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Lattice and grain boundary diffusion of Ca in polycrystalline yttria-stabilized ZrO_2 determined by employing SIMS technique¹

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Abstract

Diffusion profiles of Ca in highly densified polycrystalline yttria-stabilized (10 mol %) ZrO_2 were investigated by secondary ion mass spectroscopy (SIMS). Lattice diffusion coefficient in temperature range of 1073 to 1273 K was determined: $D_{\text{Lattice}} = 0.458 \exp[-393.3 \text{ (kJ/mol)/RT}] \text{ (cm}^2\text{/sec)}$. Grain boundary diffusion was estimated based on the Whipple's analysis. As a result, values of $D_{\text{Boundary}} \delta s$ can be represented by $D_{\text{Boundary}} \delta s = 4.85 \times 10^{-13} \exp[-185.8 \text{ (kJ/mol)/RT}] \text{ (cm}^3\text{/sec)}$, where D_{Boundary} is the grain boundary diffusion coefficient, δ the grain boundary width and s the segregation factor. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been a great deal of interests in solid oxide fuel cells (SOFC) for the generation of clean and efficient power. Yttria-stabilized zirconia (YSZ) with high oxygen ionic conductivity is often used as the electrolyte material in SOFC. Since the operating temperatures of SOFC are high around 1173 K, interfacial reactions between YSZ and electrode compounds have been pointed out to play a key role in the cell performance.

Calcium- or strontium-doped lanthanum manga-

nite (LCM) is the most promising compound for the cathode because of its high electrical conductivity and good catalysis properties. The reactions of YSZ with LCM at elevated temperatures have been investigated [1–4], and formation of $\text{La}_2\text{Zr}_2\text{O}_7$ was confirmed at the interface after an induction period. The reaction mechanism has been studied using polycrystalline and single crystal specimens of YSZ. It has been proven that the interfacial reaction proceeds in unidirectional diffusion of constituents of LCM into YSZ. Lau and Singhal [5,6] and Taimatsu et al. [7,8] have shown that polycrystals permit diffusive atoms to penetrate much deeper inside than single crystals, suggesting that the atomic transport along grain boundaries is responsible for the reactivity of polycrystalline specimens of YSZ. However,

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the kinetics of grain boundary diffusion has been little discussed for YSZ. As grain boundary diffusion is generally recognized to be several orders of magnitude faster than lattice diffusion, it seems that a knowledge of grain boundary diffusion is essential to the practical applications of polycrystalline YSZ at elevated temperatures.

Experimental methods available for studies of grain boundary diffusion are basically classified in two categories: one concerns direct methods such as radiotracer measurement, and the other indirect ones, are based on studies of phenomena such as sintering. The former is superior in accuracy in the determination of D_{Boundary} . The sectioning method, in which diffusion profiles are given through measuring the average concentrations within a section parallel to the diffusion direction as a function of penetration depth, has been long employed for the determination of diffusion coefficient, and is considered the most reliable and useful method. However, the sectioning method is limited to poor depth resolution due to the finite thickness of removed layers. Even precision-grinding method, which is one of the sectioning methods, gives removed layers as thick as a few hundred nm. Recently, SIMS has been applied to measure diffusion profiles as an alternative to the classical sectioning method, allowing the profiles to be studied at atomic level. SIMS is probably the best technique to obtain reliable data in studies of grain boundary diffusion due to its high sensitivity in detection. We have utilized SIMS technique in order to investigate cationic diffusion profiles in lattice and along grain boundaries of polycrystalline YSZ specimens. In this paper, lattice and grain boundary diffusion of Ca, which is one of the constituents of LCM, in polycrystalline YSZ will be discussed based on the diffusion profiles measured by SIMS.

2. Experimental procedure

2.1. Preparation of specimens

In order to study the grain boundary diffusion, two microstructural constraints are imposed to specimens used. One is grain size being much greater than penetration depth of diffusive atoms along grain boundaries because isolated grain boundaries have

been assumed in analytical models reported for the grain boundary diffusion [9–11]. Larger grains, however, make less contribution from grain boundaries. The other constraint is ideally pore-free specimens. The pores, especially open pores, cause unexpected diffusion profiles. Under the microstructural constraints, the authors prepared highly densified polycrystalline YSZ specimens: relative densities more than 99.8% and average grain size (= a few μm) greater than the penetration distance of Ca from the surface.

