RARE EARTH CHROMITE COATINGS FOR INCREASED H.T. OXIDATION RESISTANCE OF METALLIC SOFC INTERCONNECTS

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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 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 h. 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 x-ray diffraction analyses indicated that lanthanum chromite coated Fe-20Cr and Fe20Cr-4Al alloys were significantly more resistant to oxidation compared with the uncoated alloys. The role of La in increasing oxidation resistance of the two alloys is presented.

Keywords: SOFC interconnects, oxidation, iron-chromium alloy, iron-chromium-aluminium alloy.

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. [1] 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 electrical and thermal conductivity and high creep resistance. [2]

Until recently, doped $LaCrO_3$ based ceramic interconnects were used in fuel cells. [1] These ceramics were difficult to shape and the costs 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 1000º 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. [2] Nevertheless, the surfaces of the Fe-Cr alloys require modification to improve electrical conductivity of the chromium dioxide. [3] The addition of reactive elements such as yttrium, zirconium, or cerium to these alloys improves the protective properties of the surface oxides even more. [4-8] Rare earth oxides in the form of dispersions have also been added to these alloys to form protective surface oxides. [9] Coatings of $LaCrO_3$ have been reported to increase the adhesion of the chromium dioxide layer, reduce its growth rate and increase conductivity. [10]

This paper reports the effects of a coating of lanthanum chromite, obtained 'in situ', on the oxidation behavior of an iron-chromium and an iron-chrmium-aluminium alloy at 1000 ºC.

Methods and materials

Two alloys namely, Fe-20Cr and Fe-20Cr-4Al were prepared in an electric induction furnace and forged at 980 ºC. Specimens (10x10x2 mm) of these alloys were cut, ground to 200 mesh, degreased in acetone and weighed.

Lanthanum chromite ($LaCrO_3$) coatings were prepared using a mixture of powders of Cr_2O_3 and La_2O_3. In preliminary tests, samples of this mixture were heated for different duration at various temperatures above 600 ºC and subsequently analyzed using x-ray diffraction (XRD). In the powder mixtures heated for different duration at 600 ºC, the XRD spectra revealed un-reacted La_2O_3, Cr_2O_3, $LaCrO_4$ and La_2CrO_6. The XRD data of the powder mixture heated at 800 ºC indicated the presence of large quantities of $LaCrO_3$ and a small amount of $LaCrO_4$, besides some Cr_2O_3. This indicated that with increase in temperature to 800 ºC and time, the lanthanum compounds transformed to $LaCrO_3$. [11] On the basis of these results, 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 lanthanum chromite formed and the surface oxides were quite adherent. The average coating thickness was 10-15µm. The coated specimens were then weighed and isothermal oxidation tests carried out in a muffle furnace at 1000 ºC 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 for 7 hours at 1000 ºC followed by cooling to room temperature. The specimens were weighed after each cycle. The specimen surfaces were examined in a scanning electron microscope (SEM) and micro-regions analyzed using an energy dispersive spectroscopy (EDS) system coupled to the SEM.

Results and discussion

The x-ray diffraction spectra of the Cr_2O_3 and La_2O_3 powder mixture heated for 1, 2 and 5 h at 800º C is shown in figure 1. The $LaCrO_3$ peaks are evident in these spectra indicating its formation. The spectra also reveal Cr_2O_3 peaks, but no La_2O_3 peaks, indicating thus an excess of only the former in the mixture.

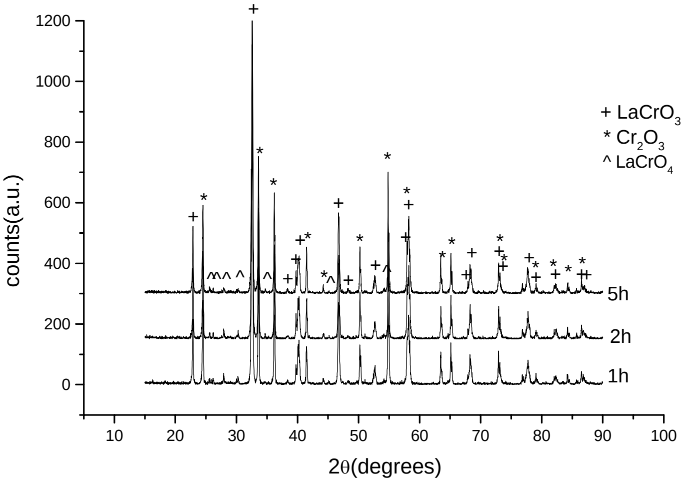


Figure 1. X-ray diffraction spectra of the Cr_2O_3 and La_2O_3 powder mixture heated in air for 1, 2 and 5h at 800 °C.

