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High temperature mechanical properties of $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ for SOFC interconnect

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Solid oxide fuel cells (SOFC) require an interconnect for fabrication into stacked cells. This is typically La(Sr, Ca)CrO_3, of which much data on the electrical and physical properties already exists. However, very little information exists on the high temperature mechanical properties of the material, which is a necessity for future design improvements. $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ samples were fabricated into green dry-pressed bars and pellets, and sintered under various heating and cooling regimes. The sinterability and high temperature mechanical properties of the material was then investigated as a function of the dopant concentration. It was observed, for example, that the modulus of rupture of the dry pressed $La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$ ($y \geqslant 0.3$) gave a value of over 110 MPa at 1000 °C. This paper will provide data on the high temperature mechanical properties of the material and its application to the SOFC system.

1. Introduction

Solid oxide fuel cells (SOFC) have the potential for producing electricity with greater efficiency than conventional systems [1, 2]. The planar SOFC system requires an interconnect, or bipolar plate, to allow for stacking the single cells into a multicellular unit. The interconnect material must possess high chemical stability under both oxidizing and reducing environments, high electronic conductivity, similar thermal expansion coefficients to the adjoining cell components, good sinterability and sufficient strength, under the likely conditions employed by the SOFC, to support other cell components [3–5]. As such, the alkaline-earth doped lanthanum chromite systems have been examined in great detail as they are considered to be the most promising candidate materials [6, 7].

The effect of sinterability of the interconnect material has been studied by a number of authors. Flandermeyer and co-workers [8] found that sintering aids such as fluoride mixtures are effective in preparing dense interconnect plates, while Tai and Lessing [9] examined the effect of sintering $La_{1-x}Sr_xCrO_3$ between two Cr_2O_3 plates, with the result of 93% relative density when fired at 1700 °C for 7 h. Chick and co-workers [10] reported 93% densification for $La_{0.76}Sr_{0.24}CrO_3$, when sintered at 1600 °C. Quite recently, Sakai and colleagues [11] discovered that a slight chromium deficiency enhances the sinterability of calcia-doped lanthanum chromite, with more than 94% theoretical density being obtained when sintered at 1400 °C for 5 h. Our recent investigation, on the sinterability of strontia-doped lanthanum chromite, has shown that 96% theoretical density can be obtained for $La_{0.7}Sr_{0.3}CrO_3$ when sintered at 1700 °C in air [12]. However, in most fabrication regimes, particularly when co-firing is employed, 1700 °C is too high a sintering temperature. Recent work has shown that the addition of a B-site dopant, such as Co, improves the sinterability of the strontia-doped lanthanum chromite system [13].

Although the sinterability of the interconnect material has been studied in great detail, the mechanical properties of the material, and particularly the high temperature mechanical properties, have not. Preliminary work by Steele [14] has shown that a value of 300 MPa could be ascertained for $LaCr_{0.8}Mg_{0.2}O_3$, although detailed information was not reported. A number of papers on the mechanical properties of the interconnect system have recently been written, as the problem of long-term mechanical integrity still needs to be solved [13, 15, 16]. Mori and colleagues [15] showed that $La_{0.9}Sr_{0.1}CrO_3$ and $La_{0.9}Ca_{0.1}CrO_3$ had 3-point bend strengths of 268 MPa and 166 MPa at room temperature and 80 and 36 MPa, at 1000 °C, respectively, thus showing the need for a large load-bearing area.

The main purpose of this paper is to provide data on the fracture strength of $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ at high temperature, and its application to SOFC systems. This paper reports on the effect of the sintering temperature on the sinterability, and high temperature mechanical properties of the system $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ for various values of x and y.

2. Experimental procedure

$La_{1-x}Sr_xCr_{1-y}Co_yO_3$ (LSCC) ($x = 0$ to 0.5 and $y = 0$ to 0.2) were synthesized from La_2O_3 (99.9%), $SrCO_3$ (99.995%), $Cr(NO)_3$ (99%) and Co_3O_4 (99.995%) using a polymer precursor method similar to that first described by Pechini [7]. The experimental details of the procedure are described elsewhere [18]; however, it involved dissolving the stoichiometric amounts of the required salts in concentrated nitric acid and

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distilled water. A 50/50 mole ratio of citric acid to ethylene glycol was then added, which formed a polymerized ester when heated to 75 °C. The polymer was then charred at 300 °C for 3 h and pulverized to form a fine particle size. Firing was then undertaken at 900 °C for 5 h and the resulting powders were then milled for 24 h. Powder X-ray analysis, using a Philips powder X-ray diffractometer and CuK_α radiation, was then undertaken on the powders to ensure that they had a single phase perovskite structure. Further sintering and milling were undertaken, where necessary. The particle size of the powders was determined using a Malvern particle size analyser.

