

High temperature oxidation resistance of rare earth chromite coated Fe-20Cr and Fe-20Cr-4Al alloys

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Abstract: 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 Fe-20Cr and Fe-20Cr-4Al alloys coated with lanthanum chromite at SOFC operation temperature was investigated. Cyclic oxidation tests were also carried out. The oxidation measurements and SEM/EDS as well as XRD analyses indicated that lanthanum chromite coated Fe-20Cr and Fe-20Cr-4Al alloys were significantly more oxidation resistant compared with the uncoated alloys.

1 INTRODUCTION

The solid oxide fuel cell (SOFC) is a multilayered structure and consists of ceramic and metallic materials. Industrial applications require hundreds of volts and to generate this, hundreds of cells and interconnects are assembled in series to form a vertical stack. Construction of a planar SOFC implies the use of interconnects to link the anode of a cell to the cathode of the next cell in the battery, to distribute the gases in the anode and cathode and also to transport electric current between the cells and in the external circuit. Hence, interconnects are an important part of SOFC for long term safe operation. (Brylewski 2001) 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 as interconnects is expected to satisfy a variety of requirements such as high density, high electric and thermal conductivity and high creep resistance. (Badwal 1997)

Until recently, doped LaCrO_3 based ceramic interconnects were widely used in fuel cells. (Badwal 1997) These ceramics presented some operational problems, were difficult to shape and it was costly to manufacture very dense interconnects. Recently the use of metallic interconnects is 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 this has made it possible to consider metallic interconnects. The use of coatings or surface treatments is considered to be a viable alternative to reduce oxidation rates and extend the useful life of alloys used as SOFC interconnects. Chromium dioxide forming iron based alloys have been considered as potential materials for interconnects. (Brylewski 2001) However, the surfaces of the Fe-Cr alloys require modification to improve electrical conductivity of the chromium dioxide. (Kadowaki 1993) Coatings of LaCrO_3 have been reported to increase the adhesion of the chromium dioxide layer, reduce its growth rate and increase electronic conductivity. (Zhu 2004).

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

The alloys, Fe-20Cr and Fe-20Cr-4Al were prepared in an electric induction furnace and forged at 980° C. Specimens with dimensions approximately 10x10x2 mm were cut, ground down to mesh 220, degreased in acetone and weighed.

A mixture of powders of Cr₂O₃ and La₂O₃ was used to prepare the LaCrO₃ coatings. In preliminary tests this mixture was heated in a muffle furnace at 600° C and 800° C for different duration and then analyzed using x-ray diffraction (XRD). At 600° C, independent of time, un-reacted La₂O₃ and Cr₂O₃ as well as LaCrO₄ and La₂CrO₆ was detected. XRD data of the powder mixture heated to 800° C indicated the presence of large quantities of LaCrO₃ and a small amount of LaCrO₄, besides some Cr₂O₃. This indicated that with increase in temperature and time, the lanthanum compounds transformed to LaCrO₃. On the basis of these results, the specimen surfaces of the two alloys were coated with the powder mixture and LaCrO₃ formed 'in situ' during the oxidation tests. The coatings were obtained 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. After heat treatment the chromite formed and the surface oxides are quite adherent. The average coating thickness was 10-15µm. The coated specimens were then weighed. The oxidation tests were carried out in a muffle furnace. The isothermal tests were carried out at 1000° C for 20, 50 and 200h. In the cyclic oxidation tests, the uncoated and coated specimens were cycled 15 times and each cycle consisted of holding the specimens at 1000° C for 7 hours followed by cooling to room temperature. The specimens were weighed after each cycle. The specimen surfaces were examined in a scanning electron microscope and micro-regions on the surface analyzed using energy dispersive spectroscopy.

3. RESULTS AND DISCUSSION

Fig. 1 shows the x-ray diffraction spectra of the Cr₂O₃ and La₂O₃ powder mixture heated for 1, 2 and 5 h at 800° C. In the spectra, the LaCrO₃ peaks are evident indicating its formation. An excess of Cr₂O₃ was observed, but no free La₂O₃.