Preparation of specimens is indicated briefly here: yttria-stabilized (10 mol %) ZrO_2 powders produced by Tosoh corporation were conventionally pressed into a disk, and then isostatically pressed at 200 MPa by employing CIP technique. The pellets were then sintered at 1673 K for 2 h in air and HIP-ed at 1473 K for 1 h under 200 MPa.

2.2. Measurement of diffusion profiles

The dense polycrystalline YSZ specimens were sufficiently polished by a diamond paste. The polished specimens were preheated at the diffusion temperature for a period much longer than the diffusion time.

Diffusive atom, Ca, was deposited on the polished side of the specimens by drying ca. 0.02 mL drop of calcium nitrate solution (1 mol/L). The specimens thus prepared were annealed at a temperature in the range of 1073 K to 1273 K for an appropriate period in air in order to impose diffusion profiles of Ca. The depth profiles of Ca^+ ions were obtained by dynamic SIMS. All measurements were performed in ultra-high vacuum using a Cameca IMS 5F magnetic sector instrument equipped with an O^- ion source. The O^- ions were accelerated to 12.5 keV and the secondary positive ions were extracted at 4.5 keV by biasing the sample, giving rise to an effective primary energy of 17.0 keV. The intensity of the primary beam was around 100 nA, rastered over an area of $250\ \mu\text{m} \times 250\ \mu\text{m}$ with a sampling area of $60\ \mu\text{m}$ in diameter. In order to reduce charging effects, the samples were coated with a thin layer of gold. The crater depth was measured by a profilometer, and linear sputtering rate was used to derive the depth scale. Both $^{40}\text{Ca}^+$ and $^{44}\text{Ca}^+$ ions were monitored to make sure that the $^{44}\text{Ca}^+ / ^{40}\text{Ca}^+$ ratio

corresponds to the correct isotope ratio. $^{40}\text{Ca}^+$ intensity was used in this paper to derive diffusion coefficients. The analyses were carried out until reaching the background level.

3. Results and discussion

In Fig. 1, a typical diffusion profile in polycrystalline specimens is illustrated, involving grain boundary diffusion. Four parts are usually observed in the profile. The grain boundary diffusion is derived from the third part based on Whipple's analysis [10] for a constant source or Suzuoka's analysis [11] for an instantaneous source. The first part is mainly attributed to lattice diffusion, since contribution from the grain boundary diffusion is negligible in this part. The second part is difficult to discuss for polycrystalline specimens because the influence of both lattice and grain boundary diffusion is comparable in this part. According to a report by LeClaire and Rabinovitch [12], the second part is due to dislocation diffusion if curves of $\text{Log } c = f(x)$ are straight lines, where c and x are concentration of diffusive atom and diffusion distance, respectively. The last part corresponds to background counts.

A representative diffusion profile in the present work is shown in Fig. 2. The annealing temperature

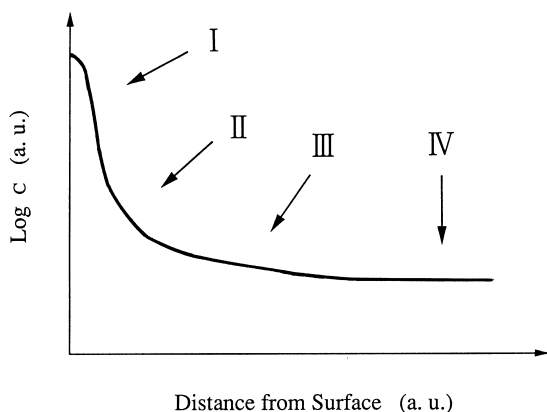


Fig. 1. Typical depth profile of diffusive atoms in polycrystalline specimens, consisting of four parts. The first (I) and third (III) parts are predominantly attributed to lattice and grain boundary diffusion, respectively. In the second (II) part, there are mixed contributions from both the lattice and grain boundary diffusion. The last (IV) part corresponds to the background noise level.

