, than commercial alloy. The scale morphology of commercial alloy shows more porous or void scale randomly detected and the thick oxide is clearly divided into two regions, where the outer layer is more porous than the inner layer, the interface between the oxide scale and the substrate. The ultimate goal of forming the LaCrO₃ on the substrate is to improve the oxidation resistance of the substrate and at the same time, to reduce Cr migration/evaporation from the oxide scale to the cathode side. However, in this study the oxidations behaviours varied for different samples, which are probably mainly due to different structures (nanocrystalline) of samples, as evidenced by the significant different oxide scale thickness of the La-implanted SPS-800 and commercial alloy (Fig. 3).
4. Conclusion

The oxidation resistance of as SPS sintered showed better quality than that of commercial alloy. The beneficial effect of La implanted sample on the oxidation resistance was clearly visible to the adherence of oxide scale. Microstructure observations revealed the effectiveness of nanocrystalline structure for improving thinner and stronger scale/substrate interface during oxidation process which presents the homogenous structure with good adherence and a uniform inter-diffusion layer between substrate and oxide scale.

Acknowledgements

This investigation was financially supported by the Ministry of Higher Education - Malaysia under FRGS Grant Scheme project with contract no. 0759. The author thanks Dr Daniela Fredrick from Thermal Technology, LLC., USA for helped us in spark plasma sintering research work.

References

[1] Fergus, JW. Metallic interconnects for solid oxide fuel cells. Mater Sci Eng A 2005;397:271-83.
[2] Zhu WZ, Deevi SC. Development of interconnect materials for solid oxide fuel cells. Mater Sci Eng A 2003;348:227-43.
[3] Huang K, Hou PY, Goodenough JB. Characterization of iron based alloy interconnects for reduced temperature solid oxide fuel cells. Solid State Ionics 2000;129:237-50.
[4] Badwal SPS, Deller R, Foger K, Ramprakash Y, Zhang JP. Interaction between chromia forming alloy interconnects and air electrode of solid oxide fuel cells. Solid State Ionics 1997;99:297-310.
[5] Tucker MC, Korokawa H, Jacobson CP, DeJonghe LC, Visco SJ. A fundamental study of chromium deposition on solid oxide fuel cell cathode materials. J Power Sources 2006;160:130-38.
[6] Linderoth S, Hendriksen PV, Mogensen M, Langvad N. Investigations of metallic alloys for use as interconnects in solid oxide fuel cell stacks. J Mater Sci 1996;31:5077-82.
[7] Zhang HW, Gopalan R, Nukai T, Hono K. Fabrication of bulk nanocrystalline Fe-C alloy by spark plasma sintering of mechanically milled powder. Scripta Materialia 2005;53:863-68.