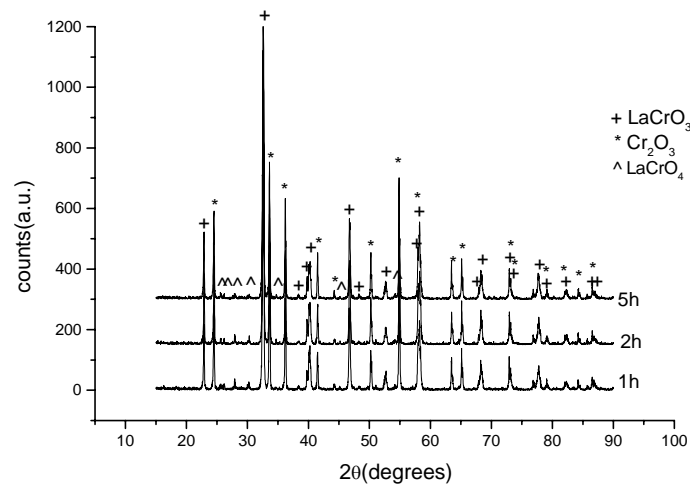


Fig. 1: X-ray diffraction spectra of the Cr₂O₃ and La₂O₃ powder mixture heated in air for 1, 2 and 5h at 800° C.

The weight gain curves of the two alloys, with and without LaCrO_3 coating, exposed for 200 h at 1000°C are shown in Fig. 2. None of the specimens exhibited oxide spallation. The Fe-20Cr alloy weight gain was the highest and the LaCrO_3 coated Fe-20Cr-4Al alloy exhibited the highest oxidation resistance. The oxide formed on the uncoated and coated Fe-20Cr alloy 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 alloys was more than that on the coated alloys. 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. (Fernandes 2004) This blocking effect is due to the higher ionic radius of the La ion, compared with the ionic radii of the substrate cations.

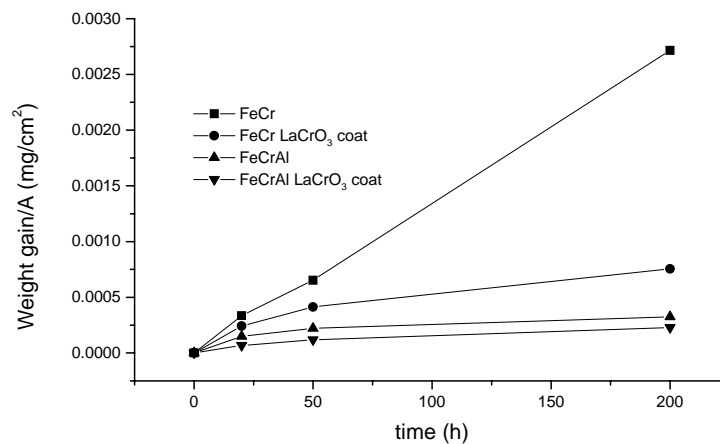


Fig. 2: Oxidation curves of alloys Fe-20Cr and Fe-20Cr-4Al with and without LaCrO_3 coating.

Fig. 3a shows the cross section of Fe-20Cr oxidized for 200h 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 indicated the presence of Cr_2O_3 and MnCr_2O_4 . These two analyses data indicate that the oxide layer is preferentially Cr_2O_3 . The outer part of surface layer consists of MnCr_2O_4 . The presence of Mn in the outer surface of the oxide layer indicates that Mn diffuses at a significantly higher rate than Cr in the Cr_2O_3 lattice. (Wild 1977) The average oxide layer thickness is about $10\ \mu\text{m}$. Fig. 3b shows the surface of LaCrO_3 coated Fe-20Cr after 200 h at 1000°C . Figure 3c is the cross section of the same specimen. The coating layer is porous and adherent. An oxide layer (grey), about $3.5\ \mu\text{m}$ thick can be observed. Particles from the initial coating can be seen embedded in the oxide that grew from the substrate. XRD analysis suggests the formation of MnCr_2O_4 , Cr_2O_3 and LaCrO_3 . On the basis of EDS and XRD analyses it can be inferred that the dark particles in the oxide layer are un-reacted Cr_2O_3 and the light particles, LaCrO_3 .

