DIFFUSION COEFFICIENT OF La$^{3+}$ IN LaCrO$_3$ DETERMINED BY SOLID STATE REACTION

Takaya Akashi*, Makoto Nanko*, Toshio Maruyama* Yuzo Shiraishi**, Jun Tanabe**

*Department of Metallurgical Engineering, Tokyo Institute of Technology 2-12-1 Ookayama, Meguro-ku Tokyo 152, Japan
**Department of Mechanical Engineering, Nippon Institute of Technology 4-1-1 Gakuendai, Miyashirocho, Minamisaitama-gun Saitama 345, Japan

ABSTRACT

The parabolic rate constant for the solid state reaction of $\frac{1}{2}$La$_2$O$_3$ + $\frac{1}{2}$Cr$_2$O$_3$ = LaCrO$_3$ was measured at temperatures between 1483 and 1688K under oxygen pressures of $2.1 \times 10^4 \sim 1.5 \times 10^{-5}$Pa. According to Wagner's theory, the diffusion coefficient of La$^{3+}$ in LaCrO$_3$ was evaluated using the parabolic rate constant and the Gibbs free energy change of the reaction. Diffusion coefficient of lanthanum ion in LaCrO$_3$ at higher oxygen pressure ($P_{O_2} > 10^{-1}$) is given by

$$D_{La^{3+}}/m^2s^{-1} = 8.19 \times 10^{-1} \cdot \exp \left( \frac{-482/kJ\text{ mol}^{-1}}{RT} \right) (P_{O_2}/Pa)^{3/16}a_{Cr_2O_3}^{1/8}$$

where $a_{Cr_2O_3}$ is activity of Cr$_2$O$_3$ and $P_{O_2}$ is oxygen pressure. On the other hand, diffusion coefficient is independent of oxygen pressure at lower oxygen pressure ($P_{O_2} < 10^{-1}$) and given by

$$D_{La^{3+}}/m^2s^{-1} = 7.87 \times 10^{-15} \cdot a_{Cr_2O_3}^{1/5} \text{ (at } T = 1695K)$$

INTRODUCTION

LaCrO$_3$ is a p-type semiconductor[1~3], and it is stable in both oxidizing and reducing atmospheres at elevated temperatures[4, 5]. Due to these properties, LaCrO$_3$ is used as an interconnector for solid oxide fuel cell (SOFC), which is attractive because of its high energy conversion efficiency and clean exhaust gas[6~8]. Since LaCrO$_3$ is used under large change of oxygen pressure at elevated temperature, it is extremely important to understand its transport properties such as demixing and creep. Oxygen ion diffusivity in several oxides with the perovskite structure has been reported[9~15]. On the other hand, cation diffusivity which is related to demixing and creep properties has been scarcely reported [16].
In this paper, the diffusion coefficient of La$^{3+}$ ion in LaCrO$_3$ was determined and the defect reaction in LaCrO$_3$ was discussed. Solid state reaction of

$$\frac{1}{2} \text{La}_2\text{O}_3 + \frac{1}{2} \text{Cr}_2\text{O}_3 \rightarrow \text{LaCrO}_3$$ (1)

was carried out in various oxygen pressures and diffusion coefficient of La$^{3+}$ in LaCrO$_3$ is determined using Gibbs’ free energy of reaction(1) by Wagner’s theory [16,17].

**EXPERIMENTAL**

Single crystals of La$_2$O$_3$ and Cr$_2$O$_3$ were cut into plate. A plane of La$_2$O$_3$ plate was polished with a polishing paper of #4000 and a plane of Cr$_2$O$_3$ plate was polished with diamond abrasive of 4$\mu$m. Diffusion couple was made by facing the polished planes of La$_2$O$_3$ and Cr$_2$O$_3$. The diffusion couple was set in a sample holder with a push rod to obtain intimate contact. Solid state reaction was carried out in the oxygen pressure range of $10^{-5}$Pa to $10^5$Pa and in temperature range of 1483K to 1695K. The oxygen pressure was controlled by air, Ar-O$_2$ or H$_2$-H$_2$O mixed gas. After the reaction, the diffusion couple was mounted in epoxy resin, cut perpendicular to the reaction interface and polished for microstructure observation using scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

