INCREASED MECHANICAL STRENGTH OF La0.8Ca0.2CrO3 BY IMPROVEMENT OF POWDER PROPERTIES AND SINTERING CONDITIONS

B. Krogh, M. Brustad, M. Dahle, J. L. Eilertsen* and R. Ødegård
Statoil R&D Center, N-7005 Trondheim, Norway

*Presently at the Department of Inorganic Chemistry,
The Norwegian Univ. of Science and Technology,
N-7034 Trondheim, Norway

ABSTRACT

By removing coarse agglomerates in La0.8Ca0.2CrO3 powder with Y2O3 as additive (Pyrox, France), we have been able to improve the mechanical strength of the sintered interconnect material at room temperature by 62% (i.e. the four-point bend strength increased from 76 to 123 MPa). The four-point bend strength at 1000°C for the improved powder showed an increase, according to the present measurements, that was proportional to the increase in the room temperature values (from 57 to 91 MPa). Creep measurements have demonstrated that this material has a considerable creep rate at 1000°C. The effect of different sintering conditions on microstructure are also discussed.

INTRODUCTION

The interconnect material in the Solid Oxide Fuel Cell must meet several extreme requirements, such as high chemical stability in both oxidizing and strongly reducing environments at high temperature, and exhibit sufficiently high electronic conductivity at these harsh conditions. Other requirements are that the thermal expansion coefficient must be close to those of the adjoining cell components, and that the expansion of the crystal lattice under an oxygen potential gradient on the reducing side of the interconnect must be sufficient small in order to minimize internal stresses which otherwise may lead to cracking of the interconnect (1,2). Since the interconnect is the main structural entity in a SOFC stack, the mechanical properties of the interconnect are very important. The fracture strength and creep characteristics of the interconnect are properties which describes whether the material meets the mechanical requirements.

In this work, powder from Pyrox, France, have been used for making interconnect plates. In 1995 mechanical testing of sintered interconnect material, in combination with stack tests (14-40 cell stacks) (3), and thermo mechanical modeling (4), lead to the conclusion that the strength of the interconnect had to be increased.
To improve the strength of the interconnect material two different options were available. The first option was to develop a new powder composition. By changing the type and amount of doping on A- and/or B-site in the perovskite structure of lanthanum chromite the expansion of the crystal can be lowered (5). The second option was to improve the mechanical properties which results when pressing and sintering the powder used throughout the whole StatOil SOFC program. In order to meet a deadline for testing of our 10 kW class SOFC pilot (3), it was decided to go for the second option. The sinteribility of sieved powder was tested and the sintering conditions varied. This resulted in changes in the amount of large agglomerates, in the size of the grains, and in the size and number of pores. The resulting mechanical strength was measured by four-point flexure tests at room temperature and at 1000°C.

EXPERIMENTAL

The powder used in this investigation is made by Pyrox, France, for production of heat elements. The powder with the nominal composition La0.8Ca0.2Cr1.5O3-y and in addition, small amounts of Y (LCCY), is made from a mixture of oxides and heat treated in air at 1000°C. Then small amounts of binder (2 wt% poly vinyl alcohol and 1,5 wt% ethyl cellulose) was added (by Pyrox). In order to be able to study the sintering properties as a function of powder size, the powder was sieved to <38, <53 and <106 μm, respectively (sieving machine in 15 minute).

Preliminary tests were done to find the optimum conditions for uniaxially compacting. Samples of the purchased powder were uniaxially pressed in a steel mould at different pressures, hold times and load cycles in order to find the optimum compacting conditions. According to these tests the powder was then compacted with 3 cycles at 80 MPa into pellets (diameter =19 mm, thickness 5 mm) or plates (90x90x8 mm) and sintered, if not otherwise mentioned, in stagnant air at 1600°C for 5 hours. The heating rate was 30°/h up to 400°C, then 200°/h to 1600°C, including a dwell in 2 hours at 800°C. The cooling rate was 80°/h. 10-20 test bars (4x4x50 mm) for four-point flexure test at room temperature were made from each plate by cutting grinded plates with a diamond saw, giving a surface roughness not greater than 5 μm. The sintering and cutting of plates were performed at Prototech AS, Bergen, Norway.

Four-point flexural test at room temperature were performed by use of a Instron universal testing machine model 1185 loaded at 0.2 mm/min. Some test bars, taken from the same plates, were sent to the Ceram Research Institute, UK, for four-point flexure test at 1000°C. The samples were heated 50°/min, and held at temperature 5 minutes prior to testing. The crosshead speed was 0.5 mm/min.

