Effects of the Grain Boundary and Its Movement on the Oxygen Self-Diffusion in CeO$_2$-ZrO$_2$ Solid Solutions

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CeO$_2$-ZrO$_2$ 固溶体における粒界および粒界移動
が酸素イオンの自己拡散におよぼす影響

1. Introduction

The knowledge of the diffusivities of component elements in ceramics during a movement of grain boundaries is important to make clear sintering mechanisms and mechanical properties. This is also important for the evaluation of diffusion coefficients obtained using powders, loosely-sintered materials and polycrystals.

The rate-controlling step for grain growth is considered to be the diffusion of atoms across a grain boundary. When sintered materials are used at temperatures which are far lower than the temperature at which the materials are sintered, the kinetics of the grain-boundary movement is normal and the rate is very slow. On the other hand, when the materials are exposed to high temperatures which are close to or higher than the sintered temperature, rapid movement of grain boundaries by the rapid grain growth frequently occurs.

It is the purpose of this work to clarify the characteristics of the oxygen self-diffusion in oxides during the movement of grain boundaries by measuring the oxygen self-diffusion coefficient. The oxygen self-diffusion is enhanced by the presence of grain boundaries in typical oxides such as Al$_2$O$_3$\textsuperscript{1)}, MgO\textsuperscript{2)} and MgAl$_2$O$_4$\textsuperscript{3)}. The change of the density of grain boundaries in a polycrystal due to grain growth results in a change of apparent diffusion coefficient when the oxygen self-diffusion coefficient is determined by measuring the total amount of $^{18}$O diffused into a specimen in a method of a gas-solid isotope exchange technique\textsuperscript{1)}. It is difficult to clarify the effect of the movement of grain boundaries on the oxygen self-diffusion using these oxides.

On the other hand, the oxygen self-diffusion is not enhanced in grain boundaries in fluorite-type oxides such as ZrO$_2$ solid solutions\textsuperscript{4,5)} and ThO$_4$\textsuperscript{4)}. The effect of the movement of grain boundaries on the oxygen self-diffusion, therefore, can be demonstrated by using these fluorite-type oxides.

In this work, 90 mol\% CeO$_2$-10 mol\% ZrO$_2$ solid solution of fluorite-type crystal structure and 14 mol\% CeO$_2$-86 mol\% ZrO$_2$ solid solution of a tetragonal structure which is close to the fluorite structure were used for the determinations under two extremely different conditions: One is...
in the condition in which the grain size does not change and the microstructure is apparently stable, and the other is in the condition in which rapid grain growth occurs.

2. Experimental

2.1 Materials

Starting powders were prepared by the co-precipitating method using Ce(NO$_3$)$_3$·6H$_2$O and ZrOCl$_2$·8H$_2$O. The compositions of the mixed powders were 90 mol% CeO$_2$-10 mol% ZrO$_2$ (90 CeO$_2$-10 ZrO$_2$) and 14 mol% CeO$_2$-86 mol% ZrO$_2$ (14 CeO$_2$-86 ZrO$_2$). The powders calcined at 1173 K for 2 h were isostatically pressed into disk-shaped samples of 10 mm diameter and 10 mm height under a pressure of 2 t/cm$^2$. The disks were sintered in air for 20 h at 1753 K. The densities of the polycrystals of 90 CeO$_2$-10 ZrO$_2$ and 14 CeO$_2$-86 ZrO$_2$ were both about 96% of the theoretical. The crystal structure of the two compositions of 90 CeO$_2$-10 ZrO$_2$ and 14 CeO$_2$-86 ZrO$_2$ were confirmed to be those of fluorite type and tetragonal, respectively, by using powder X-ray diffraction technique. These results are consistent with the phase diagram obtained by Tani et al$^7)$. Small cubes were cut from the sintered polycrystals and polished into spheres of about 4 mm diameter with diamond paste.

2.2 Determination of oxygen self-diffusion coefficient

The oxygen self-diffusion coefficient was determined by isotope exchange technique using $^{18}$O as a tracer. Before the diffusion annealing all of the samples were pre-annealed in a natural oxygen atmosphere for about 2 to 6 h at the same temperature under the same oxygen pressure ($2.0 \times 10^4$ Pa) as in the diffusion anneal. This pre-annealing time is enough to attain the equilibrium defect concentration due to the non-stoichiometry of the samples but is not enough to obtain the stable microstructure at high temperatures as will be discussed later. Diffusion annealing was conducted using an RF induction furnace with a Pt-Rh susceptor. The diffusion annealing time was about 1 to 2 h.

