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$LaCrO_3$ Composite Coatings for AISI 444 Stainless Steel Solid Oxide Fuel Cell Interconnects

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Doped lanthanum chromite-based ceramics are the most widely used interconnector material in solid fuel cells (SOFC) since they exhibit significant electrical and thermal conductivity, substantial corrosion resistance and adequate mechanical strength at ambient and high temperatures. The disadvantage of this material is its high cost and poor ductility. The aim of this study is to determine the mechanical and oxidation behavior of a stainless steel (AISI 444) with a $LaCrO_3$ deposition on its surface obtained through spray pyrolisis. Coated and pure AISI 444 materials were characterized by mechanical properties, oxidation behavior, X-ray diffraction and scanning electronic microscopy. Results indicated that the coated material displays better oxidation behavior in comparison to pure stainless steel, but no improvement in mechanical strength. Both materials indicate that deformation behavior depends on testing temperatures.

Keywords: *lanthanum chromite, interconnector, oxidation, mechanical strength, AISI 444*

1. Introduction

Solid oxide fuel cells (SOFC) are a new source of clean energy for electrical generation[1]. Planar cells consist of several cell units separated by an interconnector[2], whose main role is as an electrical connection between the cells. The interconnector must be also compatible with all cell components[3] and stable with respect to oxiding and reducing gases, present in the SOFC. Typical requirements of an interconnect material are: high electronic conductivity, chemical stability, thermal expansion match to other cell components, significant mechanical strength and- thermal conductivity, low manufacturing and material costs[4,5].Lanthanum chromite ($LaCrO_3$) doped with calcium, strontium and magnesium is the most viable material, since it exhibits relatively high electronic conductivity in both fuel and oxidant atmospheres, moderate stability in fuel cell environments and good compatibility with other cell components in terms of phase, microstructure and thermal expansion[1,4,16,17]. Reducing cell operating temperature from 1000 °C to 800 °C makes using metallic materials as interconnects an attractive alternative. The main advantages of metallic over ceramic interconnects are lower manufacturing costs[6] and higher deformation capacity[7]. Chromium- and iron-based alloys are the most widely investigated metallic interconnect materials[5,8,9]. The main drawbacks limiting use of these materials are: low oxidation resistance over the projected service lifetime (40000 h) at high operating temperature[10] and ability to develop oxide scales with sufficiently high electronic conductivity[9]; Cr volatilization, and limited strength at operating cell temperatures[8]. Studies have proposed the use of a coating on the metallic interconnector material as an oxidation layer[7,13,14,15]. Different techniques have focused on developing protective coatings for steel interconnects[11], such as, sol-gel, chemical vapor deposition[12], pulsed laser deposition, plasma spraying[14] and screen-printing[13]. Applying Co/$LaCrO_3$ coating to AISI 430 stainless steel improves oxidation resistance. However, silica networks that form at the metal-scale interface result in scale and pore formation in Co-$LaCrO_3$-coated specimens[7]. Calcium or strontium-doped lanthanum chromite thin film layers are successfully manufactured using a dipping technique, but oxidation performance was not adequate[8]. A protection layer of $MnCo_{1.9}Fe_{0.1}O_4$ spinel can be densified on ferritic steels though reactive sintering. Results show excellent structural and thermo stability of these spinel protection layers; however, the thermal expansion match between the spinel and LaSrCoFe contact layer seems to be insufficient for thermal cycling[12].

The present study describes the thermo-mechanical effect of $LaCrO_3$ as a protective coating on AISI 444 stainless steel.

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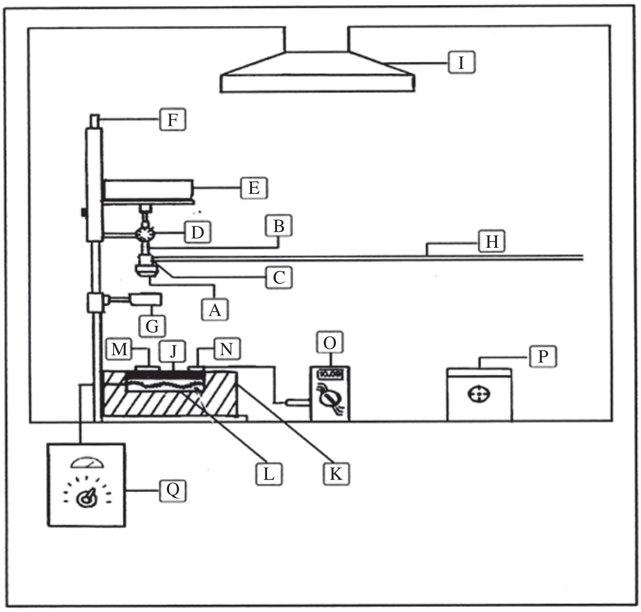


A - Atomizer nozzle
B - Solution inlet
C - Air inlet
D - Flow control valve
E - Solution recipient
F - Support
G - Shutter
H - Line of compressed air or nitrogen gas
I - Exhaustion
J - Stainless steel plate
K - Electrical resistence
M - Substrate
N - Set of thermocouple
O - Millivoltmeter digital
P - Substrate preheater
Q - AC source

Figure 1. Schematic drawing of the spray pyrolisis system.