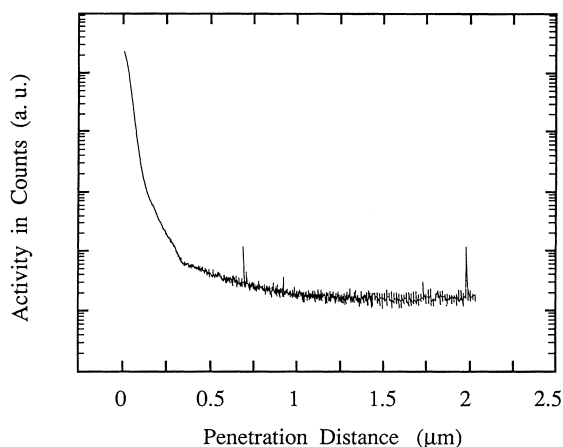


Fig. 2. Diffusion profile of Ca in highly densified polycrystalline YSZ, in which four parts involving contribution from grain boundary diffusion are observed as shown in Fig. 1.

and time were 1123 K and 25 h, respectively. As shown in Fig. 1, the profiles obtained consisted of four parts. Based on the consideration mentioned below, the D_{Lattice} and D_{Boundary} of Ca in polycrystalline YSZ are estimated from the first and third parts, respectively.

Solutions of partial differential equation in Fick's law are required to determine D_{Lattice} and D_{Boundary} , subject to boundary conditions. Since the penetration distances of Ca from the surface were incomparably short relative to the dimensions of the YSZ specimen and the Ca source, the boundary condition can be regarded as a constant source. Under the constant boundary condition, the concentration distribution of Ca due to the lattice diffusion in the annealed specimens is given by the following relation:

$$C(x, t)/C_0 = (1 - \text{erf}(x/2\sqrt{D_{\text{Lattice}}t})), \quad (1)$$

where $C(x, t)$ is the concentration of Ca as a function of both the distance from the surface and time, C_0 the Ca concentration at the surface of initially Ca-free specimens at $t > 0$ and t the annealing time. The error function, erf, is defined as $\text{erf}(x) = 2/\sqrt{\pi} \int_0^x \exp(-u^2) du$. Since the concentration of Ca is proportional to the ion intensity in SIMS analysis, D_{Lattice} can be estimated by fitting Eq. (1) to a curve of $S(x)/S_0$ versus x , where $S(x)$ and S_0 are Ca^+ ion intensities at a distance, x , from the surface and at

Table 1

Lattice and grain boundary diffusion parameters for Ca in polycrystalline yttria-stabilized (10 mol%) ZrO₂

Temp. (K)	Time (s)	D_{Lattice} (cm ² /s)	$D_{\text{Boundary}}\delta s$ (cm ³ /s)
1073	2.52E5	2.25E-18	2.11E-20
	5.18E5	3.30E-18	1.24E-20
1123	9.00E4	3.71E-17	5.59E-20
	3.60E3	2.69E-16	5.29E-19
	3.60E3	3.45E-16	1.20E-18
1223	5.76E4	2.16E-17	4.34E-18
	3.60E4	4.96E-16	5.31E-19
1273	3.60E3	4.41E-15	1.35E-19
	3.60E3	2.55E-15	6.66E-19

$x=0$, respectively. Table 1 shows estimated values of D_{Lattice} as a function of annealing temperature. Solutions to grain boundary diffusion are more complicated, although analytical models have been reported [9–11]. An exact solution has been given by Whipple [10]. The solution is, however, difficult for application. LeClaire [13] has proposed the following equation based on the Whipple's analysis:

$$D_{\text{Boundary}}\delta = (\partial \ln c / \partial x^{6/5})^{-5/3} (4D_{\text{Lattice}}/t)^{1/2} (0.78)^{5/3}, \quad (2)$$

where c is the average specific activity in a section at a distance, x , from the surface, corresponding to the ion intensity in SIMS analysis in our study. After the proposition by LeClaire, Gibbs [14] has claimed that the $D_{\text{Boundary}}\delta$ should be replaced by $D_{\text{Boundary}}\delta s$, where s is the segregation factor, because the segregation of impurities at grain boundaries has a great influence on diffusivities. According to Eq. (2), $\ln c$ varies linearly with $x^{6/5}$ in the third part of the diffusion profile, due to grain boundary diffusion. In Table 1, values of $D_{\text{Boundary}}\delta s$ estimated from the slope of the linear curve of $\ln c$ versus $x^{6/5}$ are summarized.