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Based on earlier indication that this material may show considerable creep at high temperature, we also asked the Ceram Research Institute to perform creep measurements at 1000°C. The two samples were set up in four-point flexure and heated to 1000°C at a rate of 400°/h. Once at temperature there was a dwell period of 30 minutes prior to applying the load equivalent to a stress of 22 MPa in 25 hours.

Densities of the sintered interconnect material were determined by Archimedes’ method, using distilled water as the immersion medium. Green bodies were sintered at different temperatures/time and the resulting microstructure were studied by light microscopy, equipped with Kontron image analyze system and by Electrosca...
Table I. Four-point bend strength at room temperature for two sieving fractions of \( \text{La(Ca)}\text{CrO}_3 \) (Pyrox, France). All samples (4x4x50 mm) was sintered at 1600°C for 2.5 hours.

| Sample                | Number of samples | Mean Failure stress ± standard deviation [MPa] |
|-----------------------|-------------------|-----------------------------------------------|
| Powder as received    | 29                | 76 ± 10                                       |
| Powder sieved at 53 μm| 29                | 122 ± 17                                      |
| Powder sieved at 38 μm| 27                | 112 ± 17                                      |

The result from the bend strength measurements at 1000°C are given in Table II. The Weibull plots for samples of improved powder at each temperature are shown in Figure 2. Bearing in mind that the number of samples are lower for the high temperature tests, the Weibull modules, which is an indication of the scatter in the strength, are almost the same at room temperature \( (m=9) \) and 1000°C \( (m=8) \). The strength of LCCY at 1000°C was 74 % of the strength at room temperature for the samples made of improved powder. We have also showed earlier results of three-point bend test on samples \( (6x6x70\text{mm}) \) at 1000°C made of as received powder, see Table II. The strength at 1000°C was 75 % of the strength at room temperature for the samples made of as received powder, but the difference between high temperature strength and room temperature strength was probably larger, while the three-point flexure tests generally gives larger values then four-point tests. Paulik and Armstrong \( (8) \) have done similar measurements (four-point flexural test) at RT, 600, 800 and 1000°C with \( \text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3 \) (LCC-20) and LCC with other amounts of acceptor doping. They found that the strength of LCC-20 at 1000°C was 57 % of the strength at room temperature (decreased from 97 to 55 MPa). The strength of LCC-20 remained essentially constant from 600 to 1000°C. Relative to room temperature, the proportional decrease in high temperature strengths of the LCCs increased with increasing acceptor doping. Mori et al. \( (9) \) measured the three-point bend strength of LCC-10, and found that the strength at 1000°C was only 22 % of the strength at room temperature (decreased from 166 to 36 MPa).

Table II also shows that the mean modules of elasticity (E-modulus) of LCC at 1000°C was 50 and 51 % of the E-modulus at room temperature for the samples made of as received and improved powder. Fracture analysis of the specimens tested at room temperature indicated that the source of failure were the relatively coarse grain size, and the appearance of clusters of large grains \( (10) \).
The creep in flexure at 1000°C resulted in a final deformation equal to 52 \( \mu m \) after 25 hours, or 0.057 \% creep. The \% creep are calculated by use of the strain equation:

\[
\text{\% creep} = \text{\% strain} = \frac{12dy/(3L^2-4a^2))}{100} \tag{1}
\]

where 
- \( d \) = sample depth (4 mm)
- \( y \) = sample deformation (52 \( \times \) 10\(^{-3} \) mm)
- \( a \) = the distance between the inner and outer rollers (10 mm)
- \( L \) = outer span (40 mm)

Similar measurements done earlier at Statoil R&D Center gave a final deformation of 8 \( \mu m \) after 1.5 hour (sample depth 5.3 mm, load 40 MPa).

To achieve further increase of the strength, the microstructure must be improved. We have performed some sintering measurements, and the resulting grain size distributions are presented in Figure 3. The samples (\( d \)=19 mm) were made of sieved powders and sintered at 1500°C in 10 hours, 1600°C in 5 hours and 1700°C in 1 hour, respectively. As revalued in Figure 3, a distinct shift towards smaller grain sizes can be seen with decreasing sintering temperature.