The weight gain versus time curves of the two alloys, with and without $LaCrO_3$ coating exposed for 200 h at 1000 ºC 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 specimen the least, indicating the 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 alloy specimens, 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.

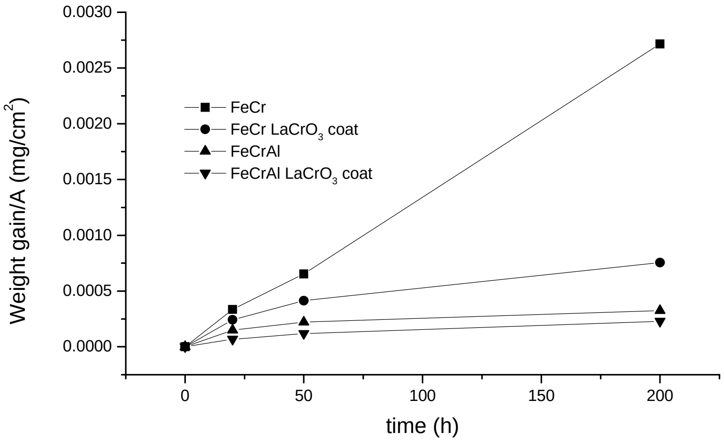
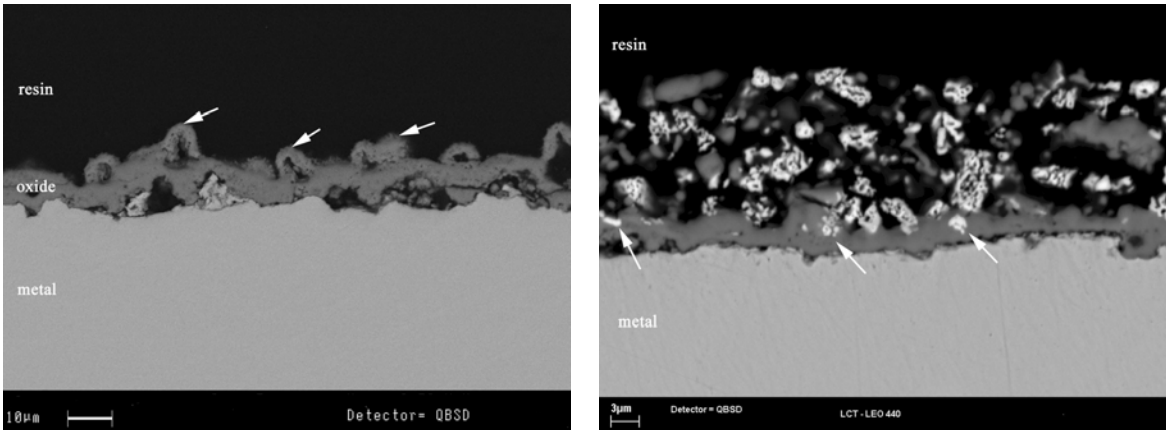


Figure 2. Oxidation curves of alloys Fe-20Cr and Fe-20Cr-4Al with and without $LaCrO_3$ coating.

Figure 3a shows the cross section of the Fe-20Cr specimen 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 data indicated that the oxide layer was mainly Cr_2O_3 and the outer part of the oxide layer contained $MnCr_2O_4$. This indicated that Mn diffused faster than Cr through the Cr_2O_3 scale. [12] The oxide layer was about 10 µm in thickness. The cross section of $LaCrO_3$ coated Fe-20Cr after 200 h at 1000 °C is shown in figure 3b. The coating is porous and adherent. The oxide layer (grey), about 3.5 µm thick, revealed embedded particles from the coating and XRD analysis of this layer indicated $MnCr_2O_4$, Cr_2O_3 and $LaCrO_3$. EDS and XRD analyses data indicated that the dark particles in the oxide layer were un-reacted Cr_2O_3 and the light particles, $LaCrO_3$. The cross sections of uncoated and coated Fe-20Cr-4Al alloy specimen oxidized for 200 h at 1000 °C are shown in figures 4a and 4b. In figure 4a, besides the α-Al_2O_3 layer, interfacial voids formed during growth of the alumina layer can be observed. [13] XRD analysis of the surface layer seen in figure 4b indicated the formation of $LaCrO_3$ and α-Al_2O_3.



(a) (b)

Figure 3. (a) Cross section of Fe-20Cr after 200h of oxidation at 1000 °C; (b) cross section of $LaCrO_3$ coated Fe-20Cr after 200h of oxidation at 1000 °C.