The $^{18}$O concentration decreasing in the gas phase was determined at scheduled intervals during the diffusion anneal by means of a mass-spectrometer. The diffusion coefficient was calculated from the $^{18}$O diffusion amount using the following equation for boundary conditions where the rate of the isotope exchange from a well-stirred fluid of a fixed volume into a sphere was controlled by both the surface exchange reaction and the diffusion in the sphere$^{8,9}$.

\[
\frac{M_t}{M_\infty} = (1 + a) \left\{ 1 - \frac{Z_1 m n Z_2}{(Z_1 - Z_2) (Z_1 - Z_3)} e \text{erfc}(Z_1 \sqrt{t}) - \frac{Z_1 m n Z_2}{(Z_1 - Z_2) (Z_1 - Z_3)} e \text{erfc}(Z_2 \sqrt{t}) - \frac{Z_1 m n Z_2}{(Z_1 - Z_2) (Z_1 - Z_3)} e \text{erfc}(Z_3 \sqrt{t}) \right\},
\]

(1)

where

\[
m = \frac{K}{\sqrt{D}},
\]

(2)

\[
n = 1 - \frac{D}{K a},
\]

(3)

$M_t$ and $M_\infty$ are the total $^{18}$O amounts diffusing into the solid for time $t$ and infinite time, respectively, $D$ is the diffusion coefficient, $K$ is the surface exchange coefficient, $a$ is the atomic ratio of oxygen in the gas and solid phases, $a$ is the spherical radius of the solid specimen, and $e \text{erfc} Z = \exp Z^2 \text{erfc} Z$.

The $Z_1$, $Z_2$ and $Z_3$ in Eq. (1) are the roots for Eq. (5).

\[
Z_1 + m n Z_2^2 + \frac{3 m^2 (1 - n)}{a} Z - \frac{3 m^2 (1 - n)^2}{a} = 0
\]

(5)

Samples of as-sintered and long-time annealed for 25 to 60 h at 1673 K were used for the determinations. Oxygen self-diffusion coefficient was determined at two temperatures of 1570 and about 1670 K.

3. Results and discussion

Oxygen self-diffusion coefficients obtained in the systems of 90 CeO$_2$-10 ZrO$_2$ and 14 CeO$_2$-86 ZrO$_2$ are shown in Table 1 and in Figs. 1 and 2, respectively. Open circles are the results of the as-sintered sample. Triangles are the samples of pre-annealed for about 25 h at about 1670 K. Closed circles are those of the samples pre-annealed for about 50 h at the same temperature.

The microstructure of 90 CeO$_2$-10 ZrO$_2$ after etching is shown in Fig. 3. The average grain size of the as-sintered sample was about 7 $\mu$m as shown in Fig. 3(a). The grain size increased to 9 $\mu$m after annealing at 1665 K for 31 h as shown in Fig. 3(b) but further grain growth was not observed in the samples annealed for 47 h. This
implies that the grain growth occurred during the annealing for 31 h.

The microstructure of 14 CeO$_2$-86 ZrO$_2$ after etching is shown in Fig. 4. The average grain size for the as-sintered sample was about 3 $\mu$m as shown in Fig. 4(a) and the size increased to 6 $\mu$m after annealing at 1670 K for 24 h as shown in Fig. 4(b) but further grain growth was not observed in the sample annealed for 64 h.

The grain size dependence of the oxygen self-diffusion coefficient is not obtained from the results at 1570 K for both systems of 90 mol% CeO$_2$-10 mol% ZrO$_2$ and 14 mol% CeO$_2$-86 mol% ZrO$_2$ as shown in Figs. 1 and 2. This clearly indicates, as predicted earlier, that the oxygen self-diffusion is not enhanced at grain boundaries in the system CeO$_2$-ZrO$_2$.

When these samples were diffusion-annealed at about 1670 K, large differences are observed
As were shown in Figs. 3 and 4 it is expected that the rapid grain growth occurred for the as-sintered samples during the diffusion annealing at about 1670 K. It is concluded, therefore, that the enhanced oxygen self-diffusion at about 1670 K for the as-sintered sample and the rapid movement of grain boundaries due to the rapid grain growth correlate to each other.

Although it is difficult to analyse the cause of the enhancement more precisely, it is considered that a fast diffusion layer was created along grain boundaries which were moving quickly. It is known that the rate of the grain-boundary movement is controlled by the diffusion of component ions across a grain boundary. As ceramics are multi-component compounds, it is considered that the rate is controlled by the diffusion of slower species. Cations are the slower species in fluorite-type oxides compared to the oxygen ions. The diffusion of cations, therefore, must be enhanced during the rapid movement of grain boundaries. The fast diffusion layer for the oxygen diffusion may also contribute to the diffusion of cations. The diffusion mechanisms in the fast diffusion layer may be different from that in the interior of the grains.

The enhancement of the self-diffusion of the oxygen ions happens only in the period when the rapid movement of grain boundaries occurs. This fact indicates that when the rapid grain growth does not occur, the fast diffusion layer is not created and there is no difference between the diffusion mechanisms in the vicinity of the grain boundaries and in the interior of the grains.

As are shown in Figs. 1 and 2 with solid lines, when the microstructure is apparently stable and the grain size does not change during the diffusion measurement we can obtain the oxygen self-diffusion coefficient and the activation energy inherent to the substance. On the other hand, when the rapid movement of grain boundaries due to the rapid grain growth occurs during the measurement, the obtained self-diffusion coefficient becomes higher than that obtained in the condition of apparently stable microstructure, and the calculated activation energy deviates from the inherent value as are shown in Figs. 1 and 2 with dashed lines. Care must be taken, therefore, to evaluate the diffusion coefficients obtained under the condition in which the microstructure rapidly changes.
References