**RESULTS**

Figure 1 shows the typical cross sectional view of the diffusion couple after reaction. The diffusion couple was easily separated at the LaCrO$_3$/Cr$_2$O$_3$ interface after cooling so that the epoxy resin is observed between LaCrO$_3$ and Cr$_2$O$_3$. Although starting materials of La$_2$O$_3$ and Cr$_2$O$_3$ are single crystals, the product of LaCrO$_3$ is polycrystalline. Figure 2 and 3 show the thickness of the LaCrO$_3$ layer produced as a function of time. It reveals that the growth rate obeys the parabolic rate law. The straight lines are drawn using the least square fits. The parabolic rate constants are obtained from the slopes. The parabolic rate constant as a function of temperature is shown in Figure 4, and is expressed as follows.

$$k_p/m^2s^{-1} = 2.84 \times \exp\left(\frac{-470/kJmol^{-1}}{RT}\right)$$ (2)

The oxygen pressure of the parabolic rate constant is shown in Figure 5. At higher oxygen pressures, the parabolic rate constant is proportional to $P_{O_2}^{3/16}$. At lower oxygen pressure, it is independent of oxygen pressure.
DISCUSSION

i) Diffusion coefficient of La$^{3+}$ ion

The electrical conduction in LaCrO$_3$ is governed by the hole conduction[1~3]. On the other hand, the lattice potential of the A-site is shallower than that of B-site in the perovskite oxide of ABO$_3$ [18,19]. This indicates that the formation of the lanthanum vacancy is much easier than that of chromium vacancy and suggests that the dissolution of Cr$_2$O$_3$ in LaCrO$_3$ is more favorable than that of La$_2$O$_3$. There are two possible defect reactions involving the dissolution of Cr$_2$O$_3$ at different oxygen pressures.

At higher oxygen pressure, the dissolution of Cr$_2$O$_3$ into LaCrO$_3$ creates the vacancy of lanthanum in the following manner,

$$\text{Cr}_2\text{O}_3 + \frac{3}{2}\text{O}_2 \rightarrow 2\text{V}_{\text{La}}^{\text{m}} + 2\text{Cr}^{\text{ox}} + 6\text{O}_2 + 6\text{h'}$$  \hspace{1cm} (3)

The equilibrium constant $K_{(3)}$ of defect reaction (3) is represented by

$$K_{(3)} = \frac{[\text{V}_{\text{La}}^{\text{m}}]^2[\text{Cr}^{\text{ox}}]^2[\text{O}_2]^{16}[\text{h}']^6}{a_{\text{Cr}_2\text{O}_3}(P_{\text{O}_2}/P_{\text{O}_2}^{\text{atm}})^{3/2}}$$  \hspace{1cm} (4)

where $a_{\text{Cr}_2\text{O}_3}$ is the activity of Cr$_2$O$_3$ in LaCrO$_3$ and $P_{\text{O}_2}^{\text{atm}}$ is the atomospheric pressure of 1.01 x 10$^5$Pa. Electroneutrality is maintained by

$$3[\text{V}_{\text{La}}^{\text{m}}] = [\text{h'}]$$  \hspace{1cm} (5)

Taking into account eq.(5), eq.(4) can be arranged as

$$[\text{V}_{\text{La}}^{\text{m}}] = \left( \frac{K_{(3)}}{3[\text{Cr}^{\text{ox}}]^2[\text{O}_2]^{16}} \right)^{1/8} \frac{(P_{\text{O}_2}/P_{\text{O}_2}^{\text{atm}})^{3/16} a_{\text{Cr}_2\text{O}_3}^{1/8}}$$  \hspace{1cm} (6)

The flux of lanthanum ion is equal to that of vacancy in the opposite direction

$$c_{\text{La}^{3+}} D_{\text{La}^{3+}} = [\text{V}_{\text{La}}^{\text{m}}] D_{\text{V}}$$  \hspace{1cm} (7)

where $D_{\text{La}^{3+}}$ and $D_{\text{V}}$ are the diffusion coefficients of lanthanum ion and lanthanum vacancy, respectively. Substituting eq.(6) into eq.(7), the diffusion coefficient of lanthanum ion is obtained by

$$D_{\text{La}^{3+}} = D'_{\text{La}}(T)(P_{\text{O}_2}/P_{\text{O}_2}^{\text{atm}})^{3/16} a_{\text{Cr}_2\text{O}_3}^{-1/8}$$  \hspace{1cm} (8)

where

$$D'_{\text{La}}(T) = \frac{D_{\text{V}}}{c_{\text{La}^{3+}}} \left( \frac{K_{(3)}}{3[\text{Cr}^{\text{ox}}]^2[\text{O}_2]^{16}} \right)^{1/8}$$  \hspace{1cm} (9)
$D_{La}^{+}(T)$ is not dependent on oxygen pressure but dependent on temperature.