The powders were die-pressed into 10 mm diameter pellets of 2 mm thickness for relative density measurements, and bars of $30 \times 10 \times 2$ mm for modulus of rupture measurements, using a conventional die press at 30 MPa. In both cases densification was carried out over the temperature range of 1100–1700 °C, using a heating and cooling rate of 5 °C min^{-1}, in a SiC element furnace. Sinterability was measured using the standard Archimedes' method and was examined in terms of the relative density (d_0/d), where d_0 was calculated using the experimental lattice parameters and the appropriate formula. The fracture strength (modulus of rupture) was measured at room temperature and 600–1000 °C, using a 3-point bend test fabricated for the purpose, with a span of 20 mm and a cross-head speed of 0.5 mm min^{-1}, using an Instron 4204 tensile testing machine interfaced to an IBM computer. All bar samples were polished using SiC and synthetic diamond compound, prior to testing, so that any edge imperfections did not affect the overall result. For measurements at high temperatures, a specially designed split-tube furnace was placed around the 3-point bend apparatus, and the sample was heated in air at a rate of 5 °C min^{-1} and held for 10 min before the measurement. A minimum of five tests were carried out for each sample at each temperature. Weibull analysis was performed on a number of samples and this required a minimum of 15 tests.

3. Results and discussion

3.1. Sintering behaviour

Fig. 1 shows the effect of strontium dopant concentration and sintering temperature on the sinterability of lanthanum chromite ($La_{1-x}Sr_xCrO_3$). The relative density was found to increase with increasing strontium content and reached an optimum value at 30 mol % ($x = 0.3$) for samples sintered at 1600 and 1700 °C, and at 40 mol % for samples sintered at 1500 °C. Further increase in the dopant concentration, however, did not appear to enhance the sinterability characteristics of the material. These results indicate that a maximum value for the sintered density of 96% could be achieved at $x = 0.3$ in $La_{1-x}Sr_xCrO_3$ when sintered at 1700 °C in air. We have also shown, in our previous paper [13], that the sintered density of the material is independent of the synthesis route and as such does not need to be considered in this work.

For practical applications, under such high sintering temperatures, fabrication is uneconomical and

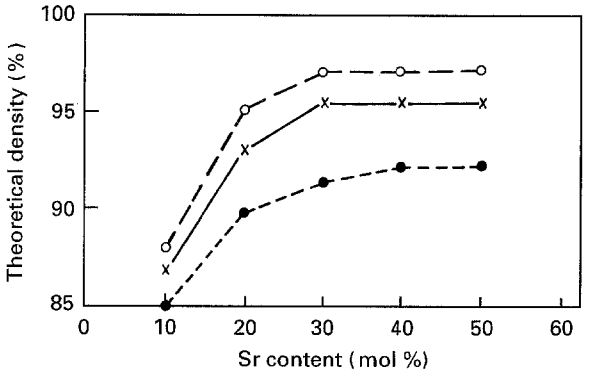

Figure 1 Effect of x in $La_{1-x}Sr_xCrO_3$ on the sinterability, as a function of sintering temperature. ○ 1700 °C; × 1600 °C; ● 1500 °C.

