SIMS ANALYSIS OF MATERIALS TRANSPORT IN LANTHANUM CHROMITE INTERCONNECTS

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ABSTRACT

The cation interdiffusion coefficient in alkaline-earth substituted lanthanum chromite is determined for the Sr\textsuperscript{2+}-La\textsubscript{0.75}Ca\textsubscript{0.25}Cr\textsubscript{3} case by using SIMS (secondary ion mass spectrometry). The bulk diffusion coefficient for interdiffusion between Sr\textsuperscript{2+} and Ca\textsuperscript{2+} is 1.2 x 10\textsuperscript{-19} m\textsuperscript{2}s\textsuperscript{-1} at 1273 K in p(O\textsubscript{2}) = 10\textsuperscript{5} Pa, 3.3 x 10\textsuperscript{-19} m\textsuperscript{2}s\textsuperscript{-1} at p(O\textsubscript{2}) = 10\textsuperscript{3} Pa, and 7.0 x 10\textsuperscript{-21} m\textsuperscript{2}s\textsuperscript{-1} at p(O\textsubscript{2}) = 10\textsuperscript{Pa}. The activation energy is 258 kJ mol\textsuperscript{-1} in the temperature range of 1173 ~ 1373 K at p(O\textsubscript{2}) = 10\textsuperscript{3} Pa. The grain boundary diffusion coefficients were found to be linear to \( p(O_2)^{\frac{1}{3}} \).

INTRODUCTION

Material transport is a substantial process in solid oxide fuel cell (SOFC) in which the flux of oxide ion or proton is converted to the electricity. The oxygen permeability determined by the ambipolar diffusion of oxide ion and hole (or electron) significantly affects the efficiency of the cell. On the other hand, the chemical degradation is caused by undesirable migration of cations, such as alkaline earth ions in lanthanum chromite, etc. All migrations are governed by chemical diffusion under a large gradient of chemical potential. Therefore, the chemical diffusion coefficient \( D_i \), abbreviated to \( D \) in this paper) is a very important property to be investigated, especially for electrolytes and interconnects which are exposed to a large \( p(O_2) \) gradient at high temperatures.

We have been interested in ceramic interconnects represented by alkaline-earth-substituted lanthanum chromites, and in mass transport which occurs in this material. Recently, the advantages of tracer diffusion technique using \( ^{18}\text{O}_2 \) in combination with analysis by secondary ion mass spectrometry (SIMS) have been discussed by several researchers for investigation of oxide ion diffusion (1, 2). We have expanded the investigation for calcium substituted lanthanum chromites over a wide range of \( p(O_2) = 10^5 \sim 10^9 \) Pa, and have suggested that the \( p(O_2) \) dependence of oxygen diffusion coefficients \( D_o \) must be taken into account to resolve the large discrepancies which had been reported among the diffusion coefficients measured by different experimental methods (3).

In contrast, the cation diffusion in lanthanum chromites has been investigated by very few researchers. This is partly because it takes long time to obtain a measurable diffusion
profile due to small diffusion coefficients $D_{M}$. However, it is noteworthy that this problem can be overcome by using a SIMS analysis with which we can obtain diffusion profiles with a wide range of depth from ca 10 nm to 1 mm. This allows us to try a variety of experimental procedures in a wide range of temperatures. The other reason for few reports is the difficulty in selection of substance as a tracer. Most of metal isotopes are too expensive to prepare the samples which is needed for making a diffusion couple. Some analogous elements having similar electron coordination can be used instead to carry out the experiments with low cost.

Recently, Horita et al. have tried to determine the diffusion coefficients of alkaline earth in $La_{0.90}Ca_{0.15}CrO_{3}$ via bulk and via grain boundary. They painted Sr(NO$_3$)$_2$ at the surface of sintered pellet, and the interdiffusion coefficient between Sr$^{2+}$ and Ca$^{2+}$ was derived from depth profile of relative strontium concentration determined by using SIMS analysis. In their paper, very high strontium concentration was observed on a fracture surface as shown in figure 1 and a large grain boundary diffusion coefficient was obtained. In the present paper, we expand this kind of investigation in a wide range of temperature and of oxygen partial pressure, $p(O_2)$. The reliability of the obtained data and analysis procedure is discussed.

EXPERIMENTAL

Sample Preparation

The composition of calcium substituted lanthanum chromites (LCC) was fixed to $La_{0.75}Ca_{0.25}CrO_{3}$. The powder was synthesized by using a liquid mixing method. A slight amount of calcium excess (less than 1 mol %) was used to obtain the samples with high density by sintering in air at 1773 K for 10 h. The relative density ($\rho/\rho_{th}$, $\rho_{th}$ is the theoretical density) is over 99 %, and XRD patterns revealed no secondary phase. No other transition metal components as impurities were detected by EDX analysis. Both surfaces of the sintered pellet were polished by using diamond paste with particle size of 3, 1, ¼ µm.

