SOLUBILITY OF CALCIUM IN LANTHANUM CHROMITE

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ABSTRACT

The solubility of Ca in LaCrO₃ versus temperature was determined using x-ray diffraction. Lattice parameters of the solid solutions ranging from 0 to 40 mol% Ca were calculated from x-ray powder diffraction data and compared with the literature.

These results show that the solubility of Ca in LaCrO₃ and the behavior of the liquid phase associated with the melting of CaCrO₄ depends on how the CaCrO₄ is distributed within the LaCrO₃. The maximum solubility occurs for the most homogeneous distribution.

The maximum solubility of Ca at 1000°C is about 30 mol% and at 900°C it decreases below 20 mol%. This implies that the optimum composition for liquid phase sintering and solid solution stability at SOFC operating temperatures lies in between 20 and 30 mol%.

1. INTRODUCTION

Calcium doped LaCrO₃ or (La,Ca)CrO₃ has been cited for use as a solid oxide fuel cell (SOFC) interconnect because of its favorable electrical conductivity, (> 10 S/cm at 1000°C), chemical stability in oxygen atmospheres as low as 10⁻¹⁸ atm and its thermal expansion compatiblity with other fuel cell components. The monolithic solid oxide fuel cell (MSOFC) design (1) requires co-sintering of all components in a single step process. Sintering should be done in air at temperatures not exceeding 1500°C to retain the desired properties of all the components. However, one of the major obstacles in fabricating the MSOFC is that (La,Ca)CrO₃ is inherently difficult to sinter to high density under the prescribed conditions.
Recently, Sakai and others (2,3) have developed a method to sinter (La,Ca)CrO$_3$ below 1400°C, in air, by adding excess La and Ca to obtain a (La+Ca)/Cr cation ratio greater than unity. They proposed that densification occurred via a liquid phase sintering mechanism.

Our investigations in this system supported their findings (4). The liquid phase was identified and characterized by SEM, X-ray diffraction (XRD) and thermal analysis techniques. It was determined that this liquid phase related directly to the CaO-Cr$_2$O$_3$ pseudo binary phase system. This liquid phase disappears after densification by redissolving into the matrix to form a solid solution, (La, Ca)CrO$_3$, thus it is considered a transient liquid. The ability of this liquid to form a solid solution depends on the Ca content as well as the temperature. The purpose of this study was to determine the solubility limit of Ca in (La, Ca)$_{0.95}$CrO$_3$ as a function of temperature, in air.

2. EXPERIMENTAL PROCEDURE

Powder specimens were prepared using the liquid mix process discussed elsewhere (5). Two series of specimens were prepared for the solubility study. The first, identified as series A, was prepared with the initial composition La$_{0.99-x}$Ca$_x$CrO$_3$, 0.1 ≤ x ≤ 0.55. Precursor chars were calcined at 800°C for 8 hr in air. The resulting powders contained a solid solution, (La, Ca)CrO$_3$, with excess CaCrO$_4$. The fraction of CaCrO$_4$ increased with increasing Ca content (x) as detected by XRD.

Series B was prepared by milling the char in reagent ethyl alcohol for 8 h and calcining at 550°C for 8 hr in argon. The powders prepared were (La$_{0.99-x}$Ca$_x$)CrO$_3$, where x = 0.2, 0.3 and 0.4. The composition x = 0.2 was single phase, whereas 0.3 and 0.4 had some excess CaCrO$_4$. For a given annealing time of 12 h, the apparent solvus temperature is expected to be higher in series A, due to segregation of CaCrO$_4$, as compared to series B where an intimate mixture of fine particles was used as the starting material.

Pellets or powder specimens were placed in a Pt boat, pushed into a heated tube furnace and annealed for 12 to 18 h at temperatures ranging from 800 to 1450°C. A specimen, x = 0.5 from series A was annealed for a longer time, 100

*For the sake of clarity, the notation La$_{0.99-x}$Ca$_x$CrO$_3$ will refer to the initial composition of the mixed cations regardless of the individual phases present. A single phase solid solution of calcium in lanthanum chromite will be denoted by (La, Ca)$_x$CrO$_3$ or more generally, (La, Ca)CrO$_3$. 

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h at 1030°C. After annealing, all specimens were quickly pulled from the furnace and quenched to room temperature in less than 60 secs. The pellets were polished to remove the outer surface prior to XRD examination. Quenched powders were ground in a mortar and pestle before XRD. There was no difference observed between the powder and the pellet specimens of the same composition.

The solvus curve was determined by the disappearing-phase method (6). Quenched specimens at a given temperature, were analyzed for the presence of CaCrO₄. Compositions that showed more than one phase were heated at higher temperatures until a single phase solid was obtained.

