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High-temperature mechanical properties of $La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$ in reducing environments

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$La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$ ($y = 0$–0.2) was synthesized so that it could be sintered at temperatures as low as 1500 °C, producing a highly dense system. The materials were fabricated into bars and mechanically tested using a four-point bend test, from room temperature to 1000 °C. High mechanical strength was obtained at 1000 °C; however, degradation of the mechanical properties was observed in the system at cobalt B-site dopant concentrations as low as 5 mol %, in reducing atmospheres at 1000 °C. $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$, for example, showed degradation after 55 min in H_2 and 75 min in H_2/3%H_2O atmospheres, with total disintegration of the sample soon after. The degradation, and hence loss in mechanical strength, was postulated as being due to reduction of the perovskite, because CoO was observed as a second phase. $La_{0.7}Sr_{0.3}CrO_3$ showed no such degradation in the mechanical strength even after 10 days in H_2 at 1000 °C. Hence, the increased sinterability of cobalt addition on the B-site of La(Sr)CrO_3 is offset by the reduction of stability (and mechanical properties) under either H_2 or H_2/3%H_2O environments.

1. Introduction

Alkaline-earth-doped lanthanum chromite has sufficient electrical conductivity, chemical stability in both reducing and oxidizing atmospheres, and reasonable sinterability, to be used as a dense interconnector in a solid oxide fuel cell (SOFC) [1, 2].

$LaCrO_3$ has poor sinterability in air, but there have been a number of significant improvements made to improve the sinterability, including the addition of sintering aids [3], substitution using A-site transition metals (including calcium or strontium) [4], B-site transition metal substitution (magnesium or cobalt) [5], chromium deficiency, and sintering in a reducing atmosphere or in a chromium-rich atmosphere (use of Cr_2O_3 plates) [6].

Sammes *et al.* [7] have shown that the densification of $La_{1-x}Sr_xCrO_3$ increased with increasing strontium content and increasing dopant concentration, and showed little variation with the powder synthesis route. They showed that 96% theoretical density could be obtained for $La_{0.7}Sr_{0.3}CrO_{3-\delta}$ when sintered at 1700 °C. Chick *et al.* [8] have reported that $La_{0.76}Sr_{0.24}CrO_3$ can be sintered to 95% theoretical density by sintering at 1550 °C, in air, while Sakai *et al.* [9] have shown that $La_{1-x}Ca_xCr_{1-y}O_3$ can be sintered to 95% theoretical density when sintered at 1550 °C in air.

The mechanical properties of doped lanthanum chromite have not been studied in great detail. Steele [10] has shown that $LaCr_{0.8}Mg_{0.2}CrO_{3-\delta}$ has a modulus of rupture of approximately 300 MPa, at room temperature. Sammes *et al.* [11, 12] have shown the effect of sinterability on the modulus of rupture of $La_{1-x}Ca_xCrO_3$ (LCC) and $La_{1-x}Sr_xCrO_3$ (LSC). The authors showed that a maximum strength of 234 and 256 MPa, for LSC and LCC, respectively, could be realized when tested in air at room temperature. Preliminary studies on $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ (LSCC) [13] have shown that a modulus of rupture of 95 MPa can be obtained for $x = 0.3$ and $y = 0.1$, when tested at 1000 °C in air. The effect of the B-site cobalt has been shown to increase the sinterability of the material, and thus the LSCC in this work was sintered at 1500 °C.

The effect of fabrication route on LSC and LSCC has also been studied [14], and the fracture strength of a dry-pressed sample has been found to not vary greatly from a sample that has been calendar rolled.

The instability of LSCC, under the reducing conditions found at the anode, have been briefly examined. $LaCoO_3$ is known to reduce in H_2 to lower oxides, due to the reduction of Co^{III}; eventually forming cobalt metal. However, the preliminary work of Koc and Anderson [15] showed that at cobalt dopant concentrations less than 30 mol % in $La_{1-x}Ca_xCr_{1-y}Co_yO_3$, the system was chemically stable. Our preliminary studies have not shown this to be the case, with $La_{1-x}Sr_xCr_{1-y}Co_yO_3$ ($x = 0.1$–0.3) reducing dramatically in mechanical integrity when tested in H_2 at 1000 °C [16].