Dilute (0.05N) aqueous solution of Sr(NO$_3$)$_2$ was used as strontium source, and it was painted on the polished surface of the sintered pellet. After drying at ca. 400 K, each sample was annealed under different conditions at $T - 1173 - 1373$ K and $p(O_2) = 10^3 - 10^5$ Pa. Oxygen partial pressure was regulated by using O$_2$-Ar balanced gas. Annealing time was regulated from 48 to 100 h to result in the diffusion depth in the range 1 ~ 5 µm.

SIMS Analysis

The depth profiles of the intensity of secondary ion, Ca$^+$, Cr$^+$, Sr$^+$, La$^+$ were obtained as a function of measuring time by SIMS (CAMECA ims5f) with O$^+$ as a primary ion (accelerating voltage = 12.5 kV, I = 300 ~ 800 nA, beam diameter = ca. 10 ~ 30 µm). Primary beam was scanned in an area of 250 x 250 µm$.^2$. The depth of sample eroded by the primary beam was subsequently measured by a surface profiler (Dektak$^3$, Veeco/Sloan Technology) An analyzed area for secondary ion is ca. φ33 µm. Intensity ratio of $I_{Sr}/I_{Cr}$ was converted to the concentration ratio $C = C_{Sr}/C_{Cr}$ by assuming that $C_{Sr}/C_{Cr} = 1$ at the surface. Concentration profile as a function of depth was fitted to the Fick's second low solved for a semi-infinite media.
where \( C \) is the concentration \( C_{S_i}/C_{Cr} \) at the depth \( x \) (m) from the sample surface, \( C_0 \) is the concentration \( C_{S_i}/C_{Cr} \) at the surface \((x = 0)\) which is assumed to be unity, \( D \) is the diffusion coefficient \((m^2s^{-1})\) and \( t \) is the annealing time (s). The diffusion coefficient along grain boundary was estimated by using the equation suggested by Le Claire (5).

\[
\left( \frac{\partial \ln C}{\partial x^2} \right)^{5/3} = \left( \frac{dD_{gb}}{0.66} \right) \left( \frac{4D}{t} \right)^{1/2}
\]

where \( d \) is the width of grain boundary (m) and \( D_{gb} \) is the grain boundary diffusion coefficient \((m^2s^{-1})\).

RESULTS AND DISCUSSION

Dependence on temperature \((T)\) and oxygen partial pressure \(p(O_2)\)

An example of raw data is shown in figure 2 as a function of sputtering time. A slight increase in the intensity of \( Ca^+ \) was observed in the vicinity of surface. A possibility of matrix effect is discounted because such an increase did not happen on other ions. Since LCC may have undetectable amount of second phases such as \( Ca_m(CrO_4)_n \) which can migrate via grain boundary at annealing temperature, the increase of \( /Ca \) represents the condensed \( Ca_m(CrO_4)_n \) at the surface. A stable intensity was obtained for \( Cr^+ \) for each measurement, which is the reason why the intensity ratio \( I_{Ca}/I_{Cr} \) is used for the following analysis.

A collected depth profile of \( C = C_{S_i}/C_{Cr} \) is shown in figure 3. The profile can be fitted to equation 1 by using a non-linear least square regression. The effect of grain boundary diffusion is observed as a long tail of the profile, and \( D_{gb} \) was calculated from the result of linear regression of \( \ln C \) and \( x^2 \) assuming the width of grain boundary \( d = 1 \) nm. The obtained diffusion coefficients, \( D \) and \( D_{gb} \) at \( p(O_2) = 10^3 \) Pa, are plotted as a function of annealing temperature in figure 4. The activation energy \((E_A)\) is 258 kJ mol\(^{-1}\) for bulk diffusion \( D \), and 217 kJ mol\(^{-1}\) for grain boundary diffusion, \( D_{gb} \). The effect of oxygen partial pressure, \( p(O_2) \) on \( D \) and \( D_{gb} \) is shown in figure 5 at 1273 K. The \( D_{gb} \) shows a linear dependence on \( p(O_2)^{1/2} \), whereas the \( D \) is not significantly affected by \( p(O_2) \).