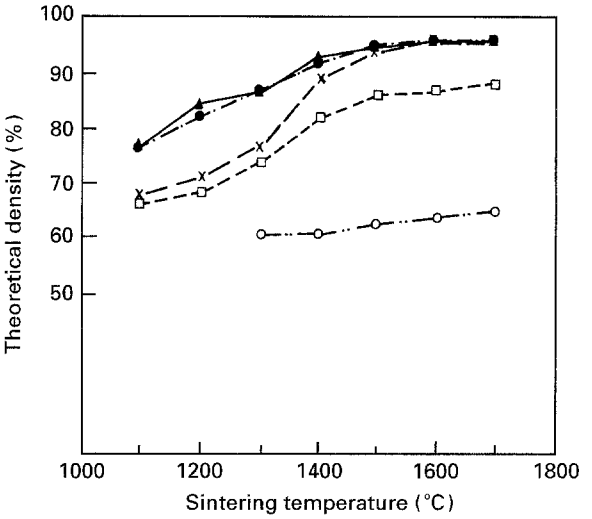

Figure 2 Sinterability of $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ as a function of sintering temperature. ○ $x = 0$, $y = 0$; □ $x = 0.1$, $y = 0$; × $x = 0.1$, $y = 0.1$; ● $x = 0.1$, $y = 0.2$; ▲ $x = 0.1$, $y = 0.3$.

detrimental to the other components which may have to be co-sintered with the interconnect. Therefore, it is important to improve the sinterability of the material in an air atmosphere.

Fig. 2 shows the effect of the sintering temperature on the sinterability of $La_{1-x}Sr_xCr_{1-y}Co_yO_3$. Doping on the B-site showed no significant improvement in the sinterability at temperatures above 1600 °C; however, there was a significant increase in the percentage theoretical density of $La_{0.9}Sr_{0.1}Cr_{1-y}Co_yO_3$ over $La_{0.9}Sr_{0.1}CrO_3$ at sintering temperatures below 1500 °C. At 1400 °C, for example, 92% theoretical density can be achieved for $La_{0.9}Sr_{0.1}Cr_{0.7}Co_{0.3}O_3$ compared to 80% for $La_{0.9}Sr_{0.1}CrO_3$. Hence, to obtain a firing regime at 1500 °C, at least 10 mol % Co must be substituted for Cr in $La_{1-x}Sr_xCr_{1-y}Co_yO_3$. Koc and Anderson [19] observed a similar phenomenon in $La_{1-x}Ca_xCr_{1-y}Co_yO_3$ and indicated that the liquid phase sintering characteristics were dependent upon the amount of Co substitution. No account has, however, been made of the long-term effects of Co substitution on the characteristics of the interconnect/electrolyte/electrode and this must be considered if the system is to be used as an interconnect material.

3.2. Mechanical properties

Fig. 3 shows the modulus of rupture (fracture strength) of strontia-doped lanthanum chromite at temperatures between 600 and 1000 °C. The error bars represent the standard deviations from five independent measurements. These materials were sintered at 1700 °C for 5 h in air. The fracture strengths at room temperature (not shown) were found to be 180, 204 and 234 MPa for $x = 0.1$, 0.2 and 0.3, respectively. In general, the fracture strength was found to decrease with increasing temperature for all samples examined.

The effect of dopant concentration on the fracture strength of $La_{1-x}Sr_xCrO_3$, at 1000 °C is shown in Fig. 4. The sample showed an initial increase in the high temperature fracture strength, with increasing x up to 0.3, which tailed off between $x = 0.3$ and 0.5. Fig. 5(a–c) shows the fracture strength of $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ (for $x = 0.1$, 0.2 and 0.3 respectively) for $y = 0$–0.2 at temperatures between 600–1000 °C. These materials were sintered in air at 1500 °C for 5 h. In general, the fracture strength was found to decrease with increasing temperature for all samples examined. For a particular Sr dopant, although the fracture strength decreases with increasing temperature, it increases significantly with increasing Co-dopant concentration, up to 10 mol %. Further increase in Co content, to 20 mol %, did not show any significant increase in fracture strength for the temperature range of 600–1000 °C.

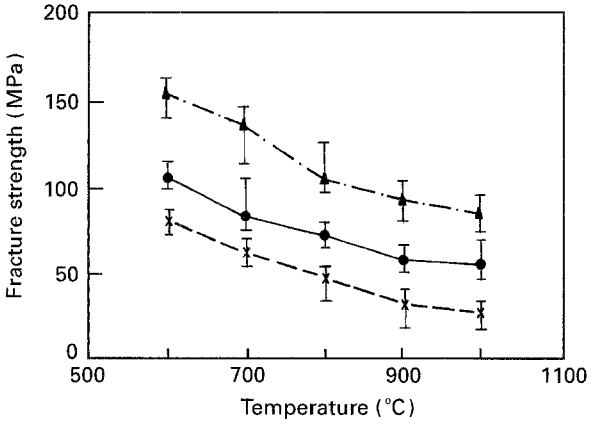

Figure 3 Fracture strength of $La_{1-x}Sr_xCrO_3$ as a function of temperature. × $x = 0.1$; ● $x = 0.2$; ▲ $x = 0.3$.

