La_{0.6}Sr_{0.4}CoO₃ Coating on AISI 430 Ferritic Stainless Steel for Application in ITSOFC Interconnects

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Abstract. In order to restrain the high temperature oxidation on metallic interconnects, a ceramic coating is deposited on its surface. For this study a AISI 430 stainless steel was coated with perovskite (La_{0.6}Sr_{0.4}CoO₃) film using the spray pyrolysis technique. Therefore, in this work, the coating morphology and composition was evaluated through X-Ray diffraction and scanning electron microscopy/energy dispersive spectroscopy analyses. The oxidation behavior was also investigated by a high temperature oxidation test. The results obtained showed that the technique employed for the coating deposition was effective, and the resultant crystalline perovskite layer acted significantly in decreasing the oxidation of the AISI 430 stainless steel. An enrichment of Sr and Cr was also observed on the alloy-coating interface, indicating a possible perovskite coating decomposition.

Key words

Interconnects, spray-pyrolysis, perovskite, ferritic stainless steel, coating.

1. Introduction

Intermediate temperature solid oxide fuel cells (ITSOFC) have got much attention in the clean energy production field. This fact may be explained by the advantages regarding its components production, knowing that in the range of its operating temperatures (600-800 °C), less expensive materials can be used for the system manufacturing [1].

The ITSOFC systems are assembled as stacks of single cells consisting of planar anode, electrolyte and cathode respectively, in order to achieve sufficient voltages for

practical applications. These single cells need to be electronically joint together by a component called interconnect. The interconnect function is the cells connection and also the promoting of both the gas distribution for the electrodes and the transportation of the generated electrical current towards the external circuit [2], [3].

AISI 430 ferritic stainless steel has been extensively researched for the ITSOFC interconnects production due to its suitable mechanical properties, high thermal and electronic conductivities, in addition to its easier fabrication and significant lower cost compared to ceramic materials and other metal alloys. However, the chromium oxide (Cr₂O₃ or chromia) scale growth on ferritic stainless steel, under the ITSOFC operating conditions, is regarded as prejudicial because of the decrease on electrical conductivity it promotes on the interconnect. Another point to be considered is the chromium migration during the possible chromia scale evaporation, which may cause problems as cathodic poisoning. Thus, to prevent the problems associated to the continuous oxide growth, a protective coating is required [4], [5], [6].

The coating studied was the conductive perovskite type oxide (La_{0.6}Sr_{0.4}CoO₃) deposited on the AISI 430 ferritic stainless steel using the spray-pyrolysis technique. Therefore, the aim of the present work is to evaluate the effectiveness of the La_{0.6}Sr_{0.4}CoO₃ film when applied as an oxidation barrier and its possible decomposition under the operational conditions.

2. Experimental Section

A. Perovskite coating deposition

To obtain the perovskite coating on AISI 430 samples, a precursor solution was previously prepared from a mixture of La, Sr and Co nitrates in the 0.6:0.4:1.0 proportion. In this case, distilled water and propylene glycol were used as solvent. The samples were heated at 550 °C and the precursor solution was then sprayed on their surface.

After the deposition process, the samples were submitted to a heat treatment at 800 °C for 2 hours to ensure the perovskite transformation, in order to obtain the desired electronic conductivity.

B. High Temperature Oxidation Test

For the oxidation test, the coated samples were exposed to synthetic air atmosphere in a furnace. The samples were then heated at a rate of 10 °C/min until the temperature of 800 °C. This temperature was maintained for many hours and different samples were removed from the furnace at predetermined intervals of 12, 24, 48 and 96 hours. The study of the oxidation kinetics was performed by measuring the samples before and after the test, therefore obtaining the difference in mass due to the oxidation process in the work conditions.

C. Coating Characterization

The analysis of the surface and cross section of the samples was carried out using JSM 5800 scanning electron microscopy (SEM) coupled with EDS analyzer. The samples morphology and chemical analysis were verified in three different cases: 1) non-treated (amorphous perovskite), 2) after the heat treatment (crystalline perovskite) and 3) after the isothermal oxidation test. The samples were also analyzed through X-ray diffraction (XRD, Bruker – AXS – Siemens D5000) Cu K α (0,154 nm) using 25 mA, 40 kV and the 2 θ angle ranged from 20 ° to 70 ° as equipment parameters.