2. Experimental procedure

$La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$ ($y = 0, 0.05, 0.1$) was synthesized from La_2O_3 (99.9%), $SrCO_3$ (99.995%),

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$Cr(NO_3)_3$ (99.9%) and Co_3O_4 (99.995%), (all Aldrich Chemicals), using a polymer precursor method similar to that first described by Pechini [17]. The experimental details of the procedure are described elsewhere [18]; however, it involved dissolving the stoichiometric amount of the required salt in concentrated nitric acid and 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 performed on the powders to ensure that they had a single-phase perovskite structure. Further sintering and milling were undertaken, where necessary. Scanning electron microscopy was undertaken using a Hitatchi S4000 system, attached to a Kevex microanalyser.

The powders were pressed into 40 mm × 12 mm × 2.5 mm bars, compacted first using a conventional hydraulic die press at 30 MPa, and then using an isostatic press at 200 MPa, and sintered for 5 h at 1500 °C [13]. This particular configuration was chosen owing to its high sinterability in air [16], with a theoretical density of over 96% attained for all samples examined.

The bars were then exposed to the anode (fuel) atmosphere. First they were placed in a high-temperature tube furnace and heated to 1000 °C at a rate of $5\,°C\,min^{-1}$ in air. On reaching 1000 °C, the samples were purged with argon for 15 min and then exposed to the fuel atmosphere ((a) H_2, (b) $H_2/3\%H_2O$). After the desired time, argon was reintroduced and the sample was cooled to room temperature at a rate of $5\,°C\,min^{-1}$.

The samples were then surface ground and polished using SiC and synthetic diamond compound, prior to testing, to remove any surface defects that may affect the results. The fracture strength was measured at room temperature and at the SOFC operating temperature of 1000 °C, using a four-point bend test fabricated for this purpose, with a span of 30 mm, using an Instron 4204 testing machine interfaced to an IBM personal computer. For high-temperature strength measurements, a specially designed split-tube furnace was placed around the four-point bend test apparatus, and the sample was heated in an argon atmosphere at a rate of $5\,°C\,min^{-1}$ and held for 15 min before the test was performed. A minimum of five tests was carried out for each sample.

3. Results

Fig. 1 shows the effect of temperature on the fracture strength of $La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$ ($y = 0$–0.2) sintered at 1500 °C for 5 h. In general, increasing the temperature at which the test was performed caused a drop in the fracture strength by approximately 40% from 600–1000 °C. This observation has previously been published for $La_{0.9}Sr_{0.1}Cr_{0.9}Co_{0.1}O_3$ [13] and $La_{1-x}Sr_xCrO_{3-x}$ [11, 12]. Increasing the B-site dopant concentration also allowed for an increased fracture strength at all the temperatures measured.

Fig. 2 shows the room-temperature fracture strength for $La_{0.7}Sr_{0.3}Cr_{0.8}Co_{0.2}O_3$, after having been subjected to H_2 at 1000 °C for times ranging from 0–10 min. There is an immediate decrease in the fracture strength of the system, falling from its original 230 MPa to below 150 MPa after only 5 min in H_2. After 9 min in H_2 the sample disintegrated so that no further measurements could be made.

Fig. 3 shows the same stoichiometric sample as Fig. 2 after having been subjected to a gas closer to that observed in the SOFC system, $H_2 + 3\%\ H_2O$ vapour at 1000 °C. This was considered to be less reducing than pure H_2 [19] towards the interconnect material. However, the sample started to lose strength after only 3 min, and after only 7 min was well below half its original value. At times greater than 10 min, the sample could no longer be tested owing to its disintegrated nature.