Table II. Four-point bend strength (samples 4x4x50 mm) at room temperature and at 1000°C for Ca- and Y-doped LaCrO\(_3\), made of as received and powder that was sieved to <53 \( \mu m \) before sintering. The samples made of as received powder tested at 1000°C (6x6x70 mm) where tested in a three-point flexure test. All samples was sintered at 1600°C. The samples made of sieved powder tested at 1000°C were sintered in 5 hours, the others in 2.5 hours.

| Temperature [°C] | Powder as received |       |       | Powder sieved at 53 \( \mu m \) |       |       |
|------------------|-------------------|-------|-------|-------------------------------|-------|-------|
| \( \text{Number of samples} \) | \( \text{Mean Failure stress [MPa]} \) | \( \text{Mean Modulus of Elasticity [GPa]} \) | \( \text{Number of samples} \) | \( \text{Mean Failure stress [MPa]} \) | \( \text{Mean Modulus of Elasticity [GPa]} \) |
| RT              | 29                | 76 ± 10 | 104 ± 23 | 78               | 123 ± 14 | 187 ± 4 |
| 1000            | 12                | 57 ± 4  | 51 ± 9   | 13               | 91 ± 11  | 96 ± 26 |

In Table III the density, average porosity and amount of secondary phase of the three different samples are given. Even if the highest density can be seen at the sample sintered at 1500°C, four point flexure test showed that the average bend strength was somewhat lower than for samples sintered at 1600°C in 5 hours.
This can be due to problems of achieving the same quality for green bodies of the large plates compared to the green body quality of the smaller pellets samples. For the sintering temperature 1500°C, the mean porosity of test bars used in the flexure test varied between 4.0-8.6 % (proportional to bend strength), while the small sample had a value of 3.5%.

The ESEM picture of a sample sintered at 1500°C in Figure 3 shows one large grain among the other much smaller ones. This large grain is evidently present even though we have removed the largest agglomerates in the powder. Large grains are probably determinant for the bend strength, and not the fact that the material consist mainly of fine grains. The smallest amount of secondary phase was found in the sample that have been sintered at the highest temperature, probably due to higher solubility of this phase in the bulk material at higher temperatures.

Table III. Microstructure, measured by image analyzes, for samples sintered at different temperatures. The theoretical density are found from lattice parameters by use of Selected Area Electron Diffraction (SAED)(11).

| Sintering conditions | Archimedes density [g/cm³] | calculated porosity (theor. density 6.34 g/cm³) [%] | measured porosity [%] | amount of secondary phase [%] |
|---------------------|-----------------------------|-----------------------------------------------|------------------------|-----------------------------|
| 1500°C, 10 h        | 6.12                        | 3.5                                           | 3.2 ± 0.4              | 2.5 ± 0.5                   |
| 1600°C, 2.5 h       | 6.09                        | 3.9                                           | 3.9 ± 0.3              | 2.4 ± 0.9                   |
| 1700°C, 1.0 h       | 6.04                        | 4.7                                           | 5.7 ± 0.3              | 1.4 ± 0.5                   |

The higher amount of secondary phase in the material sintered at the lowest temperature, may also contribute to the lower strength for the fine grain material. Sakai et al. (12, 13) have showed that in the chromium deficient LaₓCaₓCrₒ₉ᵧOₒ₃ sintered at temperatures higher than 1300°C, the secondary phase at boundaries and in the triple points consists of Caₓₗ(CrO₄)ₙ (m>n), which further reacts to CaO at sintering temperatures higher than 1600°C. EDS measurements shows that the secondary phase in our material in addition to Ca also contains higher amounts of Y than the average in the bulk phase. In the bulk phase we assume that Y (because of its size) is entering the La-sites in the lattice.
CONCLUSIONS

The chromium deficiency calcium- and yttriumdoped lanthanum chromite have been used as interconnect material in our SOFC stacks. The strength of the interconnect was increased by removing coarse agglomerates in the powder. The mechanical strength of the sintered interconnect material at room temperature are improved by 62%. The four-point bend strength at 1000°C for the improved powder showed an increase, according to the present measurements, that was proportional to the increase in the room temperature values. Creep measurements have demonstrated that this material has a considerable creep rate at 1000°C. Some effects of different sintering conditions on microstructure are also discussed, but more work have to be done to achieve knowledge of the detailed sintering properties of this material.

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Fig. 1. Pictures of sintered samples of as received powder (C), and powder sieved to <106 μm (A), <53 μm (B) and <38 μm (D). All samples were sintered at 1600°C. Length of marker: 1 mm.
Fig. 2. Weibull plot for four-point flexural strength tests at room temperature and 1000°C of interconnect samples made from improved powder. The characteristic strength, $\sigma_o = 130$ MPa at room temperature (RT) and $\sigma_o = 96$ MPa at 1000°C. Weibull modules, $m = 9$ at RT and $m = 8$ at 1000°C.
Fig. 3. ESEM pictures of fractured samples sintered at 1500°C for 10 h (A), 1600°C for 5 h (B) and 1700°C for 1.0 h (C). Included is also the respective grain size distribution found by image analyzing. Length of marker: 100 μm.