The cross section of Fe-20Cr-4Al oxidized for 200 h at 1000°C is shown in Fig.4a. Besides the $\alpha\text{-Al}_2\text{O}_3$ layer, interfacial voids, typically formed during growth of an alumina layer, can be also seen. (Tolpygo 1994). Fig. 4b shows the cross section of LaCrO_3 coated Fe-20Cr-4Al oxidized for 200 h at 1000°C . XRD analysis indicated the formation of LaCrO_3 and $\alpha\text{-Al}_2\text{O}_3$.

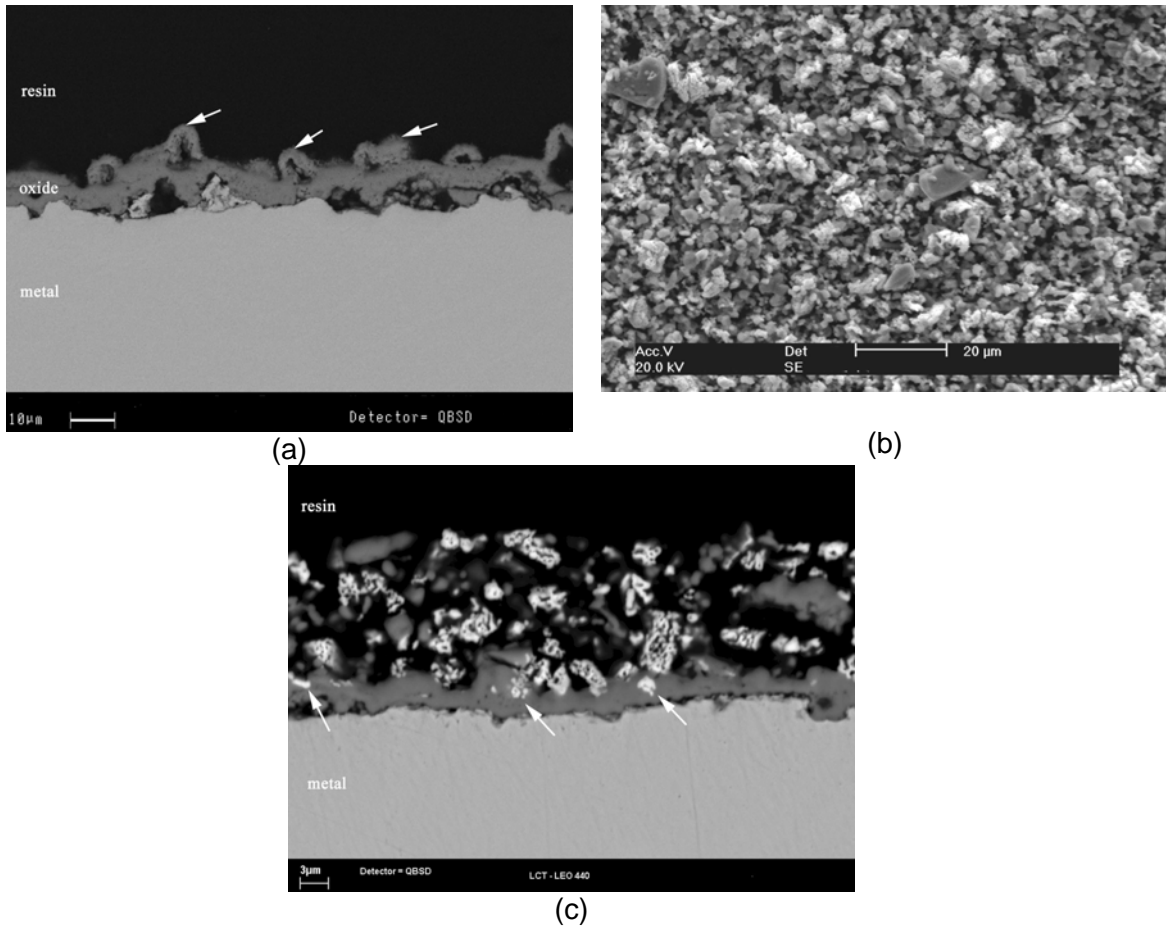


Fig. 3: (a) Cross section of Fe-20Cr after 200h of oxidation at 1000°C; (b) Surface of LaCrO₃ coated Fe-20Cr after 200h of oxidation at 1000°C; (c) cross section of (b).