Table 1. Deposition parameters used in this work.

Nozzle-substrate Distance (d)	35 cm
Solution flow (fs)	2 mL/min
Pressure carrier gas (Pg)	1.5 Kgf.cm^{-2}
Substrate Temperature (Ts)	250 °C
Deposition Time (Td)	30 min
Solution Concentration (C)	0.025 M

Table 2. Chemical composition of ASISI 444 (mass %).

C	Mn	Si	P	S	Cr	Ni	Mo
0.015	0.12	0.54	0.02	0.001	17.55	0.20	1.85
Al	**Cu**	**Co**	**V**	**Nb**	**Ti**	**N**	**O**
0.01	0.03	0.02	0.045	0.16	0.13	0.123	0.023

2. Experimental Procedure

$LaCrO_3$ thin films were deposited on the AISI 444 substrate (ferritic stainless steel, from Arcelor Mittal) using a spray-pyrolysis technique (Figure 1). Polished metallic substrates were ultrasonically cleaned in acetone for 20 minutes, rinsed in distilled water, soaked for 30 s in acetone and then dried.

Precursor solutions for the $LaCrO_3$ thin film coating were prepared from starting materials of lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$) and chromium tri-oxide (CrO_3) (Aldrich Chemicals). Precursor concentration was 0.05 M. Adequate amounts of starting materials were dissolved in distilled water and isopropyl alcohol. Operating conditions for spray pyrolisis used in this investigation are shown in Table 1. Finally, the resulting thin films were heat-treated at 900 °C for 120 minutes in a labor furnace (EDG, Brazil).

The oxidation treatment was examined at 850 and 900 °C for 1.5×10^3 minutes in air. For comparison with non-coated AISI 444, thin film coated and non-coated substrates were oxidized under the same conditions.

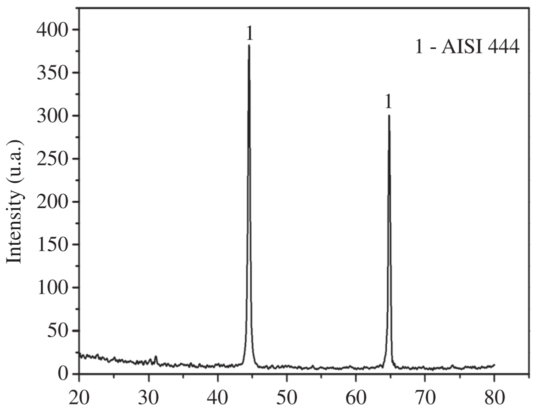
Crystallization and oxidation behavior were analyzed with X-ray diffraction (XRD 6000, Shimadzu) in order to study the stability of both materials at high temperatures.

Mechanical strength of the sintered specimens (average of five bodies for each value) was measured in 20 × 10 × 1.2 mm samples on a universal testing machine (Zwick-Roell, Germany) in three-point bending tests at a constant crosshead speed of 0.5 mm/min under high and ambient temperatures.

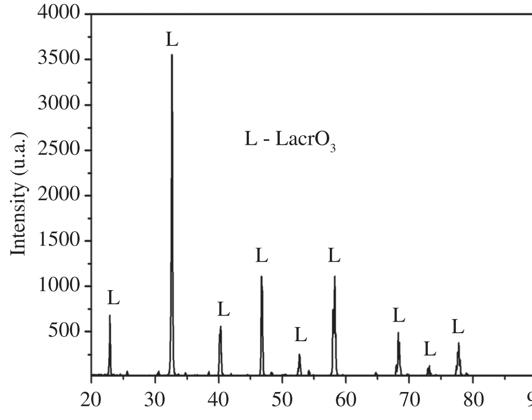
Microstructural aspects of surface and cross-sectional morphology for coated land non-coated materials were examined using optical and scanning electron microcopy (Shimadzu SSX-550).