The values of D_{Lattice} versus reciprocal of temperature are shown in Fig. 3. The D_{Lattice} can be represented as:

$$D_{\text{Lattice}} = 0.458 \exp[-393.3 \text{ (kJ/mol)/RT}] \text{ (cm}^2\text{/sec)},$$

determined by the least squares method. To the best of our knowledge, the D_{Lattice} of Ca has not been

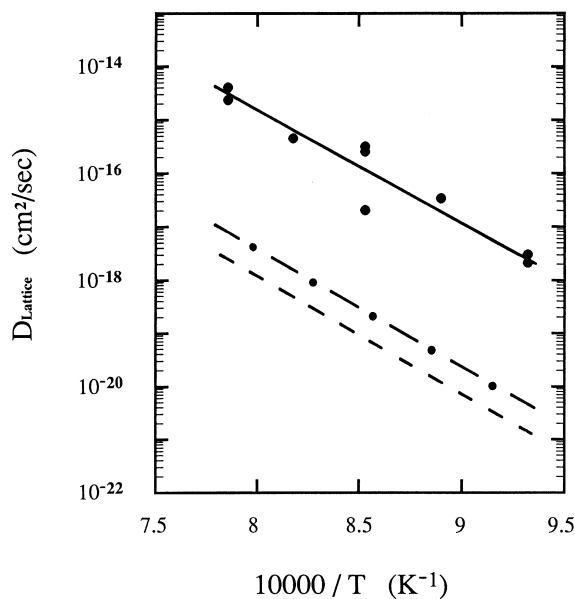


Fig. 3. Temperature dependence of lattice diffusion coefficient (D_{Lattice}) of Ca in YSZ with 10 mol % Y₂O₃. Both the broken and dot-dash lines show predicted data for calcium-stabilized ZrO₂, which were extrapolated using values above 1673 K reported by Rhodes and Carter [15] and Oishi and Ichimura [16], respectively.

previously reported for YSZ containing 10 mol % Y₂O₃. Lau and Singhal [5] have studied lattice diffusion of Mn and La using single crystals of YSZ with the same composition as our specimens and reported the D_{Lattice} of order of 10⁻¹⁶ (cm²/sec) at 1273 K. The values for Ca are about one order of magnitude higher than those for insoluble Mn and La atoms into fluorite structure of ZrO₂. The solubility of diffusive atoms may be related to the differences in their diffusivities. In Fig. 3, D_{Lattice} of Ca in calcium-stabilized ZrO₂ (CSZ) is shown for comparison, which was extrapolated using values of D_{Lattice} above 1673 K [15,16]. In the comparison, the D_{Lattice} of Ca in YSZ was about 10³ times higher than that in CSZ, although no significant difference in activation energies of Ca diffusion was found between the former and latter. The influence of chemical potential gradient of Ca in our study might be considered as a cause for the difference between our and published data. A previous report [16] has, however, shown for Ca diffusion in CSZ that interdiffusion coefficients measured under strong chemical potential gradient are similar to self-diffusion

coefficients under no chemical potential. Since it is, at the present stage, difficult to estimate how large the influence of chemical potential gradient is on our data, further investigation is needed in order to make a clear explanation for why Ca atoms move much faster in YSZ than in CSZ.