3. Preliminary Results

A. X-ray diffraction (XRD)

Figure 1 shows the XRD patterns for as-deposited films and for the coatings after heat treatment for 2 h at 800 °C. While the as-deposited sample did not show any detectable crystalline phase, the coatings heated treated at 800 °C presented the formation of crystalline $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ phase. These results show the influence of the temperature on the structure transformation and apparently, the temperature of 800 °C is enough to obtain the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ phase in the coating.

Fig. 1. XRD patterns of the films as-deposited and after heat-treatment at 800 °C for 2 hours

B. Coating Morphology and Composition

By the energy dispersive spectroscopy (EDS), it is possible to observe that the spray-pyrolysis technique is effective to obtain a protective perovskite layer with thickness of ~ 4,2 μm . The adhesion of the films to the substrate was checked by sticking a scotch tape to the film and removing it (standard method ABNT NBR 11003-2009). The films showed very good adhesion, because no trace of the film was found on the tape after its removal. The coating after heat treatment and its EDS spectra are shown in Figure 2.

Fig. 2. (a) SEM micrograph of the cross-section of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ coated ferritic stainless steel and (b) EDS spectra taken from point 1.

C. High Temperature Oxidation Behavior of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ Coating

Figure 3 presents the oxidation kinetics of the coated AISI 430 and of the bare AISI 430 oxidized at 800 °C in

air for up to 96 h. In the two cases, the square of specific area mass gain caused by oxidation increases linearly with the oxidation time, satisfying the diffusion-controlled parabolic law as described by equation 1:

$$(\Delta M/A)^2 = K_p \cdot t \quad \text{Equation (1)}$$

Where ΔM is the sample mass gain, A is the sample surface area, t is the oxidation time, and k_p is the parabolic rate coefficient. The values for the mass gain of coated samples showed a significant reduction ($\sim 52\%$ lower) when compared to uncoated samples, presenting an evident protective behavior by the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ coating. The mass gain of the coated sample can be associated to the oxygen inward diffusion and chromium diffusion from the alloy through the coating [7] [8]. From the slope of those lines, it is possible to estimate the oxide scale growth rate, k_p , for the coated and uncoated substrate. The parabolic constant of the substrate coated with $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ was about 77.3% smaller than the parabolic constant for the bare substrate. The calculated values of k_p for 96 h are listed in Table I.

Fig. 4. SEM micrograph and element profiles of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ contact layer on AISI 430 stainless steel after 48 h exposure at 800°C in synthetic air.

Table I: Parabolic constants at 800°C in air for 96 h.

Samples	$k_p (\times 10^{-13} \text{ g}^2\text{cm}^{-4}\text{s}^{-1})$
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ coated	2.63
Bare substrate	11.6

Figure 4 shows the cross section of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ coated ferritic stainless steel oxidized for 48 h. It was possible to observe from line scans (Figure 4b) the chromium diffusion through the coating, and its enrichment close to the interface coating/substrate. And it was also possible to verify the enrichment of Sr on the substrate/coating interface. This result indicates a $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ coating decomposition and possible formation of the Sr/Cr oxides, mentioned by other authors [9].

Figure 5 shows the XRD patterns for the coated substrate after 48h of oxidation test. The diffractogram indicates the presence of a Cr an Mn spinel oxide, normally observed in ferritic stainless steels, and also an oxide composed of Sr and Cr (SrCrO_4). The formation of this oxide can be due to the film decomposition resulting of Sr diffusion from the film towards the metal/substrate interface combined with the Cr diffusion from the substrate to metal/substrate interface. The SrCrO_4 is mentioned by literature as beneficial if formed within the former chromia layer, it is due to the high conductive Sr oxide scale obtained [9]. It is also possible to observe the variation on the film composition based on the film stoichiometry after the oxidation test.

Fig. 5: XRD patterns of $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ -coated AISI 430 substrate oxidized at 800 °C for 96 h in synthetic air.

4. Conclusion

The results showed that spray-pyrolysis technique was effective in obtaining the perovskite coating on AISI 430 stainless steel samples. The coated AISI 430 presented considerable reduction on its oxidation at 800 °C compared to the uncoated ones at the same condition, indicating that the coating obtained is a good oxidation barrier. And a film decomposition was observed.

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