Fig. 4 shows the fracture strength at 1000 °C for the sample described above, after having been subjected

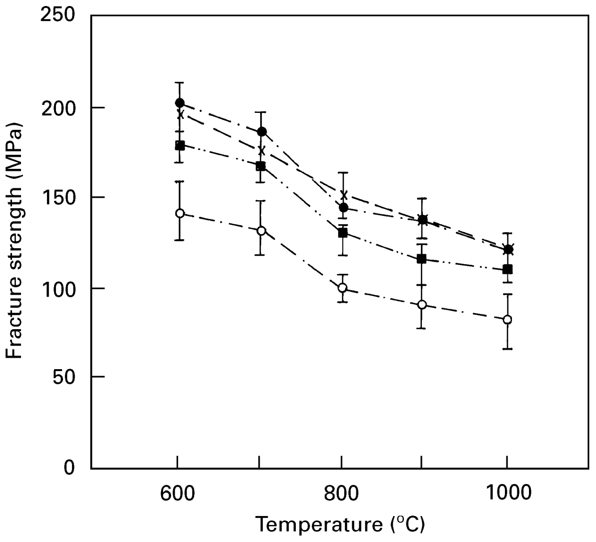

Figure 1 The effect of temperature on the fracture strength of $La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$. y = (○) 0, (■) 0.05, (×) 0.1, (●) 0.2.

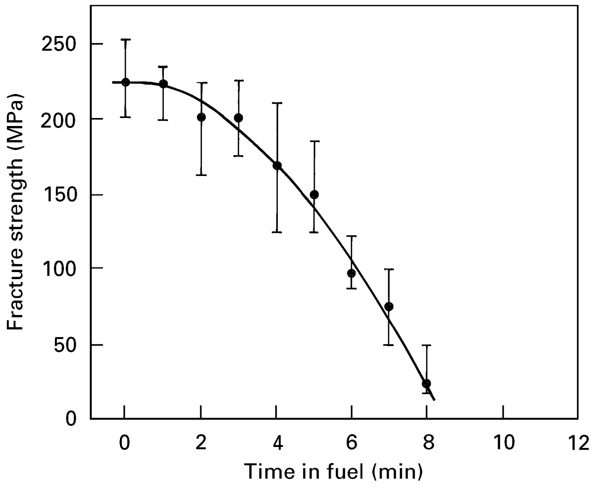

Figure 2 Room-temperature fracture strength of $La_{0.7}Sr_{0.3}Cr_{0.8}\cdot Co_{0.2}O_3$ in H_2 for various times.

to $H_2/3\%H_2O$ at 1000 °C. It is interesting to note that the decrease in fracture strength follows the same trend as that observed for the room-temperature strength; the decrease is again observed after only 3 min in the fuel gas stream.

For comparative purposes, $La_{0.7}Sr_{0.3}CrO_3$ was subjected to a H_2 gas stream at 1000 °C, and the data are shown in Fig. 5. As is apparent from the figure, there is no degradation in the strength of the sample even after 110 min. It should be noted that the sample has been examined after 10 days at 1000 °C, in a H_2 stream, and no loss in strength was observed.

Figs 6–8 show similar results as those of Figs 2–4; however, $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ was examined. As was seen for $La_{0.7}Sr_{0.3}Cr_{0.8}Co_{0.2}O_3$, the effect of H_2 was slightly more marked than that of $H_2/3\%H_2O$. In fact the sample observed in this work

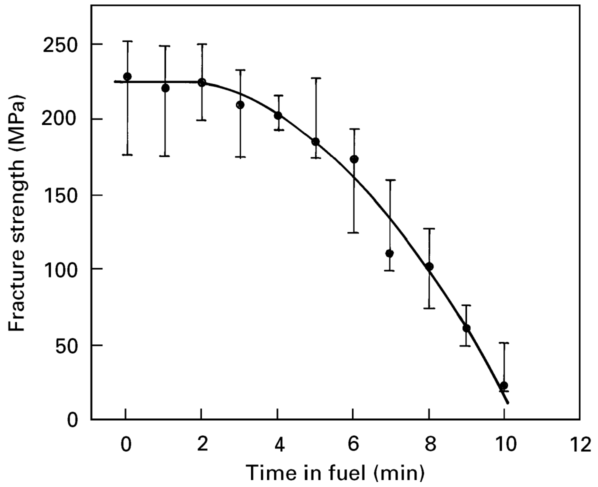

Figure 3 Room-temperature fracture strength of $La_{0.7}Sr_{0.3}Cr_{0.8}\cdot Co_{0.2}O_3$ in $H_2/3\%H_2O$ for various times.