Temperature dependence of $D_{\text{Boundary}}\delta s$ for grain boundary diffusion of Ca in polycrystalline YSZ is shown in Fig. 4. The values of $D_{\text{Boundary}}\delta s$, determined by the least squares method, can be represented by

$$D_{\text{Boundary}}\delta s = 4.85 \times 10^{-13} \times \exp[-185.8 \text{ (kJ/mol)/RT}] \text{ (cm}^3\text{/sec)}.$$

There are no data on grain boundary diffusion in YSZ to compare with our results. The activation energy of grain boundary diffusion is about a half of that of lattice diffusion. This is probably due to less packing of atoms at the grain boundaries, resulting in greater atomic mobility than in the lattice. The value of δ is usually assumed to be constant and independent of temperature though the determination of δ is complicated. Atkinson and Taylor [17] have studied δ for Ni grain boundary diffusion in NiO.

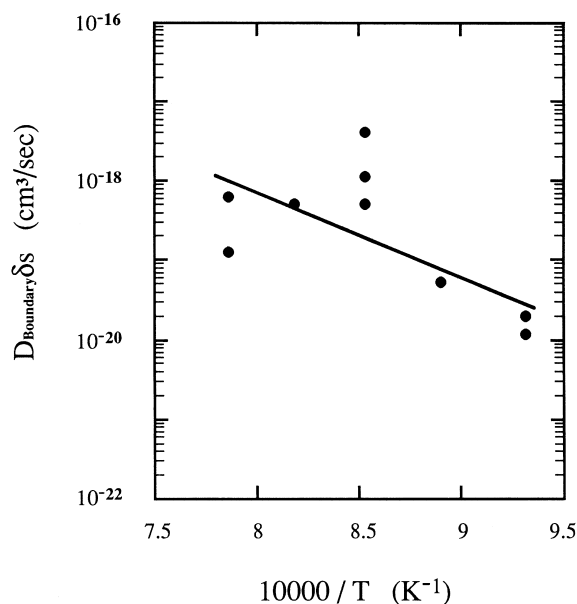


Fig. 4. Values of $D_{\text{Boundary}}\delta s$ for Ca grain boundary diffusion in polycrystalline YSZ versus reciprocal of temperature.

The value of δ was ca. 0.7 nm, which was comparable to reported values for metallic systems, although δ of nonmetallic systems was believed to be much thicker than that of metallic systems. Although δ for the Ca grain boundary diffusion has not yet been disclosed, D_{Boundary} of Ca is estimated in this paper assuming that the effective δ is a constant value of order of 10^{-9} m. It is not easy to determine the value of s , as well as δ , precisely. A general understanding for the s is that the value is highly affected by solubility of diffusive atoms into the host lattice. As Ca, the diffusive atom in the present work, shows high solubility in ZrO_2 , no significant segregation at grain boundaries is expected in the YSZ specimens. Hence, the value of s can be taken as 1 in the present work. Based on these assumptions, diffusion enhancement factors by grain boundaries ($D_{\text{Boundary}}/D_{\text{Lattice}}$) are roughly estimated to be of the order of 10^4 – 10^5 . This estimation clearly indicates that Ca diffuses much faster along the grain boundaries than in the lattice during the interfacial reaction between YSZ and LCM at the operating temperatures of SOFC.

4. Conclusions

In the present work, the SIMS technique was applied to measure diffusion profiles of Ca in polycrystalline YSZ, prepared with two microstructural constraints in order to determine the grain boundary diffusion. The obtained diffusion profiles have a typical shape, consisting of four parts including contributions from lattice and grain boundary diffusion. The D_{Lattice} and $D_{\text{Boundary}}\delta s$ in the temperature range of 1073 to 1273 K, which corresponds to the operation temperature range of SOFC with YSZ electrolytes, can be represented by

$$D_{\text{Lattice}} = 0.458 \exp[-393.3 \text{ (kJ/mol)/RT}] \text{ (cm}^2\text{/sec)},$$

and

$$D_{\text{Boundary}}\delta s = 4.85 \times 10^{-13} \times \exp[-185.8 \text{ (kJ/mol)/RT}] \text{ (cm}^3\text{/sec)},$$

respectively. The determination of $D_{\text{Boundary}}\delta s$ was

carried out based on the Whipple's analysis. Assuming that the δ and s are constant values of the order of 10^{-9} m and 1, respectively, diffusion enhancement factors by grain boundaries were roughly determined to be of the order of 10^4 – 10^5 . These data have not been previously reported.

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