3. Results and Discussion

Table 2 displays the chemical composition of the stainless steel studied. As expected, the material consists primarily of iron (bal.), carbon (0,025 wt. (%)), manganese (1,0 wt. (%)), phosphorus (0,040 wt. (%)), sulfur (0,030 wt. (%)), silicon (1,00 wt. (%)), nickel (1,00 wt. (%)) and chromium (17.55 wt. (%)). Figure 2 shows the X-ray diffraction pattern of both investigated materials. As expected, pure and coated AISI 444 material indicates the presence of the Fe-Cr phase (AISI 444) and $LaCrO_3$ respectively. No evidence of other phases was found. Figure 3 depicts the microstructural aspects of both materials. As shown, the $LaCrO_3$ material presents a homogeneous grain size distribution, with a grain size of approximately 0.7 µm. Microstructural aspects of the transverse cross-section of AISI 444 with $LaCrO_3$ deposition are presented in Figure 4. The spray pyrolysis process produced a regular $LaCrO_3$ layer along the surface with a layer depth of approximately 100 µm.

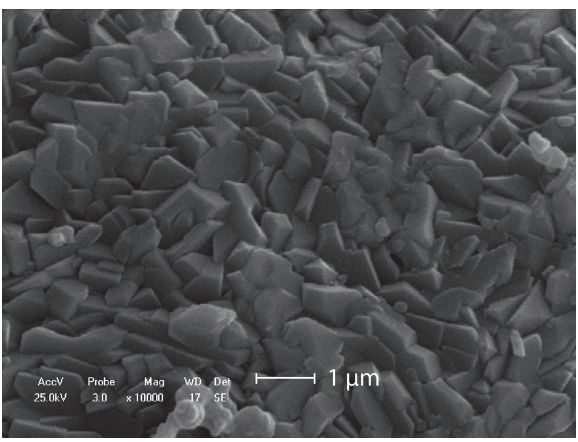


(a)



(b)

Figure 2. X-ray diffraction of: a) AISI 444 and b) AISI 444 with $LaCrO_3$ deposition.



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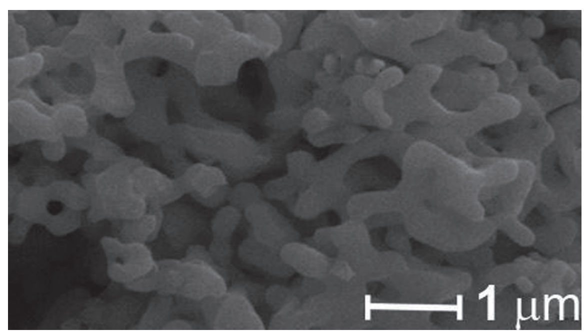
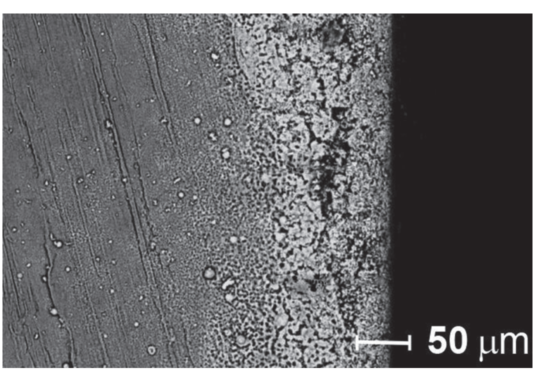


(b)

Figure 3. Surface micrograph of: a) AISI 444 b) AISI 444 with $LaCrO_3$ deposition.



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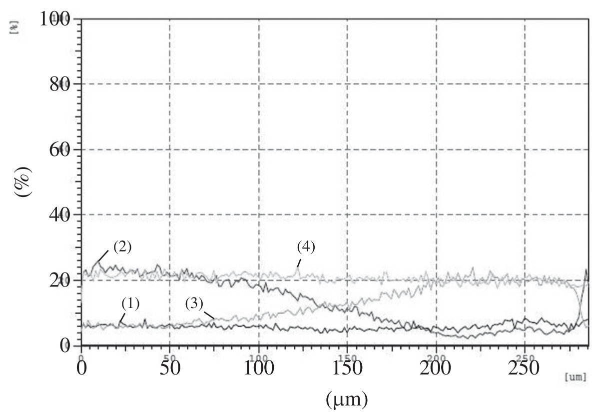


(b)

Figure 4. Transversal section of the coated material.