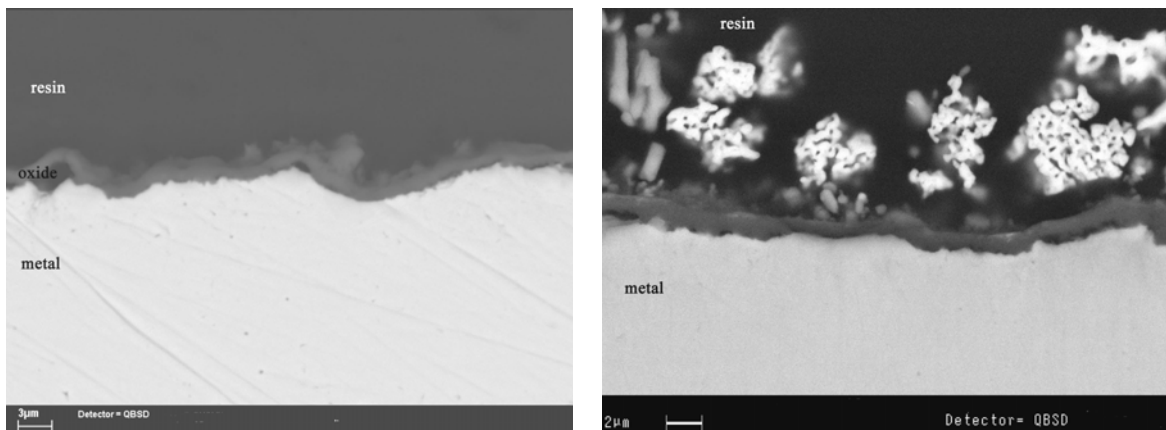


Fig. 4: Cross section Fe-20Cr-4Al oxidized for 200 h at 1000°C. (a) Uncoated; (b) LaCrO₃ coated.

The cyclic oxidation curves of the two alloys, with and without the LaCrO₃, are shown in Fig. 5. Neither of the alloys, with or without the coatings exhibited oxide spalling. The coated alloys exhibited a marked change in weight gain after the second cycle, where as the uncoated alloy specimens exhibited the change in weight gain right after the first

cycle and maintained this weight gain even after 15 cycles. This could be attributed to formation of lanthanum chromite and initiation of scale formation during the first cycle followed by further scale growth during the second cycle. The peak in change in weight gain of the uncoated Fe-20Cr alloy after the 6th cycle is due probably to oxide cracking and formation of new oxide.

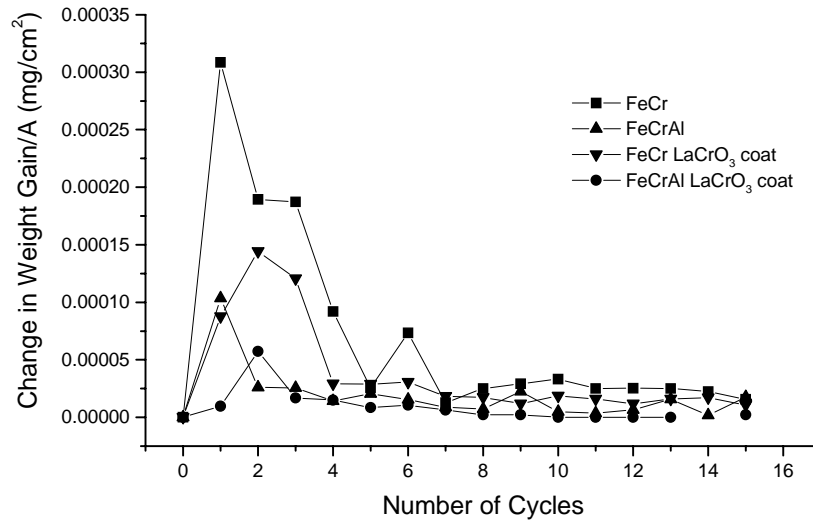


Fig. 5: Cyclic oxidation curves of the coated and uncoated alloys. Each cycle consisted of 7h at 1000°C followed by cooling to room temperature.

Fig.6a shows the cross section of Fe-20Cr after 15 cycles of oxidation at 1000°C. Voids, both interfacial and in the oxide can be observed, features similar to those observed in specimens oxidized isothermally. Fig. 6b is a cross section of the same alloy coated with LaCrO₃.