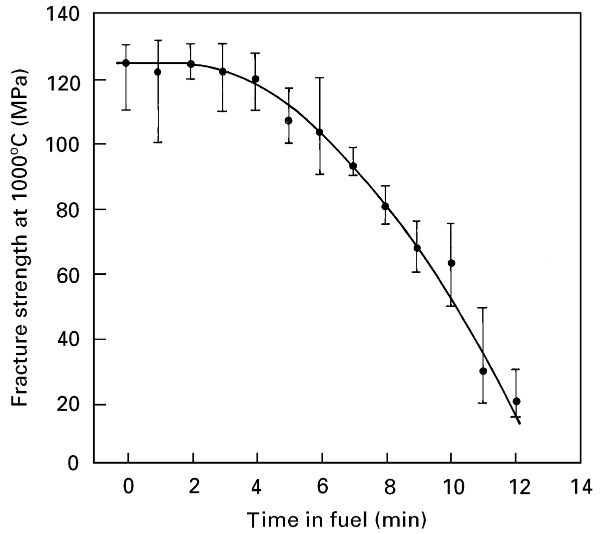

Figure 4 Fracture strength at 1000 °C for $La_{0.7}Sr_{0.3}Cr_{0.8}Co_{0.2}O_3$ in $H_2/3\%H_2O$ for various times.

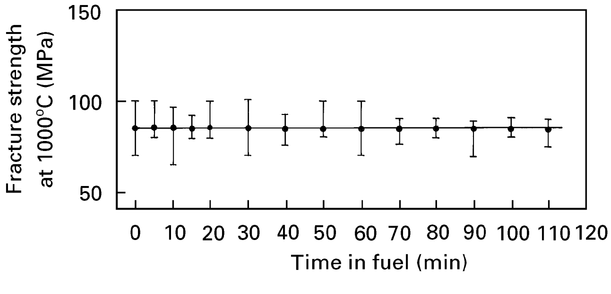

Figure 5 Fracture strength at 1000 °C for $La_{0.7}Sr_{0.3}CrO_3$ in H_2 for various times.

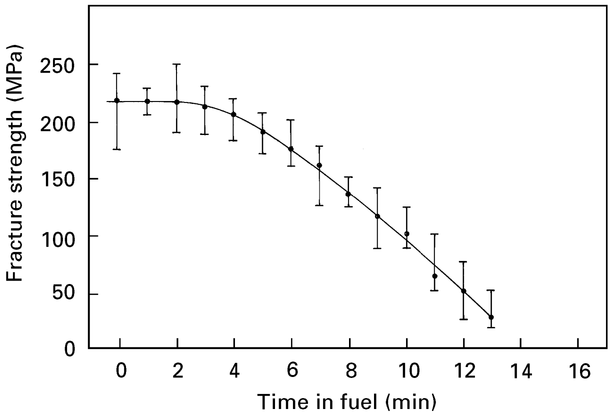

Figure 6 Room-temperature fracture strength of $La_{0.7}Sr_{0.3}Cr_{0.9}\cdot Co_{0.1}O_3$ in H_2 for various times.