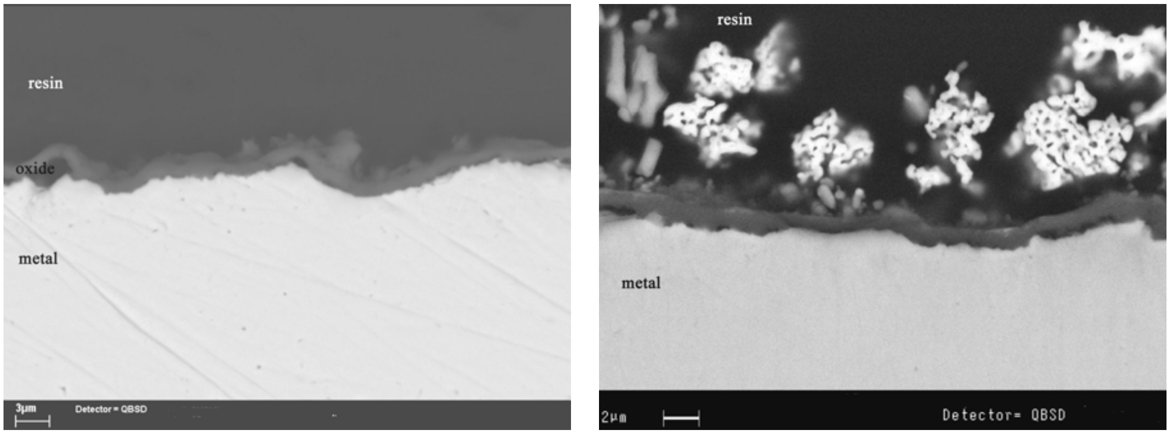


Figure 4. Cross section Fe-20Cr-4Al oxidized for 200 h at 1000 °C. (a) Uncoated; (b) $LaCrO_3$ coated.

The results of cyclic oxidation of the two alloys, with and without the $LaCrO_3$, are shown in figure 5. Neither of the alloys, with or without the coatings exhibited oxide spalling. The coated and uncoated alloys exhibited marked weight gains after the second and first cycle, and thereafter remained constant for up to 15 cycles. This weight change could be attributed to formation of lanthanum chromite and the initiation of scale formation during the first cycle followed by further scale growth during the second cycle. The peak in the change in weight gain of the uncoated Fe-20Cr alloy after the 6th cycle was due to oxide cracking and formation of new oxide.

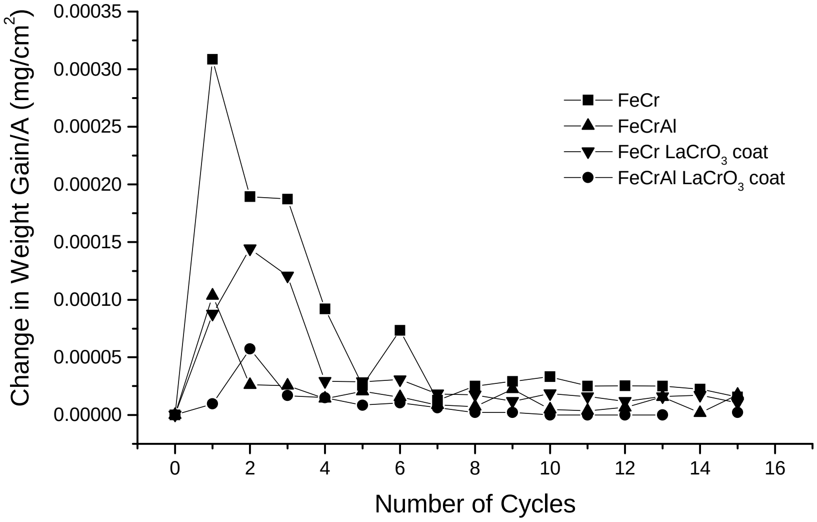
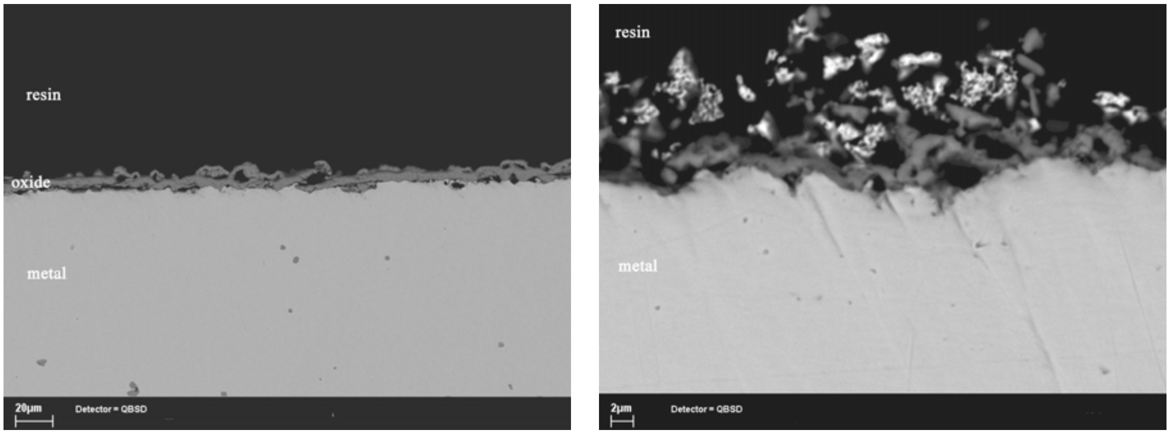


Figure 5. Cyclic oxidation curves of the coated and uncoated alloys. Each cycle consisted of 7h at 1000 °C followed by cooling to room temperature.

