Self-Diffusion of Oxygen Ion in MgAl_2O_4 Single Crystal

By

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1. Introduction

The diffusion coefficient of oxygen in metallic oxides is one of the important factors affecting their properties. In most cases the rate of mass transport during sintering or solid-state reaction is directly determined by diffusion of constituent ions.

Bratton studied the initial- and intermediate-stage sintering of MgAl_2O_4 and concluded that the densification was controlled by a volume diffusion mechanism^{(1),(2)}. However, for lack of the information on self-diffusion coefficients of constituent ions, the rate controlling species of mass transport during sintering has not been clearly elucidated. Determination of the self-diffusion coefficient of oxygen ion in the spinel will give a clearer insight to the kinetics of sintering and solid-state reaction for the spinel.

2. Experimental

The specimen was a single crystal of spinel prepared by the Verneuil method. The highest impurity content in the starting material was approximately 10 ppm of Si. The single crystal was crushed to 60 to 70 mesh grains. The average diameter of the grains was 230 μm . The composition of the spinel was confirmed to be $\text{MgO} \cdot \text{Al}_2\text{O}_3$ by an X-ray diffraction technique using the relation of composition and lattice parameter^{(3),(4)}.

The self-diffusion coefficient of oxygen ion in the single-crystal grains of the spinel was determined by a gas solid exchange technique using O^{18} as a tracer. Diffusion annealing of the spinel specimen was carried out in an oxygen atmosphere enriched with 5% O^{18} for a specified time at a specified temperature. The oxygen in the specimen was reduced to CO and converted to CO_2 . The diffusing amount of O^{18} in the spinel was calculated from the $\text{CO}_2(46)/\text{CO}_2(44)$ ratio determined with a mass-spectrometer. The relation between the amount of diffusion and the diffusion coefficient is given by Eq. (1).

$$\frac{M_t}{M_\infty} = (1 + \alpha) \left[1 - \frac{\tau_1}{\tau_1 + \tau_2} e \operatorname{erfc} \left\{ \frac{3\tau_1}{\alpha} \left(\frac{Dt}{a^2} \right)^{1/2} \right\} - \frac{\tau_2}{\tau_1 + \tau_2} e \operatorname{erfc} \left\{ -\frac{3\tau_2}{\alpha} \left(\frac{Dt}{a^2} \right)^{1/2} \right\} \right] \dots (1)$$

where

$$e \operatorname{erfc} Z = \exp Z^2 \operatorname{erfc} Z \dots (2)$$

$$\tau_1 = \frac{1}{2} \left\{ \left(1 + \frac{4}{3}\alpha \right)^{1/2} + 1 \right\} \dots (3)$$

$$\tau_2 = \tau_1 - 1 \dots (4)$$

M_t and M_∞ are the diffusing amounts of O^{18} in the solid specimen at time t and time of infinity, α is the ratio of numbers of oxygen atoms in the gas and the solid phases, D is the diffusion coefficient, t is the diffusion time, a is the radius of specimen particle, and τ_1 and τ_2 are related to α as given by Eqs. (3) and (4). The volume of the gas phase was 309 cc and the oxygen pressure of the gas phase was 153 mmHg at room temperature. The amount of spinel specimen was about 10 mg. The apparatus and techniques were similar to those employed for aluminum oxide⁽⁵⁾ and periclase⁽⁶⁾. In analysis of experimental results, an assumption was made that the reaction rate of exchange at the gas solid interface was much faster than the diffusion in the solid phase as was true with many oxides, *e.g.* $\alpha\text{-Al}_2\text{O}_3$ ⁽⁵⁾, MgO ⁽⁶⁾, NiCr_2O_4 ⁽⁷⁾, $\alpha\text{-Fe}_2\text{O}_3$ ⁽⁷⁾, $\alpha\text{-Cr}_2\text{O}_3$ ⁽⁸⁾, and $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ ⁽⁹⁾.

3. Results

The determined self-diffusion coefficients of

Fig. 1. Self-diffusion coefficients of oxygen ion in MgAl_2O_4 single crystal.

oxygen ion in the MgAl_2O_4 single crystal are shown by Fig. 1 as a function of temperature between 1420° and 1630°C. The results over the temperature range studied can be represented by an Arrhenius equation :

$$D = 1.5 \times 10^3 \exp(-136 \times 10^3/RT) \text{ cm}^2/\text{sec}. \quad \dots\dots\dots (5)$$

The probable errors are calculated as ± 6.0 kcal/mol for the activation energy, and ± 1.07 for $\log D_0$.

4. Discussions

In the magnesium aluminate spinel, the oxygen ions are in a nearly closest packing structure similar to that of MgO and $\alpha\text{-Al}_2\text{O}_3$. Cations in MgO and $\alpha\text{-Al}_2\text{O}_3$ are in octahedral sites while cations in spinel are in octahedral sites and tetrahedral sites. Similarity in diffusion behavior of oxygen ions is expected to these oxides which have similar crystal structures.