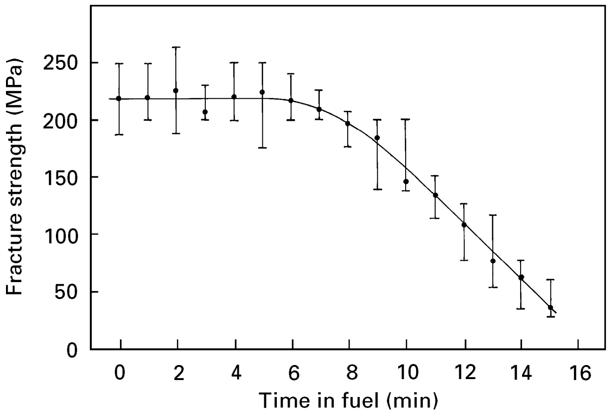

Figure 7 Room-temperature fracture strength of $La_{0.7}Sr_{0.3}Cr_{0.9}\cdot Co_{0.1}O_3$ in $H_2/3\%H_2O$ for various times.

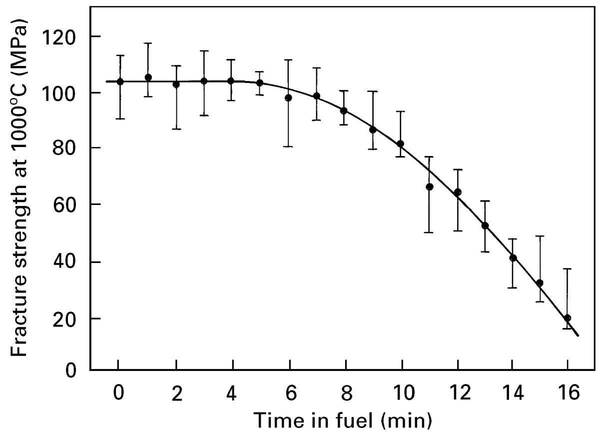

Figure 8 Fracture strength at 1000 °C for $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ in $H_2/3\%H_2O$ for various times.

showed degradation after only 6 min in $H_2/3\%H_2O$ and was apparent for both room-temperature fracture strength and the fracture strength at 1000 °C.

$La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$ was therefore fabricated to try and reduce the amount of B-site cobalt dopant added. The work of Koc and Anderson [20] suggested that the limit for cobalt addition to allow for La(Ca)CrO_3 with stability, was below 30 mol %. From Figs 9–11 it can be seen that this was not the case for La(Sr)CrO_3. Figs 9–11 show $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$ tested under the same conditions as Figs 2–7. In Fig. 9 the fracture strength at room temperature was greatly reduced after the sample had been subjected to only 60 min in H_2 at 1000 °C, and after only 75 min in $H_2/3\%H_2O$ at 1000 °C (Fig. 10). Fig. 11 again showed a similar trend to Fig. 10, where the fracture strength was found to fall from 100 MPa to less than 40 MPa after 100 min.

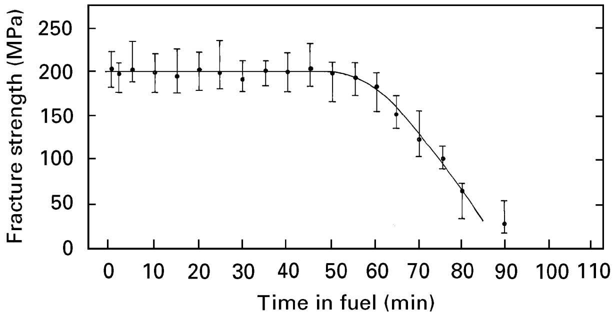

Figure 9 Room-temperature fracture strength of $La_{0.7}Sr_{0.3}Cr_{0.95}\cdot Co_{0.05}O_3$ in H_2 for various times.

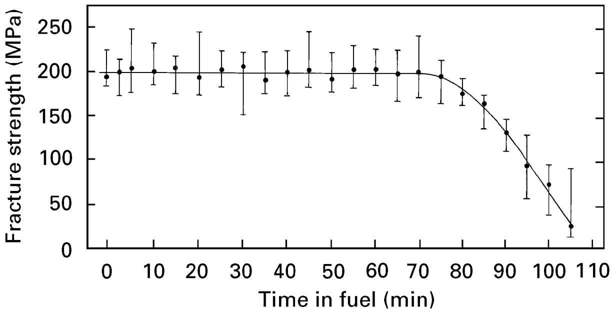

Figure 10 Room-temperature fracture strength of $La_{0.7}Sr_{0.3}Cr_{0.95}\cdot Co_{0.05}O_3$ in $H_2/3\%H_2O$ for various times.