On the other hand, at lower oxygen pressure the dissolution of Cr$_2$O$_3$ into LaCrO$_3$ is

$$\text{Cr}_2\text{O}_3 \rightarrow 2V_{La}^{m'} + 2\text{Cr}^{x'} + 3\text{O}_2 + 3V_{0}^{''}$$  \hspace{1cm} (10)

In the same way, diffusion coefficient of lanthanum ion at lower oxygen pressure is obtained by

$$D_{La}^{+} = D_{La}^{+}(T)q_{Cr_2O_3}^{1/5}$$  \hspace{1cm} (11)

where

$$D_{La}^{+}(T) = \frac{D_{o}}{c_{La}^{+}} \left( \frac{K_{10}}{\left( \frac{3}{2} \right)^{3} |\text{Cr}^{+}_{2O}_3|^2 |\text{O}_2|^3} \right)^{1/5}$$  \hspace{1cm} (12)

$K$ is the equilibrium constant of defect reaction (10) and $D_{La}^{+}(T)$ is not dependent on oxygen pressure but dependent on temperature.

ii) Parabolic rate constant

Using the solid state reaction between La$_2$O$_3$ and Cr$_2$O$_3$, LaCrO$_3$ layer was produced by reaction (1). The thickness of the product layer is written as

$$x^2 = 2k_{p}t$$  \hspace{1cm} (13)

where $t$ is the reaction time and $k_{p}$ is the parabolic rate constant. In the case that the reaction is controlled by diffusion of La$_{3+}$ in LaCrO$_3$, parabolic rate constant is written as

$$k_{p} = -\frac{v}{RT} \int_{\mu_{La}(La)}^{\mu_{La}(Cr)} D_{La}^{3+}c_{La}^{3+} d\mu_{La}$$  \hspace{1cm} (14)

where $v$ is the increase in volume of the reaction layer resulting from the transport of one equivalent of ions through the reaction products, $\mu_{La}(Cr)$ is the chemical potential of La at Cr$_2$O$_3$/LaCrO$_3$ interface and $\mu_{La}(La)$ is chemical potential of La at La$_2$O$_3$/LaCrO$_3$ interface. Substituting eq.(8) into eq.(14) and taking into account $v = 1/c_{La}^{3+}$, parabolic rate constant at higher oxygen pressure is obtained by

$$k_{p} = -\frac{D_{La}^{+}(T)(P_{O_2}/P_{O_2}^*)^{3/16}}{RT} \int_{\mu_{La}(La)}^{\mu_{La}(Cr)} c_{Cr_2O_3}^{1/8} d\mu_{La}$$  \hspace{1cm} (15)

The following reactions are considered

$$2\mu_{La} + 3/2\mu_{O_2} = \mu_{La_2O_3}$$  \hspace{1cm} (16)

and

$$\mu_{La_2O_3} + \mu_{Cr_2O_3} = 2\mu_{LaCrO_3}$$  \hspace{1cm} (17)
Taking into account the fixed chemical potentials of oxygen \(d\mu_{O_2} = 0\) and \(LaCrO_3\) \((d\mu_{LaCrO_3} = d\mu_{LaCrO_3})\), following relation is obtained:

\[
2d\mu_{La} = d\mu_{La_2O_3} = -d\mu_{Cr_2O_3} = -RTd\ln a_{Cr_2O_3} \tag{18}
\]

Substituting eq.(18) into eq(15), parabolic rate constant at higher oxygen pressure is represented by

\[
k_p = \frac{D'_{La}(T)(P_{O_2}/P_{O_2}^*)^{3/16}}{2} \int_{\ln a_{Cr_2O_3(La)}}^{\ln a_{Cr_2O_3(Cr)}} a_{Cr_2O_3} d\ln a_{Cr_2O_3} = 4D'_{La}(T)(P_{O_2}/P_{O_2}^*)^{3/16} \left( a_{Cr_2O_3(Cr)}^{1/8} - a_{Cr_2O_3(La)}^{1/8} \right) \tag{19}
\]

The parabolic rate constant is proportional to \(P_{O_2}^{3/16}\).

