HIGH TEMPERATURE MECHANICAL PROPERTIES OF CALENDAR-ROLLED LANTHANUM CHROMITE INTERCONNECT MATERIAL.

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ABSTRACT

La$_{1-x}$Sr$_x$Cr$_{1-y}$Co$_y$O$_3$ was fabricated using a calendar rolling technique. The green tapes were cut into bars and fired under various heating and cooling regimes. The high temperature mechanical properties of the material were then investigated as a function of the fabrication conditions employed. It was observed, for example, that the modulus of rupture of calendar-rolled La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$Co$_{0.1}$O$_3$, 95MPa at 1000°C, was similar to the dry pressed sample which gave a value of 105MPa at 1000°C. This paper will describe the significance of this result, and other results, in relation to the stacked planar SOFC system.

INTRODUCTION

In recent years, solid oxide fuel cells (SOFC) have gained significant attention because of their very high generating efficiency and the possibility of utilizing a large variety of fuels such as natural gas and methanol (1,2). In the planar design, the interconnect, or bi-polar plate, is an important component of the SOFC as it allows single cells to be stacked into a multi-cellular unit (3). The interconnect must possess high chemical stability in both the oxidising and reducing environments, high electronic conductivity, good sinterability and a thermal expansion coefficient similar to the adjoining cell components (4). The interconnect must also possess significant strength to support the other cell components, particularly in the planar design where the interconnect is considered the load bearing component.

Alkaline-earth doped lanthanum chromites are considered to be the most promising candidates for the interconnect material (5,6). Since it must have sufficient strength to support the other cell components, considerable attention has been paid to improve its sinterability and strength (3).

Our recent investigation, on the sinterability of strontia-doped lanthanum chromite, has shown that 96% theoretical density can be achieved for La$_{0.7}$Sr$_{0.3}$Cr$_3$O$_7$ (LSC) when sintered at 1700°C in air (7). However, in most fabrication processes, 1700°C is too high particularly if a co-firing regime is required. We have also shown that this sintering temperature can be further lowered to 1500°C when 10 mole % Co is added to LSC as a B-site dopant (8).
Although the sinterability of the interconnect material has been studied in great detail, the mechanical properties, especially at high temperature, have not. Quite recently, Mori et al (9) showed that dry-pressed La0.9Sr0.1CrO3 had a three-point bend strength of 268MPa and 80MPa at room temperature and 1000°C respectively. Most sintered bodies, for fabrication into interconnect plates, are produced by slip casting, calendar rolling or other similar techniques. This paper reports on the room temperature and high temperature mechanical properties of calendar rolled La1-xSrxCr1-yCo3O3 (LSCC) system for various values of x and y. A comparison between the strength of the LSCC sample fabricated by dry-pressing and calendar rolling is also reported.

EXPERIMENTAL METHODS

La1-xSrxCr1-yCo3O3 systems (x=0 to 0.5, y=0 to 0.2) were synthesised from La(NO3)2 (99.999%), Sr(NO3)2 (99.995%), Cr(NO3)3 (99.99%) and Co(NO3)2 (99.99%) provided by Aldrich chemicals, using a glycine-nitrate pyrolysis method. The experimental details of the procedure are described elsewhere (10). However, the method involved mixing the solutions of the cation nitrates, in the appropriate stoichiometric proportions, with the correct proportion of glycine, as a fuel, in a granular form or as a solution. The prepared solution was then heated on a hot-plate to evaporate the water, at which point it ignited leaving behind a fine powder which was then fired at 900°C, for 12 hours, to ensure complete formation of the perovskite phase. The resulting powders were then subjected to powder x-ray diffraction, using a Philips powder x-ray diffractometer and Cu Kα radiation, to ensure that they were of a single phase. The surface area of the powders was determined using a NOVA 1000 surface area analyser. Scanning electron microscopy was undertaken using a Hitachi S4000 system, attached to a Kevex microanalyser.

The calendar rolled samples were fabricated by mixing the ceramic powder with a solvent (a mixture of toluene and iso-propyl alcohol) and dispersant, KD1 (ICI C and P Ltd), and milled, using fully stabilised zirconia balls as the milling media, for 12 hours. The plasticizer (see Table 1) and binder (PVB) were then added, and the whole was milled for a further 12 hours.

TABLE 1

| Requirement | Additive          | wt % (relative to the ceramic powder) |
|-------------|------------------|--------------------------------------|
| Dispersant  | KD1              | 2.3                                  |
| Plasticiser | Di-butyl phthalate (DBP) | 7                                    |
|             | Di-octyl phthalate (DOP) | (DBP:DOP:PEG 2:2:1)                  |
|             | Polyethylene glycol (PEG) |                                      |
| Binder      | PVB              | 8                                    |

The slip was then poured into a container and the solvent evaporated off at room temperature, until a plastic mass was obtained. The plastic mass was then calendar-
rolled to the required thickness and shape using a 2-roll mill system (11), producing a material with a relative green density of approximately 65% dense. 30 mm x 10 mm x 2 mm bars were cut from the calendar-rolled tape and sintered at 1700°C for 5 hours \((\text{La}_{1-x}\text{Sr}_x\text{CrO}_3)\) and 1500°C for 5 hours \((\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3)\). The fracture strength (modulus of rupture) was measured at room temperature and 600-1000°C, using a 3-point bend test fabricated for this purpose, with a span of 20 mm and a cross-head speed of 0.5 mm/min, using an Instron 4204 tensile testing machine interfaced to an IBM micro-computer. For high temperature measurements, a specially designed split-tube furnace was placed around the 3-point bend apparatus, and the samples were heated at a rate of 5°C/min, and held for 10 minutes before the measurements were taken. All the bar samples were polished using SiC paper and synthetic diamond paste on a polishing wheel, prior to testing, to ensure that any surface or edge flaws did not affect the overall results. A minimum of 5 tests were carried out for each sample at each temperature.

