High Temperature Oxidation Resistance of Rare Earth Chromite Coated Fe-20Cr and Fe-20Cr-4Al Alloys

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Doped lanthanum chromite has been used in solid oxide fuel cell (SOFC) interconnects. The high costs involved in obtaining dense lanthanum chromite have increased efforts to find suitable metallic materials for interconnects. In this context, the oxidation behavior of lanthanum chromite coated Fe-20Cr and Fe-20Cr-4Al alloys at SOFC operation temperature was studied. Isothermal oxidation tests were carried out at 1000 °C for 20, 50 and 200 hours. Cyclic oxidation tests were also carried out and each oxidation cycle consisted of 7 hours at 1000 °C followed by cooling to room temperature. The oxidation measurements and the results of SEM/EDS as well as XRD analyses indicated that lanthanum chromite coated Fe-20Cr and Fe-20Cr-4Al alloys were significantly more resistant to oxidation compared with the uncoated alloys.

Keywords: interconnects, fuel cells, coating, cyclic oxidation

1. Introduction

The solid oxide fuel cell (SOFC) is a multilayered structure and consists of ceramic and metallic materials. Many industrial applications require hundreds of volts and to generate this using SOFC, hundreds of cells and interconnects are assembled in series to form a vertical stack. Interconnects in SOFC link the anode of a cell to the cathode of the next cell in the battery, distribute the gases in the anode and cathode and it also transports electric current between the cells and in the external circuit. Hence, interconnects are an important part of SOFC for long term safe operation. Over the years, a number of metals and ceramic materials have been considered and tested for use as interconnects of planar SOFCs. So far no satisfactory solution has been found. The material used for interconnects is expected to satisfy a variety of requirements such as high density, high electrical and thermal conductivity and high creep resistance.

Until recently, doped LaCrO$_3$ based ceramic interconnects were used in fuel cells. These ceramics were difficult to shape and the cost involved in manufacturing dense interconnects was very high. In recent years the use of metallic interconnects has been gaining ground due to availability of a variety of manufacturing techniques, low shaping costs and adequate thermal conductivity. SOFCs generally operate at around 1000 °C. A number of studies are being carried out to reduce the operating temperatures of SOFCs and the lower temperatures permit metallic interconnects to be considered. The use of coatings or surface treatments is a viable alternative to reduce oxidation rates and extend the useful life of potential alloys as SOFC interconnects. Chromium dioxide forming iron based alloys have been studied as potential materials for interconnects. Nevertheless, the surfaces of the Fe-Cr alloys require modification to improve electrical conductivity of the chromium dioxide. The addition of reactive elements such as yttrium, zirconium or cerium to these alloys improves the protective properties of the surface oxides even more. Rare earth oxides in the form of dispersions have also been added to these alloys to form protective surface oxides. Coatings of LaCrO$_3$ have been reported to increase the adhesion of the chromium dioxide layer, reduce its growth rate and increase electronic conductivity.

This paper reports the effect of a coating of lanthanum chromite, obtained ‘in situ’, on the oxidation behavior of an iron-chromium and an iron-chromium-aluminium alloy at 1000 °C.

2. Methods and Materials

Two alloys namely Fe-20Cr and Fe-20Cr-4AI were prepared in an electric induction furnace and forged at 980 °C. Specimens of these alloys with approximate dimensions of 10 x 10 x 2 mm were cut, ground to 220 mesh, degreased in acetone and weighed.

Lanthanum chromite (LaCrO$_3$) coatings were prepared using a mixture of powders of Cr$_2$O$_3$ and La$_2$O$_3$. In preliminary tests, samples of this mixture were heated for different duration at 600 and 800 °C and subsequently analyzed using X-ray diffraction (XRD). In the powder mixtures, the XRD spectra revealed un-reacted La$_2$O$_3$ and Cr$_2$O$_3$ and a small amount of LaCrO$_3$. The XRD data of the powder mixture heated at 800 °C indicated the presence of large quantities of LaCrO$_3$ and a small amount of La$_2$Cr$_2$O$_7$. The coating was applied on the alloy specimen surfaces were coated with the powder mixture and LaCrO$_3$ was formed ‘in situ’ during the oxidation tests. The specimens were coated by spraying a suspension of the powder mixture in ethanol. Five sides of the specimens were coated and one side remained uncoated. This procedure was adopted due to poor adhesion of the coating. However, after heat treatment the chromite formed and the surface oxides were quite adherent. The average coating thickness was 10-15 µm. The coated specimens were then weighed and isothermal oxidation tests carried out in a muffle furnace at 1000 °C for 20, 50 and 200 hours in the cyclic oxidation tests, the uncoated and coated specimens were cycled 15 times and each cycle consisted of holding the specimens for 7 hours at 1000 °C.

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followed by cooling to room temperature. The specimens were weighed after each cycle. The specimen surfaces were examined in a LEO scanning electron microscope (SEM) and micro-regions analyzed using energy dispersive spectroscopy (EDS).