On the other hand, parabolic rate constant at lower oxygen pressure is

\[
k_p = \frac{5}{2} D'_{La}(T) \left( a_{Cr_2O_3(Cr)}^{1/5} - a_{Cr_2O_3(La)}^{1/5} \right) \tag{20}
\]

The parabolic rate constant is not dependent on oxygen pressure.

iii) Calculation of diffusion coefficient of La\(^{3+}\) ion from parabolic rate constant

Because the phase diagram[23] shows that the solubility of La\(_2O_3\) in LaCrO\(_3\) is extremely low, the activity of Cr\(_2O_3\) in LaCrO\(_3\) at the Cr\(_2O_3\)/LaCrO\(_3\) interface is

\[
a_{Cr_2O_3(La)} = 1 \tag{21}
\]

The activity of Cr\(_2O_3\) in LaCrO\(_3\) at the La\(_2O_3\)/LaCrO\(_3\) interface can be calculated from Gibbs free energy change of reaction (1)[5] and activity of La\(_2O_3\) in LaCrO\(_3\) at the La\(_2O_3\)/LaCrO\(_3\) interface \((a_{Cr_2O_3(La)} = 1)\). The activity of Cr\(_2O_3\) is expressed as

\[
a_{Cr_2O_3(La)} = \exp \left( \frac{2\Delta G^o}{RT} \right) \tag{22}
\]

Substituting eq.(21) and eq.(22) into eq.(19), the parabolic rate constant is represented by

\[
k_p = 4D'_{La}(T)(P_{O_2}/P_{O_2}^*)^{3/16} \left( 1 - \exp \frac{\Delta G^o}{4RT} \right) \tag{23}
\]

Because the parabolic rate constant \((k_p)\) is obtained by eq(2), \(D'_{La}(T)\) is calculated using eq.(23) as

\[
D'_{La}(T)/m^2s^{-1} = 7.11 \cdot \exp \left( \frac{-482/kJ\text{ mol}^{-1}}{RT} \right) \tag{24}
\]

Substituting \(D'_{La}(T)\) into eq.(8), diffusion coefficient of La\(^{3+}\) is obtained by

\[
D_{La^{3+}}/m^2s^{-1} = 8.19 \times 10^{-1} \cdot \exp \left( \frac{-482/kJ\text{ mol}^{-1}}{RT} \right)(P_{O_2}/Pa)^{3/16}a_{Cr_2O_3}^{1/8} \tag{25}
\]
Diffusion coefficient of \( \text{La}^{3+} \) ion in \( \text{LaCrO}_3 \) was obtained from parabolic rate constant and Gibbs free energy change of eq.(1). Figure 6 shows diffusion coefficient of \( \text{La}^{3+} \) in \( \text{LaCrO}_3 \) at \( P_{O_2} = 2.12 \times 10^4 \text{Pa} \) with the reported values of that of cation in perovskite type oxides. Because diffusion coefficient of \( \text{La}^{3+} \) is a function of activity of \( \text{Cr}_2\text{O}_3 \) as shown in eq.(25), two diffusion coefficients of \( \text{La}^{3+} \) are calculated at both \( \text{La}_2\text{O}_3 \) side and \( \text{Cr}_2\text{O}_3 \) side.

Diffusion coefficient of lanthanum ion at lower oxygen pressure is obtained by

\[
D_{\text{La}^{3+}}/m^2s^{-1} = 7.87 \times 10^{-15} \cdot a_{\text{Cr}_2\text{O}_3}^{1/5} \quad (T = 1695\text{K})
\]

(26)

The present technique allows the determination of upper and lower limits of the diffusion coefficient of the rate-determining species in the product compound.

CONCLUSION

The diffusion coefficient of \( \text{La}^{3+} \) ion in polycrystalline \( \text{LaCrO}_3 \) is obtained using solid state reaction between \( \text{La}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3 \) at 1483~1688K in air, and at 1695K in oxygen pressure range of \( 10^{-5} \sim 10^{5}\text{Pa} \). By investigating the oxygen pressure dependence of diffusion coefficient, the predominant defect reaction in the formation of the lanthanum vacancy at higher oxygen pressure is

\[
\text{Cr}_2\text{O}_3 + \frac{3}{2}O_2 \rightarrow 2V_{\text{La}}'' + 2\text{Cr}_\text{Cr}^\alpha + 6\text{O}_\text{O}^\alpha + 6h^+ \quad (P_{O_2} > 10^{-1})
\]

(27)

and the predominant defect reaction at lower oxygen pressure is

\[
\text{Cr}_2\text{O}_3 \rightarrow 2V_{\text{La}}'' + 2\text{Cr}_\text{Cr}^\alpha + 3\text{O}_\text{O}^\alpha + 3V_0^\alpha \quad (P_{O_2} < 10^{-1})
\]

(28)