Phase analysis was performed on a Scintag XDS 2000 X-ray diffractometer using Cu Kα radiation, λ = 1.5406 Å, at 45 kV and 40 mA. Patterns were run in the step-scan mode with a step size of 0.03° 2θ and with a 1 second time constant. The resolution of the diffractometer was determined by preparing mechanical mixtures of LaCrO₃ and CaCrO₄ using an iterative mixing procedure, and then scanning in the range of the 100% relative intensity peak (20 to 34° in 2θ) for CaCrO₄. Compositions ranged from 0.1 to 5.0 wt% (0.002 to 0.020 mol%) CaCrO₄. The resolution of the diffractometer is illustrated in Figure 1. The 100% intensity peak of the CaCrO₄ phase occurs at 24.6° 2θ. The smallest amount of CaCrO₄ detected was 0.25 wt % (0.004 mol%).

Lattice parameters were calculated for LaCrO₃ and for single phase solid solutions of La₀.₉₉₅CaₓCrO₄, x = 0.1, 0.2, 0.3, and 0.4. The procedure involved mixing the powders with a Si standard followed by slow scanning through the orthorhombic 440, 008, 044, and 404 hkl reflections at step intervals of 0.01° 2θ, with a 4 second time constant. The scan range was chosen to include a Si reflection so that the error in 2θ could be corrected.

3. RESULTS AND DISCUSSION

The cation ratio (La+Ca)/Cr of 0.99 was selected to minimize problems related to the hygroscopic nature of both La₂O₃ and CaO.

The solvus curve, determined from XRD is plotted in Figure 2. The dotted line represents the solubility limit of series A after a 12 hour anneal. Above and to the left of this line, XRD showed a single phase solid solution of orthorhombic (La,Ca)CrO₃. Below and to the right, (La,Ca)CrO₃ was found mixed with CaCrO₄. Similarly, the dashed line represents the solubility limit of series B (low temperature powder). In this case, the solubility limit of Ca approaches the eutectic at 1022°C in the CaO-Cr₂O₃ pseudo binary system (7).
The differences between series A and B may be due to processing. Series A powders were a mechanical mixture of two phases. The CaCrO₄ nucleated, grew and segregated from the (La,Ca)CrO₃ matrix during the calcination process as can be seen in the top center of the SEM micrograph of Figure 3. This was further identified by energy dispersive analysis. When series A was heated above the eutectic temperature, the CaCrO₄ melted, forming pools of liquid within the compact. This liquid did not dissolve into the matrix until the temperature was increased enough to speed up diffusion kinetics.

On the other hand, Series B powders began as a homogeneous mixture of (La₁₀₀Caₓ)₀₉₉CrO₄ solid solution and a slight excess of CaCrO₄. When this series was pushed into the furnace, it was quickly heated past the two phase region into the high temperature solid solution region, allowing very little time for further phase segregation. This series best represents equilibrium conditions.

To further illustrate the difficulty of reforming a solid solution after CaCrO₄ had segregated from the matrix, a series A powder containing 50 mol% Ca, was pushed into a heated furnace at 1030°C and annealed for 100 h. According to the solubility data from the B powder this should have formed a solid solution, obviously it did not. In Figure 4, the XRD data shows that the CaCrO₄ from the 100 h anneal (shaded peaks) did not completely dissolve into the matrix.

Figure 4 also shows that (La,Ca)CrO₃ was quenched in the rhombohedral structure. This is evident by the double peak with the largest intensity. In pure LaCrO₃, the orthorhombic structure is stable to about 240°C above this temperature, it changes to the rhombohedral structure (8). In Ca doped LaCrO₃, the prominent crystal structure was orthorhombic. In most quenched specimens the orthorhombic structure was formed. However, as in the above example, the rhombohedral phase was occasionally quenched to room temperature. At the present time we have no explanation for this behavior.

The lattice parameters were calculated from quenched specimens which formed a complete solid solution crystallizing in the orthorhombic structure. The orthorhombic form has three different parameters a, b and c. The angles α, β and γ are 90° with respect to each other. The lattice parameters and the hkl reflection planes are related to the d-spacing by:

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]  \hspace{1cm} (1)

the lattice parameters were determined by solving three simultaneous equations with three unknowns.

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Lattice parameters and XRD densities of the solid solution La$_{0.99-x}$Ca$_x$CrO$_3$ are listed in Table I. These values are within the error of Berjoan's data (9), furthermore, pure LaCrO$_3$ compares well with the neutron diffraction data of Khattak and Cox (10). Khattak and Cox suggested that the difference between the lattice parameters of La$_{0.99}$CrO$_3$ and LaCrO$_3$ is within experimental error. Therefore, comparing LaCrO$_3$ with La$_{0.99-x}$Ca$_x$CrO$_3$ is justifiable. Figure 5 is a plot of the cell volume vs. Ca content. The line through the data is a least squares fit, having an $r^2 = 0.998$. These data follow Vegard's law which states that the cell volume of a solid solution varies linearly with composition.

4. CONCLUSIONS

The results show that the solubility of Ca in LaCrO$_3$, and the behavior of the liquid phase associated with the melting of CaCrO$_4$, depends on how the CaCrO$_4$ is distributed within the LaCrO$_3$. This is the only difference between series A and B. In series A the CaCrO$_4$ had segregated into crystals as large as 3 µm prior to reheating in the solubility study. In series B most of the CaCrO$_4$ was in solid solution with LaCrO$_3$ and any exsolved CaCrO$_4$ was homogeneously mixed in the system. Evidently the longer diffusion paths associated with the segregated system (series A) impeded the rate of solid solution formation of (La,Ca)CrO$_3$ as compared to the homogeneous system (series B).