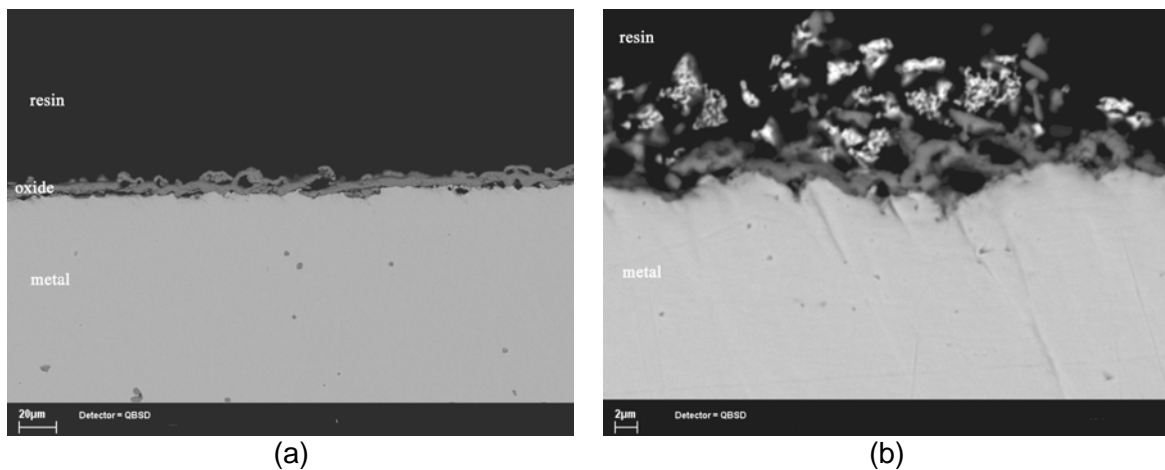


Fig. 6: Cross section of Fe-20Cr after 15 cycles of oxidation in air at 1000°C. (a) Uncoated; (b) LaCrO₃ coated.

Figs. 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.

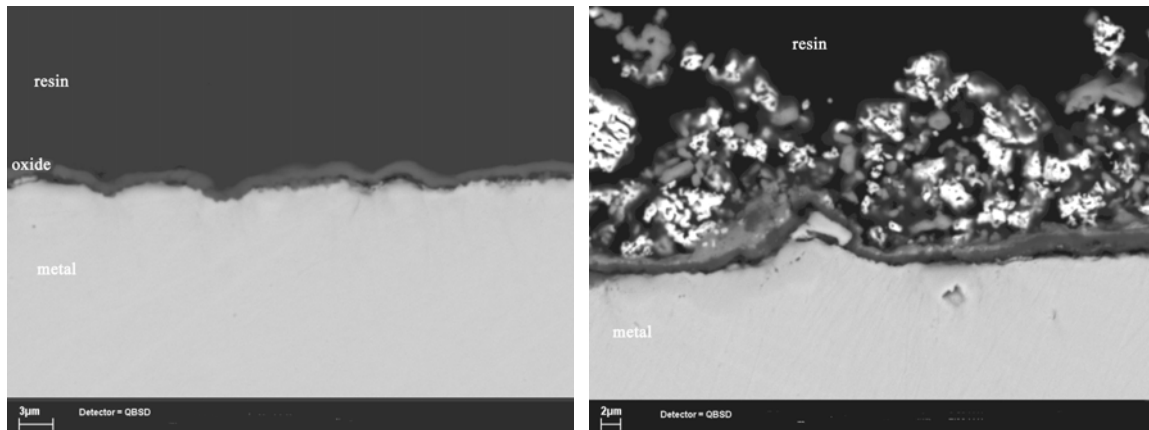


Fig. 7: Cross section of Fe-20Cr-4Al after 15 cycles of oxidation in air at 1000°C. (a) uncoated; (b) LaCrO₃ coated.

4. CONCLUSIONS

1. Lanthanum chromite was synthesized 'in situ' at 800°C from a mixture of La₂O₃ and Cr₂O₃.
2. The lanthanum chromite coated Fe-20Cr and Fe20Cr-4Al alloys were significantly more resistant to oxidation and can therefore be considered for use as interconnects in SOFC.

5. REFERENCES

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