The cross sections of uncoated and $LaCrO_3$ coated Fe-20Cr specimens after 15 cycles of oxidation at 1000 °C are shown in Figures 6a and 6b. In Figure 6a, voids, both interfacial and within the oxide can be observed. These features are similar to those observed in specimens oxidized isothermally.



(a) (b)

Figure 6. Cross section of Fe-20Cr after 15 cycles of oxidation in air at 1000 °C: (a) Uncoated; (b) $LaCrO_3$ coated.

Figures 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.

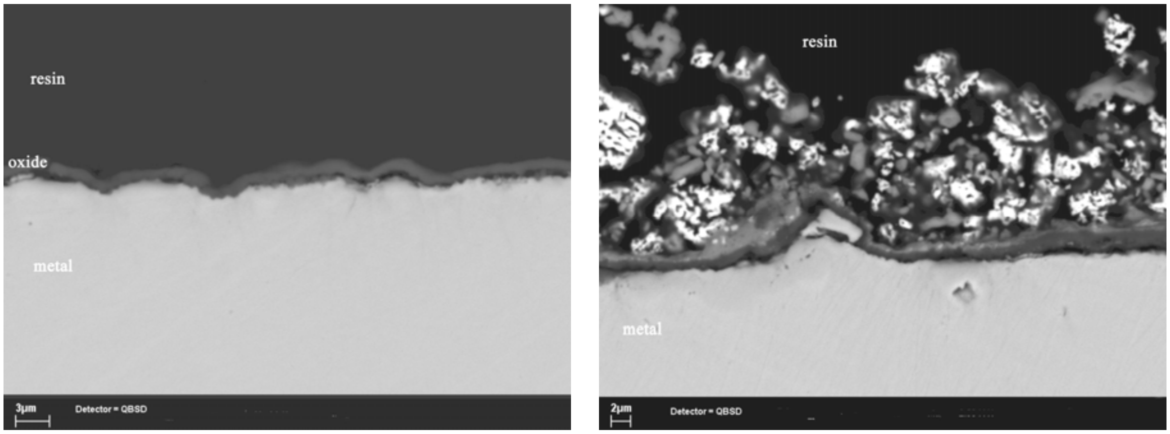


Figure 7. Cross section of Fe-20Cr-4Al after 15 cycles of oxidation in air at 1000 °C: (a) uncoated; (b) $LaCrO_3$ coated.

General discussion

The mechanism by which $LaCrO_3$ coated alloy specimens acquire increased oxidation resistance is the same for the chromium dioxide forming Fe-Cr alloy and the aluminium oxide forming FeCrAl alloy. The surface deposited $LaCrO_3$ gets incorporated into the growing scale, the La ions segregate to the grain boundaries in the scale and diffuse through the scale, to the gas interface. [14] Segregation of the La ion to the scale grain boundaries is driven by forces acquired by it due to its larger ionic radius, compared with that of the Cr or Al ion. [15] Proof of this was shown after prolonged oxidations. [15] The diffusion rate of La through the chromia and the alumina layer vary, being significantly slower in the latter. [16-23] The presence of the La ion at the oxide scale grain boundaries results in two effects. The first effect is inhibition of normal outward short-circuit transport of alloy cations along the scale grain boundaries due to the slower diffusion of the large RE ions. Besides the new rate-limiting step of the overall oxidation process being the inward transport of O^- ions along the scale grain boundaries, the time taken to form the critical scale thickness for spallation to take place is significantly longer. During much of this period, the scale formed is thin, more plastic, more adherent to the alloy and therefore capable of withstanding stresses associated with scale growth and temperature cycling. Similar observations were reported with respect to scale growth on ceria coated Fe-Cr alloys. [24, 25]

The second effect is reduction in oxide scale grain growth and this is due a solute-drag effect of the La ions that are at the scale grain boundaries. [26] This results in small grained oxides on the $LaCrO_3$ coated specimens compared with that formed on the uncoated alloy specimens. [27]

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_2O_3 and Cr_2O_3.
2. The isothermal and cyclic oxidation tests revealed that the lanthanum chromite coated Fe-20Cr and Fe20Cr-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 mitigation of alloy cation diffusion.
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.

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