The maximum solubility of Ca at 1000°C is about 30 mol % and at 900°C it decreases below 20 mol %. This implies that the optimum composition for liquid phase sintering and solid solution stability at SOFC operating temperatures lies in between 20 and 30 mol%. Lattice parameter measurements show that, at least for the 40 mol % Ca, the solid solutions of (La,Ca)CrO$_3$ exist just above 1030°C.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. D.C. Fee, R.K. Steunenberg, T.D. Claar, R.B. Poeppel, and J.P. Ackerman, p. 74, 1983 Fuel Cell Seminar, Courtesy Associates, Washington DC (1983).
2. N. Sakai, T. Kawada, H. Yokokawa, M. Dokiya, and T. Iwata, "Sinterability and Electrical Conductivity of Calcium-Doped Lanthanum Chromites", J. Mater. Sci. 25, 4531-4534 (1990).

3. M. Mori, N. Sakai, T. Kawada, H. Yokokawa, and M. Dokiya, "Low Temperature Air-Sinterable Lanthanum Calcium Chromite with Chromium Deficit for SOFC Separator", Denki Kagaku, 59[4], 314-319 (1991).

4. J.D. Carter, "The Low-Temperature Sintering Behavior of (La,Ca)CrO₃: Densification of Calcium Doped Lanthanum Chromite via Transient Liquid Phase Sintering", Ph.D. Dissertation, University of Missouri-Rolla (1992).

5. L. Tai, and P. Lessing, "Modified Resin-Intermediate Processing of Perovskite Powders: Part II. Processing for Fine, Nonagglomerated Sr-doped Lanthanum Chromite Powders", J. Mater. Res., 7[2], 511-519 (1992).

6. B.D. Cullity, Elements of X-ray Diffraction, 2nd Ed., (Reading MA: Addison-Wesley, 1978).

7. Z. Pánek, "Phase Equilibria in the System Ca-Cr-O", Silikáty, 25, 169-171 (1981).

8. S. Srilomsak, D.P. Schilling, and H.U. Anderson, "Thermal Expansion Studies on Cathode and Interconnect Oxides", pp. 129-140 in Proc. of the 1st Intl. Symp. on Solid Oxide Fuel Cells, Vol. 89-11. Ed. by S.C. Singhal. The Electrochem. Soc., Pennington, NJ (1989).

9. R. Berjoan, C. Romand, and J.-P. Coutures, "Oxygen Reactivity of La₂O₃-Cr₂O₃-CaO MHD-Related Materials", High Temp. Sci., 13, 173-188 (1980).

10. C.P. Khattak, and D.E. Cox, "Structural Studies of the (La,Sr)CrO₃ System", Mat. Res. Bull., 12 463-472 (1977).
Table I: Lattice Parameters and XRD Densities of (La<sub>x</sub>Ca<sub>y</sub>)CrO<sub>3</sub> Solid Solutions

| Composition x/y | a (Å) ± 0.001 | b (Å) ± 0.001 | c (Å) ± 0.001 | D<sub>x</sub> (g/cm<sup>3</sup>) ± 0.003 |
|-----------------|--------------|--------------|--------------|-------------------------------------|
| 1.0/0           | 5.526        | 5.480        | 7.762        | 6.76                                |
| 0.89/0.1        | 5.494        | 5.467        | 7.739        | 6.54                                |
| 0.79/0.2        | 5.480        | 5.453        | 7.710        | 6.32                                |
| 0.69/0.3        | 5.457        | 5.438        | 7.687        | 6.09                                |
| 0.59/0.4        | 5.435        | 5.421        | 7.671        | 5.86                                |

Figure 1: Mechanical mixtures of LaCrO<sub>3</sub> and CaCrO<sub>4</sub> illustrating the resolution of phase detection in the Scintag x-ray diffractometer. La = LaCrO<sub>3</sub> and Ca = CaCrO<sub>4</sub>.

La = LaCrO<sub>3</sub>  
Ca = CaCrO<sub>4</sub>
Figure 2: The phase boundary between (La,Ca)CrO$_3$ solid solution and a mixture of the solid solution and CaCrO$_4$.

Figure 3: La$_{40}$Ca$_{50}$CrO$_3$ powder calcined at 800°C for 8 h. A ~3 µm CaCrO$_4$ crystal is seen at the top-center of the photo.
Figure 4: XRD data of La$_{49}$Ca$_{50}$CrO$_3$ showing CaCrO$_4$ second phase before (white peaks) and after (shaded peaks) a 100 h anneal at 1030°C. La = LaCrO$_3$ and Ca = CaCrO$_4$. 
Figure 5: Unit cell volume of LaCrO$_3$ vs. Ca content and complete solid solutions of (La$_{0.99}$Ca$_x$)CrO$_3$ where 0.1 $\leq x \leq$ 0.4.