Bulk diffusion

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The present absolute value of $D$ at 1273 K is slightly larger than the $D$ for Sr$^{2+}$-L$_{0.90}$Ca$_{0.13}$Cr$_{0.3}$ reported by Horita et al (4) as shown in figure 5. This indicates that the interdiffusion mechanism of Sr$^{2+}$ and Ca$^{2+}$ is almost the same in both cases, whereas some effect of different Ca$^{2+}$ content in LCC may exist. Furthermore, the absolute values and activation energy of bulk diffusion coefficient are comparable with the data of diffusion coefficient of yttrium in YCrO$_3$ reported by Kawamura et al (6). They carried out precise measurement by using a diffusion couple of Y$_2$O$_3$ and Cr$_2$O$_3$ single crystals, and reported a slight difference of diffusion coefficient and activation energy of yttrium in the Y$_2$O$_3$ and the Cr$_2$O$_3$ sides. The $E_A$ was 290 kJ mol$^{-1}$ in the Y$_2$O$_3$ side, and 272 kJ mol$^{-1}$ in the Cr$_2$O$_3$ side. The present diffusion coefficient and activation energy revealed very good agreement with those of yttrium in the Cr$_2$O$_3$ side reported by Kawamura et al. It indicates that the present experimental method and analysis procedure can be useful although they use very rough treatments and unclarified assumptions, for example, $C_{Sr}/C_{Cr} = 1$ at $x = 0$. Such an assumption indicates that strontium originated from Sr(NO$_3$)$_3$ first reacts with chromium component of LCC surface, forming the strontium chromate, SrCrO$_4$.

Grain boundary diffusion

The present data revealed that the effect of grain boundary diffusion was not negligible at each temperature. Assuming the width of the grain boundary to be 1 nm, $D_{gb}$ is $10^5 \sim 10^6$ times larger than bulk diffusion coefficient, $D$. This result can be easily expected because SrCrO$_4$ is the analogue of CaCrO$_4$ which may turn into Ca$_m$(CrO$_4$)$_n$. We previously reported the fast migration and precipitation of Sr-rich compounds in L$_{0.9}$Sr$_{0.1}$Cr$_3$O$_7$ sintered body under the SOFC operating condition(7). It is most reasonable to expect that the strontium component at grain boundary migrates as a form of Sr-Cr-O liquid phase.

The present data of grain boundary diffusion coefficients $D_{gb}$ are compared with previous data of $D_{gb}$ reported by Horita et al in figure 5. The present data have good compatibility with their $D_{gb}$ determined by line scanning method analyzing the strontium concentration profile in the vicinity of grain boundary (= fracture surface) as shown in figure 1. Note that the literature data are somewhat scattered. When the equation 2 is used to estimate $D_{gb}$, the slope of $\ln C$ vs. $x^{\frac{1}{3}}$ should be determined by using a linear regression. However, the slope is very small and it may easily change with the fitting range which is used for linear regression. Furthermore, there remains a question about the value of grain boundary width $d$. In a line scanning method, precise determination of the distance from the fracture surface (= grain boundary) should have been required to derive $D_{gb}$. The distance from the fracture surface shown in figure 1 is about 40 nm, which is generally very difficult to be measured with good accuracy. The uncertainty of the distance may cause some changes in the derived $D_{gb}$.

It is noteworthy that the $D_{gb}$ has a linear dependence with $p(O_2)^{\frac{1}{3}}$. A similar tendency was obtained by Kajimura et al. for the oxide ion conductivity ($\sigma_i$) of L$_{0.87}$Sr$_{0.13}$Cr$_3$O$_7$ (8) in which they suggested the effect of fast ion transport via grain boundary. However, the mechanism is much complicated for the case of cation diffusion. One qualitative explanation can be made in relation with the chemical stability of the Sr-Cr-O

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phase at grain boundary. Since Sr-Cr-O decomposes into SrO and Cr$_2$O$_3$ in reducing atmosphere(7), such precipitates at triple point may prevent the comprehensive connection of diffusion path. However, further experimental data and information are required for quantitative and complete explanation.

CONCLUSION

The experimental method used in the present paper had proven to be useful to investigate diffusion phenomena with simple procedures. The obtained data revealed sufficient accuracy for bulk diffusion coefficients, although several simple assumptions were adopted. The problems lie in the determination of grain boundary diffusion coefficients, and the precise estimation of the width of grain boundary is highly required.

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Figure 1 The concentration map of strontium in the vicinity of the grain boundary of La_{0.93}Ca_{0.13}CrO_3 (ref. 4).

Figure 2 Raw data of depth profile: $T = 1273$ K, $p(O_2) = 10^3$ Pa.
Figure 3  Relative concentration of strontium to chromium ($C = C_{Sr} / C_{Cr}$) as a function of the distance from the surface ($x$): $C$ is assumed to be unity at $x = 0$.

Figure 4  Diffusion coefficient via bulk ($D$) and via grain boundary ($D_{gb}$) as a function of temperature. $p(O_2) = 10^3$ Pa.
Figure 5  Diffusion coefficient via bulk \((D)\) and via grain boundary \((D_{gb})\) as a function of oxygen partial pressure. \(T = 1273\) K. ■ O, the Present data; ◆ + x, Horita et al. (4), ◆, \(D\); +, \(D_{gb}\) determined by depth profile method; x, determined by line scanning method.