The diffusion coefficient of \( \text{La}^{3+} \) ion in polycrystalline \( \text{LaCrO}_3 \) at higher oxygen pressure is

\[
D_{\text{La}^{3+}}/m^2s^{-1} = 8.19 \times 10^{-15} \cdot \exp \left( -\frac{482/\text{kJ mol}^{-1}}{RT} \right) \cdot (P_{O_2}/P_a)^{3/16} \cdot a_{\text{Cr}_2\text{O}_3}^{1/8} \quad (P_{O_2} > 10^{-1})
\]

(29)

and at lower oxygen pressure diffusion coefficient is

\[
D_{\text{La}^{3+}}/m^2s^{-1} = 7.87 \times 10^{-15} \cdot a_{\text{Cr}_2\text{O}_3}^{1/5} \quad (T = 1695\text{K}, P_{O_2} < 10^{-1})
\]

(30)

REFERENCE

[1] D. B. Meadowcroft, Br. J. Appl. Phys. (J. Phys. D), Ser.2, 2, 1225 (1969).

[2] G. V. Subba Rao, B. M. Wanklyn, and C. N. T. Rao, J. Phys. Chem. Solids, 32, 345 (1971).
[3] D. P. Karma and A. T. Aldred, *Phys. Rev. B*, 20, 2255 (1979).

[4] Tetsuro Nakamura, G. Petzow and L. J. Gauckler, *Mat. Res. Bull.*, 14, 649 (1979).

[5] A. M. Azad, R. Suds, and O. M. Sreedharan, J. the Less-Common Metals, 166, 57 (1990).

[6] Harlan U. Anderson, *Solid State Ionics*, 52, 33 (1992).

[7] W. Schafer and Schmidberger, *High Tech Ceramics*, 1737 (1987).

[8] N. M. Sammes and R. Ratnaraj, *J. Mater. Sci.*, 30, 4523 (1995).

[9] A. E. Paladino, L. G. Rubin, and J. S. Waugh, *J. Phys. Chem. Solids*, 26, 391 (1965).

[10] A. E. Paladino, *J. Am. Ceram. Soc.*, 48, 476 (1965).

[11] A. Yamaji, *J. Am. Ceram. Soc.*, 58, 152 (1975).

[12] D. B. Schwarz and H. U. Anderson, *J. Electrochem. Soc.*, 122, 707 (1975).

[13] S. Shirasaki, H. Yamaura, H. Haneda, K. Kakegawa, and J. Moori, *J. Chem. Phys.*, 73, 4640 (1980).

[14] T. Ishigaki, S. Yamauchi, J. Mizusaki, K. Fueki and H. Tamura, *J. Solid State Chem.*, 54, 100 (1984).

[15] M. C. Kim, S. J. Park, H. Haneda, J. Tanaka, T. Mitsuhashi and S. Shirasaki, *J. Mater. Sci. Lett.*, 9, 102 (1990).

[16] Ken-ichi Kawamura, Atushi Saiki, Toshio Maruyama and Kazuhiro Nagata, *J. Electrochem. Soc.*, 142(9), 3073 (1995).

[17] C. Wagner, *Z. Phys. Chem.*, 34, 309 (1936).

[18] W. Van Gool and A. G. Piken, *J. Mater. Sci.*, 4, 95 (1969)

[19] M. Yoshimura, T. Nakamura, and T. Sata, *Bull. Tokyo Inst. Technol.*, 120, 13 (1974).

[20] A. Garcia-Verduch and R. Lindner, *Arkiv Kemi.*, 5, 313 (1953).

[21] P. Turlier, P. Bussiere, and M. Prettre, *C. R. Acad. Sci.*, 250, 1649 (1960).

[22] W. H. Rhodes and W. D. Kingery, *J. Am. Ceram. Soc.*, 49, 521 (1966).

[23] V. N. Pavlikov, A. V. Shevchenko, L. M. Lopato, and S. G. Tresvyatskii, p.57 in *Chemistry of High Temperature Materials*. Edited by N. A. Toropov; translated by C. B. Finch. Consultants Bureau, New York, 1969.
Fig. 1. Cross sectional view of diffusion couple after reaction for 432ks at 1688K in air.

Fig. 2. The square of the reaction layer thickness as a function of time at different temperatures.
Fig. 3. The square of the reaction layer thickness as a function of time at different oxygen pressures.

Fig. 4. Parabolic rate constant as a function of reciprocal temperature.
Fig. 5. Oxygen pressure dependence of parabolic rate constant.

Fig. 6. Diffusion coefficients of cations in perovskite type oxides.