Figure 4 shows mapping of the principal elements across the transverse section of stainless steel with lanthanum chromite deposition. Results indicate the constant presence of Cr in the stainless steel, along the interface and in deposition. As expected, the concentration of lanthanum is low in the steel region and high in the deposited layer. The amount of Fe element is elevated in the steel and not present in the coated region. Figure 5 presents the strength behavior at ambient and high-temperatures. Both materials exhibited very similar behavior, regardless of temperature. Strength values of the composite materials at ambient temperature are higher when compared to $LaCrO_3$ (180-260 MPa)[4], but similar at 900 °C (50-100 MPa)[10]. At 900 °C, the materials display significantly higher deformation values in comparison to ambient temperature, which is characteristic of metallic behavior (Figure 5). No significant difference was found between materials, which may indicate that deposition has notable effect on strength behavior of metallic substrate. Similar strength behavior was observed for creeping tests in high-Cr ferritic steels[6].

Figure 6 illustrates the oxidation behavior of the investigated materials. Results demonstrated that deposition of $LaCrO_3$ improved oxidation resistance of pure AISI 444, regardless of oxidation temperature. Weight gain of coated materials was significantly lower in relation to stainless steel.

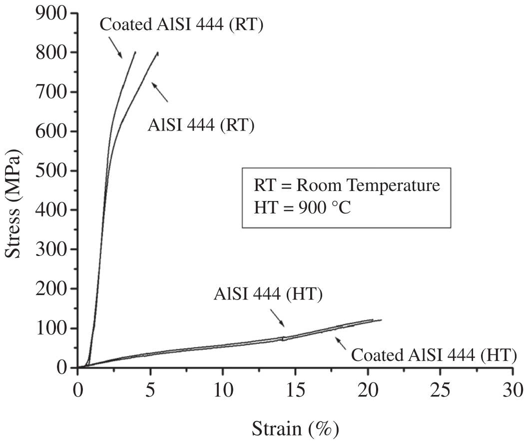


Figure 5. Strength behavior of the pure and coated AISI 444 stainless steel material.

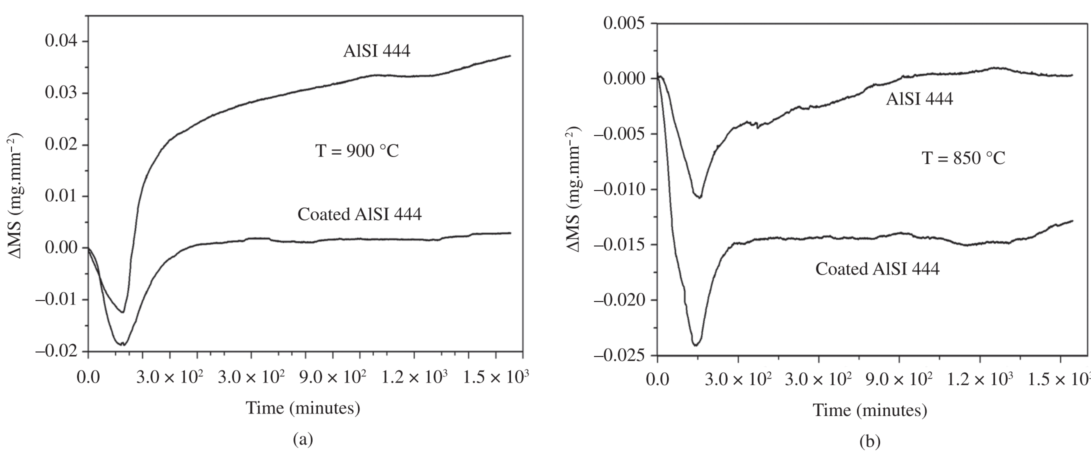


Figure 6. Oxidation behavior at: a) 900 °C and b) 850 °C.