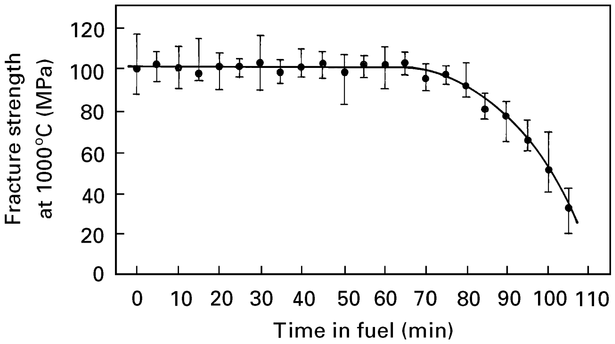

Figure 11 Fracture strength at 1000 °C for $La_{0.7}Sr_{0.3}Cr_{0.95}\cdot Co_{0.05}O_3$ in $H_2/3\%H_2O$ for various times.

SEM analyses of the fracture surfaces of $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ and $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$, tested at room temperature are shown in Fig. 12a and b, respectively. Analysis of the micrographs shows that the failure was transgranular. However, defects approximately 2–3 μm diameter were also present, which are possibly the sources of failure for these samples.

The fracture surfaces of $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ and $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$ samples were tested at 1000 °C in air then analysed, using the SEM, and are shown in Fig. 13a and b. The magnification is the same as that for Fig. 12a and b. The source of failure is very difficult to determine; however, it is apparent that failure was intergranular.

4. Discussion

The present study has revealed that $La_{0.7}Sr_{0.3}Cr_{1-y}\cdot Co_yO_3$ ($y = 0$–0.2) has high mechanical strength when tested at temperatures up to 1000 °C as shown in Fig. 1. This has been previously shown to be due to the high sinterability of the lanthanum chromite system when B-site dopants are added [15, 16]. In fact, previous studies have shown that very high densities, and hence high room-temperature strength, could be realized for samples that had been sintered at temperatures as low as 1400 °C [21]. Previous studies on the

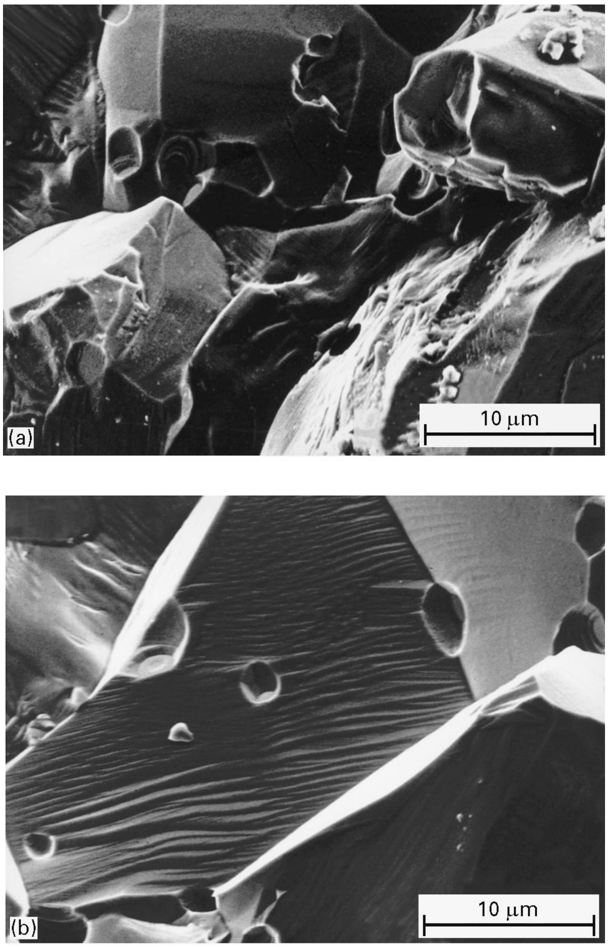

Figure 12 Scanning electron micrographs of the fracture surfaces of (a) $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ and (b) $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$ tested at room temperature.