Table 1 shows the activation energies and pre-exponential terms for the self-diffusion of oxygen ion in single-crystal spinel obtained in the present study together with $\alpha\text{-Al}_2\text{O}_3$ ⁵⁾ and MgO ⁶⁾ which have been reported. The activation energy of

136 kcal/mol for MgAl_2O_4 is about 80 kcal/mol larger than that for extrinsic diffusion in $\alpha\text{-Al}_2\text{O}_3$ (57.6 kcal/mol) and for that in MgO (62.4 kcal/mol). The value is rather close to the value for intrinsic diffusion in $\alpha\text{-Al}_2\text{O}_3$ (152 kcal/mol). Moreover, the pre-exponential term of $D_0 = 1.5 \times 10^3 \text{ cm}^2/\text{sec}$ for MgAl_2O_4 is close to the value for intrinsic diffusion in $\alpha\text{-Al}_2\text{O}_3$ ($D_0 = 1.9 \times 10^3 \text{ cm}^2/\text{sec}$). Consequently the self-diffusion coefficient of oxygen ion in MgAl_2O_4 single crystal determined in the present investigation is interpreted to be due to intrinsic diffusion where the concentration of oxygen vacancies is dependent on temperature with assumption of a vacancy mechanism.

Bratton has calculated apparent diffusion coefficients from the densification rates for initial sintering over the temperature range of 1050° to 1300°C as Eq. (6) :¹⁾

$$D_{s1} = 18.6 \exp(-116 \times 10^3/RT) \text{ cm}^2/\text{sec} \dots (6)$$

and for intermediate stage sintering over the temperature range of 1300° to 1600°C as Eq. (7) :²⁾

$$D_{s2} = 157 \exp(-118 \times 10^3/RT) \text{ cm}^2/\text{sec} \dots (7)$$

In Fig. 2, D_{s1} (extrapolated from the lower temperature range) and D_{s2} are compared with the self-diffusion coefficient for oxygen ion and that for magnesium ion determined by Lindner and Åkerström¹⁰⁾.

The diffusion coefficients calculated from the sintering rates are smaller by 4 to 6 orders of magnitude than the self-diffusion coefficient of magnesium ion and closer to that of oxygen ion, though the activation energy for sintering is smaller by about 20 kcal/mol than that for self-diffusion of oxygen ion.

The self-diffusion coefficient of aluminum ion in MgAl_2O_4 has not been measured. Since the self-diffusion coefficients of two constituent cations, however, tend to be close to each other in other binary oxides, *e.g.* ZnFe_2O_4 ¹⁰⁾, NiCr_2O_4 ¹¹⁾, ZnCr_2O_4 ¹¹⁾, and $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ ⁹⁾ the self-diffusion coefficient of aluminum ion in MgAl_2O_4 is also assumed to be close to that of magnesium ion. With this assumption the results obtained in the present investigation and Bratton's works confirm that the mechanism of sintering for MgAl_2O_4 is volume diffusion and the rate controlling species is oxygen ion which has the smallest self-diffusion coefficient.

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Table 1. Activation energies and pre-exponential terms for self-diffusion of oxygen ion in single crystals of MgAl_2O_4 , $\alpha\text{-Al}_2\text{O}_3$ and MgO

Substance	Temperature range (°C)	D_0 (cm ² /sec)	Q (kcal/mol)	Diffusion mechanism	Reference
MgAl_2O_4	1350~1600	1.5×10^3	136	intrinsic	This work
$\alpha\text{-Al}_2\text{O}_3$	1600~1800	1.9×10^3	152	intrinsic	5
$\alpha\text{-Al}_2\text{O}_3$	<1600	6.3×10^{-8}	57.6	extrinsic	"
MgO	1300~1750	2.5×10^{-6}	62.4	extrinsic	6

Fig. 2. Temperature dependences of the self-diffusion coefficients of oxygen and magnesium ions in MgAl_2O_4 and the apparent diffusion coefficients calculated from the initial.¹⁾ and intermediate.²⁾ stage sintering rates.

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単結晶 MgAl_2O_4 中の酸素イオンの自己拡散

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MgAl_2O_4 単結晶中の酸素イオンの自己拡散係数を温度 1420°C から 1630°C の範囲にわたって測定した。測定はトレサーとして O^{18} を用いる気-固相交換法によった。得られた自己拡散係数の温度依存性は実験温度範囲内において次式のように表わされる。

$$D = 1.5 \times 10^3 \exp(-136 \times 10^3/RT) \text{ cm}^2/\text{sec}$$

これは intrinsic な拡散によるものと考えられる。またこの酸素イオンの自己拡散係数の絶対値は MgAl_2O_4 中のマグネシウムイオンの自己拡散係数の絶対値より数桁小さく、 MgAl_2O_4 の焼結速度から求めたみかけの自己拡散係数に近い。

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