3. Results and Discussion

Figure 1 shows the X-ray diffraction spectra of the Cr$_2$O$_3$ and La$_2$O$_3$ powder mixture heated for 1, 2 and 5 hours at 800 °C. In the spectra, the LaCrO$_3$ peaks are evident indicating its formation. The spectra also reveals Cr$_2$O$_3$ peaks, but no La$_2$O$_3$ peaks, indicating thus an excess of only the former in the mixture.

The weight gain vs. time curves of the two alloys, with and without LaCrO$_3$ coating at 1000 °C are shown in Figure 2. None of the specimens exhibited oxide spallation. The weight gain of the Fe-20Cr alloy specimen was the highest and that of the LaCrO$_3$ coated Fe-20Cr-4Al alloy specimens the lowest, indicating higher oxidation resistance of the latter. The oxide formed on the uncoated and coated Fe-20Cr alloy specimens was mainly chromium dioxide and that on the Al containing alloys, aluminium oxide. The amount of chromium dioxide or aluminium oxide formed on the uncoated alloy specimens was more than that on the coated alloy specimens. Growth of chromium dioxide or aluminium oxide on the coated alloy specimens was inhibited by incorporation of La$^{2+}$ ions in the growing scale. This La ion segregates to the grain boundaries in the scale and blocks substrate-cation diffusion, thus inhibiting scale growth$^{11}$. This blocking effect is due to the higher ionic radius of the La ion, compared with the ionic radii of the substrate cations.

Figure 3a shows the cross section of Fe-20Cr specimens oxidized for 200 hours at 1000 °C. The surface layer is irregular with voids,
both at the interface and in the alloy. EDS indicated Mn in the outer surface of the layer (arrows). XRD data indicated that the oxide layer was mainly Cr$_2$O$_3$ and the outer part of the oxide layer contained MnCr$_2$O$_4$. This indicates that Mn diffuses faster than Cr through the Cr$_2$O$_3$ scale. The oxide layer was about 10 µm in thickness. The surface and cross section of LaCrO$_3$ coated Fe-20Cr after 200 hours at 1000 °C are shown in Figures 3b and 3c. The coating is porous and adherent. The oxide layer (grey), about 3.5 µm thick, revealed particles from the coating and XRD analysis of this layer suggests the formation of MnCr$_2$O$_4$, Cr$_2$O$_3$ and LaCrO$_3$. EDS and XRD analysis data indicated that the dark particles in the oxide layer were un-reacted Cr$_2$O$_3$ and the light particles, LaCrO$_3$.

The cross section of uncoated and coated Fe-20Cr-4Al alloy specimens oxidized for 200 hours at 1000 °C are shown in Figures 4a and 4b. In Figure 4a, besides the α-Al$_2$O$_3$ layer, interfacial voids, formed during growth of the alumina layer, can be observed. XRD analysis of the surface layer seen in Figure 4b indicated the formation of LaCrO$_3$ and α-Al$_2$O$_3$.

The cross sections of uncoated and LaCrO$_3$ coated Fe-20Cr specimens oxidized for 200 hours at 1000 °C are shown in Figures 6a and 6b. In Figure 6a, voids, both interfacial and in the oxide can be observed. These features are similar to those observed in specimens oxidized isothermally.

Figure 7a and 7b show the cross sections of the uncoated and coated Fe-20Cr-4Al specimens after 15 cycles of oxidation at 1000 °C. Most of the features are identical to those observed in specimens of this alloy that were oxidized isothermally. Particles of the coating can be seen in the oxide layer that grew from the alloy substrate.

4. Conclusions

1. Lanthanum chromite coatings on Fe-20Cr and Fe-20Cr-4Al alloy specimens were obtained by 'in-situ' synthesis at 800 °C from a mixture of La$_2$O$_3$ and Cr$_2$O$_3$;

2. The isothermal and cyclic oxidation tests revealed that the lanthanum chromite coated Fe-20Cr and Fe-20Cr-4Al alloy specimens were significantly more resistant to oxidation than the uncoated specimens of the same alloys;

3. The XRD and SEM/EDS measurements on oxidized lanthanum chromite coated Fe-20Cr and Fe-20Cr-4Al alloy specimens revealed the formation of thin adherent chromium dioxide and alumina respectively;

4. The increased oxidation resistance of lanthanum chromite coated specimens is due to incorporation of La ions in the oxide scales formed during oxidation; and

5. The results of this investigation indicate that lanthanum chromite coated Fe-Cr and Fe-Cr-Al alloys can be considered for use as interconnects in SOFC.

![Figure 4. Cross section of Fe-20Cr-4Al oxidized for 200 hours at 1000 °C. a) Uncoated; and b) LaCrO$_3$ coated.](image)

![Figure 5. Cyclic oxidation curves of the coated and uncoated alloys. Each cycle consisted of 7 hours at 1000 °C followed by cooling to room temperature.](image)
References


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Figure 6. Cross section of Fe-20Cr after 15 cycles of oxidation in air at 1000 °C. a) Uncoated; and b) LaCrO$_3$ coated.

Figure 7. Cross section of Fe-20Cr-4Al after 15 cycles of oxidation in air at 1000 °C. a) uncoated; and b) LaCrO$_3$ coated.