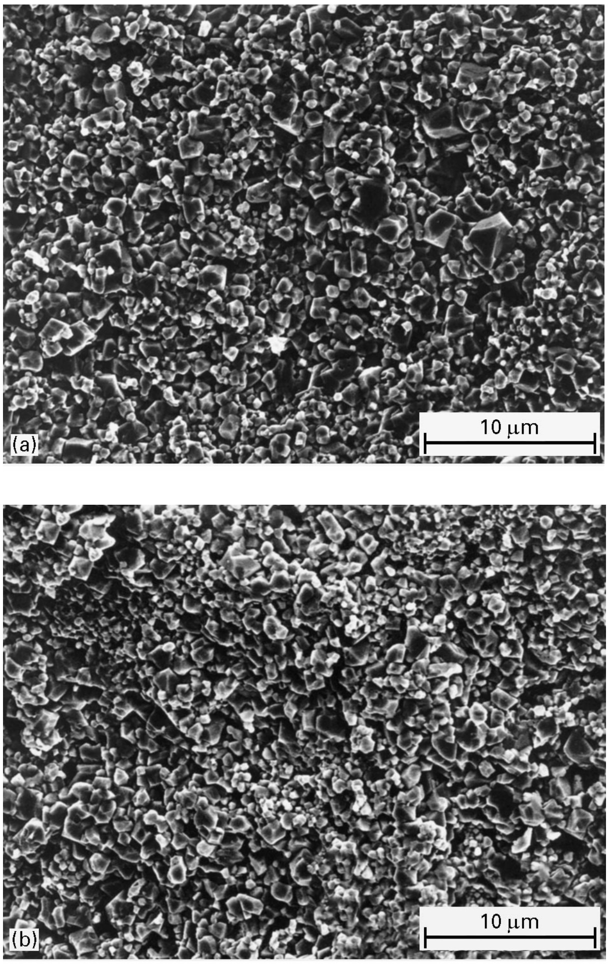

Figure 13 Scanning electron micrographs of the fracture surfaces of (a) $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ and (b) $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$ tested at 1000 °C in air.

TABLE I

Cobalt dopant concentration, y	Degradation time (min)	
	H_2	$H_2/3\%H_2O$
0.05	55	75
0.1	3	6
0.2	< 1	2

sinterability of lanthanum chromite interconnects have primarily concentrated on A-site dopants or slightly non-stoichiometric systems. Sakai *et al.* [9, 22] showed that $(La_{1-x}Ca_x)$ $(Cr_{1-y}Co_y)$ O_3 could be sintered to high density at temperatures as low as 1500 °C in air, and they perceived the formation of chromium deficiency to be the main cause of the high sinterability.

La(Sr) CrO_3 has also been studied, and the increase in sinterability, and hence modulus of rupture, has been postulated as being due to the formation of $SrCrO_3$, which forms a liquid phase, at the sintering temperature, within the first 10 min of sintering [23].

Cobalt substituted lanthanum chromite has been studied by a number of authors. Christiansen *et al.* [21] studied $La_{0.7}Ca_{0.3}Cr_{1-y}Co_yO_3$ ($y = 0$–0.1) and found that high sinterability could be realized at temperatures as low as 1300 °C. However, the authors found that even at cobalt dopant concentrations as low as 5 mol %, some segregation of intermediate and secondary phases was apparent when reducing gases were used. Nakumura *et al.* [24] have, however, previously suggested that A-site substitution of strontium, in $La_{1-x}Sr_xCoO_{3-\delta}$, allows for some stability of the system to reduction due to the resultant charge compensation by the oxidation of Co^{3+} to Co^{4+}. Koc and Anderson [20] also suggested that $La_{1-x}Ca_xCr_{1-y}Co_yO_3$ remained a single phase after reduction at 10^{-19} atm O_2, provided that the B-site cobalt dopant remained below 30 mol% ($x < 0.3$) and perhaps as low as 10 mol%. At higher dopant concentrations, however, they found that $LaCrO_3$ and CoO were the primary phases.