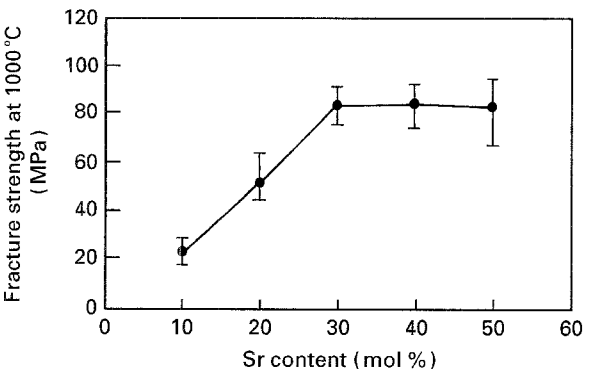

Figure 4 Effect of x in $La_{1-x}Sr_xCrO_3$ on the fracture strength, at 1000 °C.

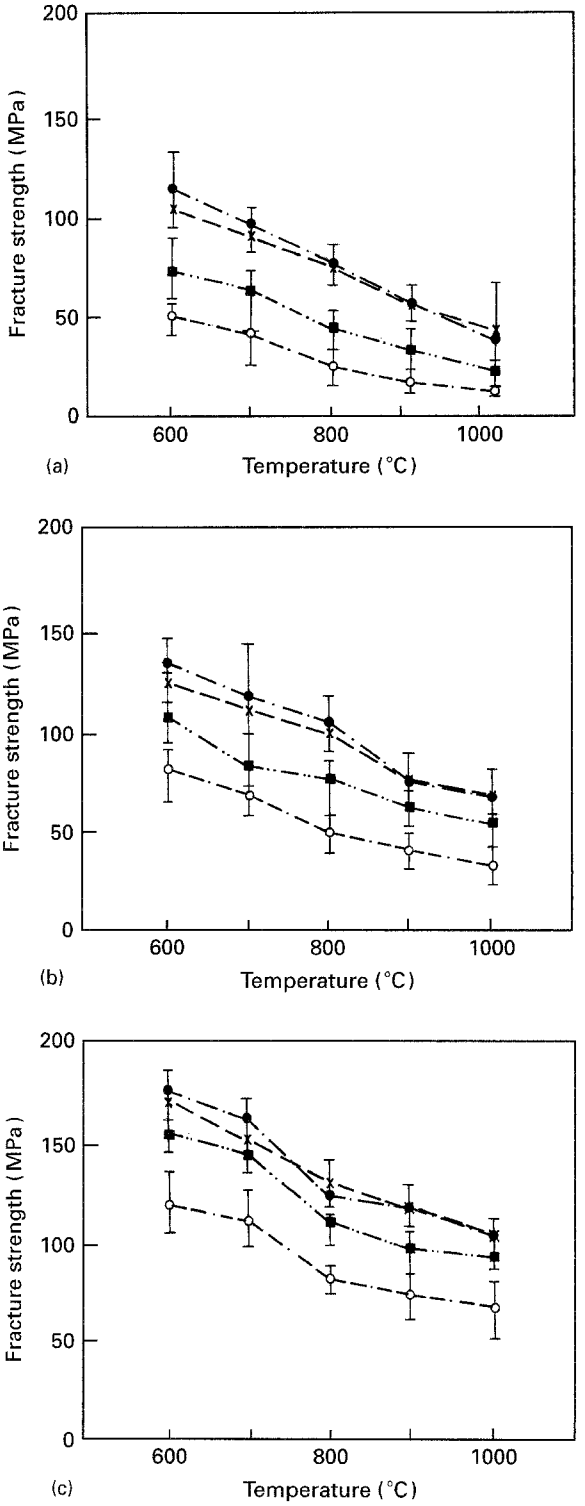

Figure 5 Fracture strength of dry-pressed (a) $La_{0.9}Sr_{0.1}Cr_{1-y}Co_yO_3$, (b) $La_{0.8}Sr_{0.2}Cr_{1-y}Co_yO_3$ and (c) $La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$, with increasing y (to 0.2) as a function of temperature. ○ $y = 0$; ■ $y = 0.05$; × $y = 0.1$; ● $y = 0.2$.