RESULTS AND DISCUSSION

Fig. 1. shows the modulus of rupture (fracture strength) of the calendar rolled \(\text{La}_{1-x}\text{Sr}_x\text{CrO}_3\), at temperatures between 600 and 900°C. The error bars represent the standard deviation from five independent measurements. These samples were sintered at 1700°C for 5 hours in air. Generally, the fracture strength of calendar rolled \(\text{La}_{1-x}\text{Sr}_x\text{CrO}_3\) was found to decrease with increasing temperature for all samples examined. The fracture strength of the calendar rolled samples was found to be 172 MPa, 186 MPa and 224 MPa, for \(x = 0.1, 0.2\) and 0.3 respectively, compared to 180 MPa, 204 MPa and 234 MPa, for the dry-pressed samples.

The effect of dopant concentration on the fracture strength at 1000°C, for the dry-pressed and calendar rolled samples of the general formula, \(\text{La}_{1-x}\text{Sr}_x\text{CrO}_3\), sintered at 1700°C, is shown in fig. 2. In both cases, calendar rolled and dry-pressed, the samples showed an initial increase in the high temperature fracture strength, with increasing \(x\), up to 0.3, which then tailed off between \(x = 0.3\) and 0.5. The calendar rolled sample had a value of 74 MPa at a Sr level of 30 mole% or above, and the dry-pressed sample gave a slightly higher value of 82 MPa, for the same Sr level.

Fig. 3. (a-c). shows the fracture strength of \(\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Co}_y\text{O}_3\) (LSCC), calendar rolled and sintered at 1500°C for 5 hours, for \(x = 0.1, 0.2\) and 0.3 respectively, at temperatures between 600 and 1000°C. In general, the fracture strength of the calendar rolled material was found to decrease with increasing temperature for all the samples examined. For a particular Sr dopant concentration, although the fracture strength was found to decrease with increasing temperature, it significantly increased with increasing Co concentrations up to 10 mole%. Further increase in the Co concentration, above 20 mole%, did not show any significant effect on the fracture strength in the temperature range examined. The reason for this effect is not well understood, but is partly due to the increase in the sinterability of the material (12), resulting from a possible transient liquid phase. There is some concern about the stability of the system containing Co (13), but our work (8) and the work of Koc and Anderson (12) seems to show that if the
Co content is kept low then the system is stable. Further work is underway to investigate the long term stability of the LSCC system.

The effect of B-site dopant concentration, Co, on the fracture strength of calendar rolled and dry-pressed La_{0.7}Sr_{0.3}Cr_{1.9}Co_{0.1}O_{3}, at 1000°C, is shown in fig. 4. In both cases, the high temperature fracture strength initially increased with increasing Co concentration up to 10 mole%, but then tailed off between 20 and 40 mole%. It can also be seen that the high temperature strength of the dry-pressed samples have a slightly higher fracture strength than for the calendar rolled samples.

Although the dry-pressing method gave a higher high-temperature strength than the calendar rolled method, it does have a number of limitations, especially with respect to the fabrication of interconnect plates. From this investigation, we have shown that in the development of planar solid oxide fuel cells, a non dry-pressed method (calendar rolling, in this particular case) of fabricating the interconnect plates can be employed without any significant loss in the overall strength of the material. Further studies are underway to examine the effect of pre-treating the interconnect materials in different fuel environments, before measuring the mechanical strength.

SUMMARY

The high temperature mechanical properties of calendar rolled La_{1-x}Sr_{x}Cr_{1-y}Co_{y}O_{3} have been studied using a 3-point bend test. The effect of A and B-site dopants, in the ABO_{3} perovskite, were found to increase the room temperature and high temperature fracture strength of the material. An optimum fracture strength of 95 MPa could be realised for calendar rolled La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_{3} at 1000°C, while the dry-pressed sample gave a value of 105 MPa.

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Fig. 1. Fracture strength of calendar rolled La$_{1-x}$Sr$_x$CrO$_3$, sintered at 1700°C, as a function of temperature.

Fig. 2. Effect of x in dry pressed and calendar rolled La$_{1-x}$Sr$_x$CrO$_3$, sintered at 1700°C.
Fig. 3(a). Fracture strength of calendar rolled La$_{0.9}$Sr$_{0.1}$Cr$_{1-y}$Co$_{y}$O$_3$, sintered at 1500°C, as a function of temperature.

Fig. 3(b). Fracture strength of calendar rolled La$_{0.8}$Sr$_{0.2}$Cr$_{1-y}$Co$_{y}$O$_3$, sintered at 1500°C, as a function of temperature.
Fig. 3(c). Fracture strength of calendar rolled La$_{0.7}$Sr$_{0.3}$Cr$_{1-y}$Co$_y$O$_3$, sintered at 1500°C, as a function of temperature.

Fig. 4. Effect of $y$ in La$_{0.7}$Sr$_{0.3}$Cr$_{1-y}$Co$_y$O$_3$, sintered at 1500°C, on the fracture strength at 1000°C.