Figs 2–4 show the effect of H_2 and $H_2/3\%H_2O$ on $La_{0.7}Sr_{0.3}Cr_{0.8}Co_{0.2}O_3$ when tested both at room temperature and at 1000 °C. It is very clear that the sample is highly unstable under these reducing environments even for $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ (Figs 6–8) and $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$ (Figs 9–11) under H_2 or $H_2/3\%H_2O$. It is interesting to note that as the B-site dopant concentration is lowered, the stability is slightly increased; the degradation time for different dopant concentrations is summarized in Table I.

What is very apparent is that even for relatively low dopant concentrations ($x = 0.05$), the stability time is still very low. $La_{0.7}Sr_{0.3}CrO_3$ (Fig. 5), however, shows excellent stability in even the most reducing atmosphere, that of pure H_2.

Nakamura *et al.* [25] and Seppanen *et al.* [26] have suggested that the reduction of $LaCoO_3$ at 1000 °C involves a three stage process

$$2LaCoO_3 \rightarrow La_2CoO_4 + CoO + \frac{1}{2}O_2 \tag{1}$$

$$La_2CoO_4 + CoO \rightarrow La_2CoO_4 + Co + \frac{1}{2}O_2 \tag{2}$$

$$La_2CoO_4 \rightarrow La_2O_3 + Co + \frac{1}{2}O_2 \tag{3}$$

The authors found that $LaCoO_3$ was stable across the range 1–10^{-7} atm O_2, and that the later work of Sis *et al.* [27], for example, discovered that this reduction process proceeded through the formation of a series of oxygen-deficient structures of the general formula $LaCo_xO_{3-y}$ ($0 < x \leq 0.08$ and $0 < y \leq 0.5$).

It is, therefore, quite apparent that the amount of cobalt-doping in the lanthanum chromite system must be minimized, and perhaps not used at all.

This work has revealed that high-strength lanthanum chromite materials can be fabricated at sintering temperatures as low as 1500 °C. At B-site dopant concentrations as low as 5 mol% under H_2/H_2O atmospheres, room-temperature strengths in excess of 200 MPa can be realized (Fig. 10) and over 100 MPa at 1000 °C (Fig. 11). Unfortunately, even these systems were only stable for 60–70 min in reducing environments. It was difficult to determine the reason for the degradation. However, preliminary work using EDAX analysis revealed an increase in CoO concentration. No metallic cobalt was apparent in any of the samples examined, even after complete loss of mechanical integrity, which is in accordance with the work of Christiansen *et al.* [21]. A full analysis of the reduction products has, as yet, not been carried out. However, it is very apparent that complete loss of mechanical integrity occurs in all samples where cobalt is present. Further work will be carried out to examine the effect of cobalt additions present in extremely low concentrations (< 1 mol %), and also the mechanism of failure.

5. Conclusions

$La_{0.7}Sr_{0.3}Cr_{1-y}Co_yO_3$ ($y = 0$–0.2) showed high mechanical strength at 1000 °C in air. However, when the samples were pre-treated, at increasing times, in either H_2 or $H_2/3\%H_2O$ at 1000 °C, the mechanical strength dropped dramatically. $La_{0.7}Sr_{0.3}Cr_{0.95}Co_{0.05}O_3$, for example, degraded after only 55 min in H_2 and 75 min in $H_2/3\%H_2O$. The loss in mechanical integrity was postulated as being due to the reduction of the sample forming CoO as a second phase. When no cobalt B-site dopant was added, for example $La_{0.7}Sr_{0.3}CrO_3$, the sample showed stability in H_2 after 10 days at 1000 °C. Hence, the added advantages of lower sintering temperature with cobalt additions are well outweighed by the reduction in H_2 or $H_2/3\%H_2O$ at dopant concentrations as low as 5 mol %.

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