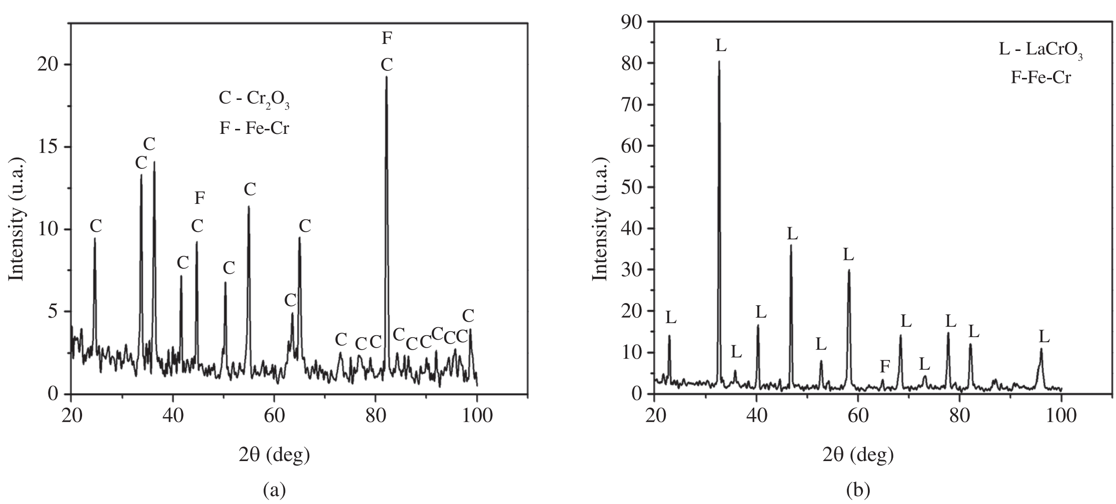
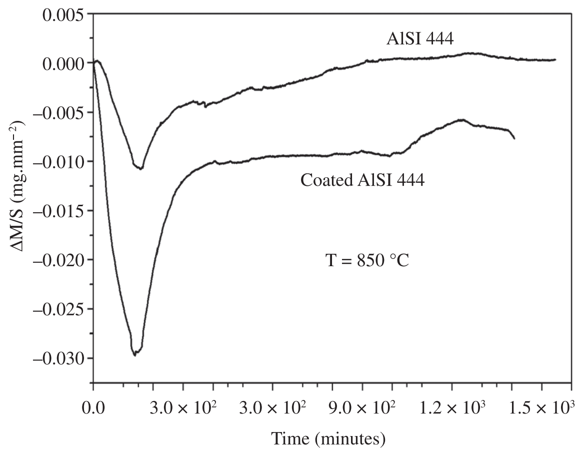
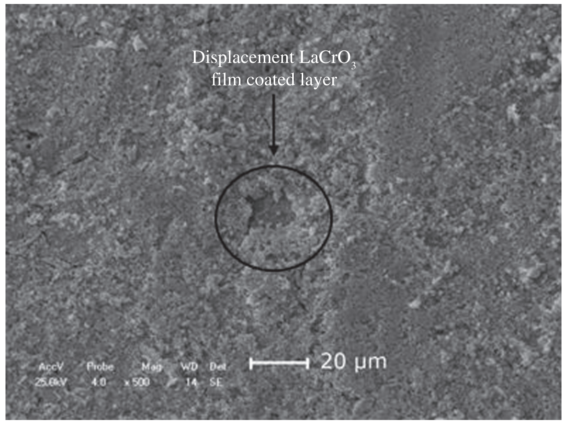


Figure 7. X-ray diffraction pattern of no-coated (a) and coated (b) stainless steel material (after oxidation).



(a)



(b)

Figure 8. Defect on the surface deposition and its consequence.

Application of (La,Sr)FeO_3 protection layers on ferritic steel also resulted in some improvement in oxidation resistance[15].

Figure 7 shows the X-ray diffraction patterns of stainless steel and the coated material after oxidation tests. Analyses indicated the AISI 444 material exhibits formation of a new crystalline phase (Cr_2O_3) at high temperatures. The presence of Cr_2O_3 and similar oxidation behavior was also observed in the literature[8,13]. Furthermore, the coated material displays a new crystalline phase (Fe-Cr), which is evidence of Fe diffusion from the steel across the steel/$LaCrO_3$ interface. Analogous results were also observed elsewhere[7]. No presence of Fe_2O_3 was identified in X-ray diffraction patterns. Figure 8 shows a surface defect on the AISI 444 surface produced during spray pyrolisis. The absence of the protection layer ($LaCrO_3$) on the metal base increases steel oxidation. The coated material demonstrates an abrupt increase in mass gain during analysis (Figure 8). The spray pyrolisis process must be improved in order to avoid such surface defects.

Further studies are still underway in order to optimize the quality of the spray pyrolisis process and its consequent properties. Creep tests should be also performed.

4. Conclusions

Lanthanum chromite thin film layers are successfully manufactured using a spray pyrolisis technique from precursor solutions. Nevertheless, this process needs to be improved in order to avoid the deposition defect observed on the surface and resulting decrease in the oxidation resistance. A denser microstructure is observed for the $LaCrO_3$ thin film on the AISI 4444 substrate. The use of $LaCrO_3$ coating on the AISI 444 stainless steel significantly improves oxidation resistance. Thermo-mechanical properties of the composite are strongly dependent on the temperature. The material shows substantial strengths and low deformation values at ambient temperature. Increasing test temperature results in a loss of mechanical resistance and greater deformation.

Acknowledgement

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