The effect of Co and Sr dopant concentration on the fracture strength of $La_{1-x}Sr_xCr_{1-y}Co_yO_3$, at 1000 °C, is shown in Fig. 6. For a given Sr concentration, the LSCC sample showed a linear increase in the high temperature fracture strength, with increasing Co concentration, up to 10 mol %, and this tailed off between 10 and 30 mol %. For a fixed Co concentration, the fracture strength was found to increase with increasing Sr content up to 30 mol %. Further increase in the Sr content did not make any significant improvement on the fracture strength.

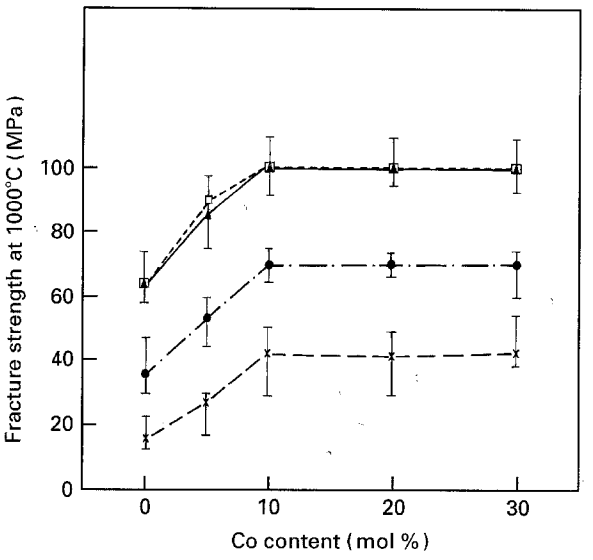

Figure 6 Effect of x and y in $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ on the fracture strength at 1000 °C. × $x = 0.1$; ● $x = 0.2$; ▲ $x = 0.3$; □ $x = 0.4$.

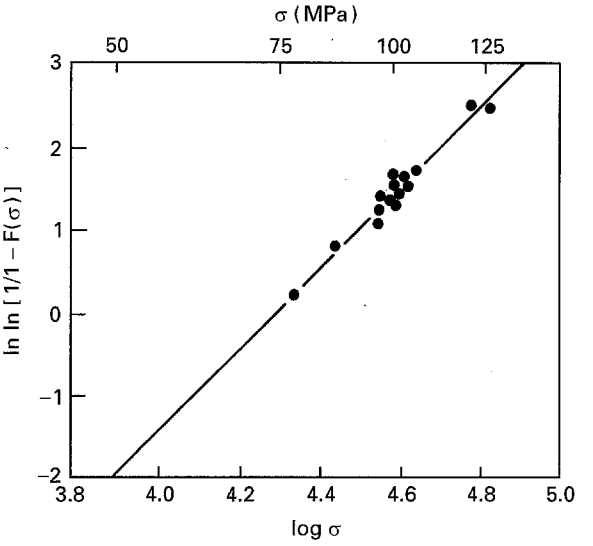

Figure 7 Weibull analysis on the fracture strength values for $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$, tested at 1000 °C. $\sigma_m = 103$ MPa; $m = 9.7$.

A Weibull analysis was undertaken on the fracture strength of $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ at 1000 °C, obtained from the 3-point tests and is given in Fig. 7. The details of this analysis are described elsewhere [20, 21]. A regression coefficient of 0.94 was obtained for this Weibull plot. The range of fracture strengths recorded for the material was relatively small, as indicated by the Weibull modulus ($m = 9.7$), showing that these data points were reliable for the design considerations. However, there are no other data available for this material to compare with the results of the present work.

4. Conclusions

The high temperature mechanical properties of dry-pressed $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ have been studied using a 3-point bend test. The effect of A and B site dopants, in the ABO_3 perovskite, increase the high temperature mechanical properties and the sinterability of the material. An optimum strength of 110 MPa could be realized for $La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$ for $y \geqslant 0.1$, which the Weibull modulus for $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ was reported as being 9.7, showing that the data were reliable.

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