

# Oxygen self-diffusion in single and polycrystalline magnesio-ferrites

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Self-diffusion coefficients of oxygen ion in polycrystalline and single-crystal magnesio-ferrites have been measured by a gas–solid isotopic exchange technique using  $^{18}\text{O}$  as a tracer at temperature in the range 975 to 1465° C. A new method was considered for the oxygen volume diffusion in polycrystalline magnesio-ferrite, and its reliability is discussed. The volume diffusion coefficients of polycrystalline magnesio-ferrite ( $\text{MgO}/\text{Fe}_2\text{O}_3 = 0.95$  in mole ratio) can be expressed as  $D = 1.51 \times 10^{-1} \exp(-78\,600/RT) \text{ cm}^2 \text{ sec}^{-1}$  (1135 to 1465° C) and  $D = 1.2 \times 10^{-7} \exp(-38\,000/RT) \text{ cm}^2 \text{ sec}^{-1}$  (975 to 1135° C). The volume diffusion coefficients of the polycrystal in the high temperature range were very close to those of single crystal ferrite of the same composition as the polycrystal. The activation energy of grain-boundary diffusion in this polycrystal was expected to be greater than that of the volume diffusion. A possible interpretation of this unusual behaviour is given in terms of an increased enrichment of  $\text{Fe}^{2+}$  ion along the grain boundary with temperature elevation, by which oxygen vacancies increase.

## 1. Introduction

Magnesio-ferrite has an extensive application as a microwave and square-loop ferrite. However, there have been no data available on the oxygen diffusion coefficients of this material, which are important in understanding the processes of sintering, creep and solid state reaction, and defect chemistry of this ferrite. The present study deals with the characteristics of volume and grain-boundary diffusion of oxygen in this material.

The solid–gas exchange technique using  $^{18}\text{O}$  as a tracer has been used to study the oxygen diffusion in many single and polycrystalline oxides. For single crystals,  $^{18}\text{O}$  concentration in the gaseous phase was traced as a function of time in the exchange experiments; resultant diffusion coefficients were restricted to values greater than  $10^{-14} \text{ cm}^2 \text{ sec}^{-1}$  [1]. Because of this limitation, one cannot often detect extrinsic diffusion of materials appearing at low temperatures. If the solid–gas exchange experiments are performed using polycrystalline materials where the grain size is small enough and the grain-boundary diffusion is faster than that of volume diffusion, the exchange

amounts increase, and a very low level of diffusivities may be detected. The method of obtaining volume diffusion coefficients from exchange amounts between a polycrystalline oxide and oxygen gas was reported previously [2, 3]. In the present study, the reliability of this method was examined experimentally.

It is not easy to calculate accurately grain-boundary diffusion coefficients,  $D_b$ , in a solid. In the present study the relative magnitudes of  $D_b$  and volume diffusion coefficients,  $D_1$ , of the polycrystalline magnesio-ferrite were qualitatively determined, in which the defect structure along grain-boundaries is speculated.

## 2. Experimental details

### 2.1. Sample preparation

Polycrystalline ferrite ( $\text{MgO}/\text{Fe}_2\text{O}_3 = 0.95$  in mole ratio) was prepared by the usual ceramic method. 3 N-Mg(OH) $_2$  and 3 N-Fe $_2\text{O}_3$  were used as starting materials. Desired amounts of these reagents were wet-mixed and then calcined at 1100° C for 1 day in air. The resultant powder was milled, pelletized under a pressure of 2 t cm $^{-2}$ , and then finally fired

at 1400°C for a week in air. The fired materials were quenched in air to room temperature and crushed to particles; these were screened by sieves. The average grain size was determined by SEM in the usual manner and found to be 15 μm.

Single crystal ferrite was prepared by a traveling solvent floating-zone melting technique (TSFZ) [4]. The powdered mixture was hydrostatically pressed to about 1 t cm<sup>-2</sup> to obtain a rod (~ 8 mm diameter and 80 mm long), whose composition was nearly the same as that of the polycrystalline magnesio-ferrite. The rod was then sintered at 1450°C in oxygen, and then positioned in an infrared radiation convergence apparatus with 1.5 kW halogen lamp radiation source, to prepare single crystal magnesio-ferrite by TSFZ. Two shafts were counter-rotated at 30 rpm, and were simultaneously driven downwards at a speed from 2 to 8 mm h<sup>-1</sup>. Pure oxygen gas was introduced into the chamber. The resultant single crystal was crushed and then screened, as for the polycrystalline ferrite. These particles, prior to the diffusion experiments, were annealed at 1400°C for 1 day in air to remove metastable defects [5] expected in the as-grown crystal, and were screened again by sieves.

## 2.2. Measurement of oxygen diffusion

The self-diffusion coefficients of oxygen in magnesio-ferrites were determined by measuring the rate of gas–solid exchange of <sup>18</sup>O over the temperature range 975 to 1465°C in oxygen gas enriched with 5 to 20% <sup>18</sup>O at a pressure of about 40 torr. Prior to each diffusion annealing, the exchange system was preheated at 700°C for 15 min. The amount exchanged was followed as a function of diffusion time by analysis of the <sup>18</sup>O-content of the gaseous phase using a mass-spectrometer. Details of the experimental apparatus and procedures have been described previously [6]. The total amount of <sup>18</sup>O,  $M_t$ , in the sphere sample after time,  $t$ , is expressed as a fraction of the corresponding quantity,  $M_\infty$ , after infinite time by the following relation [7]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(1+\alpha) \exp(-Dq_n^2 t/A^2)}{9 + 9\alpha + q_n^2 \alpha^2} \quad (1)$$

where  $q_n$  are the non-zero roots of  $\tan(q_n) = 3q_n/(3 + \alpha q_n^2)$ ,  $A$  is the radius of sample sphere, and  $\alpha$  the gram atom ratio of oxygen present in the solid to that in gaseous phase. This equation is approximated by following equations [8]:

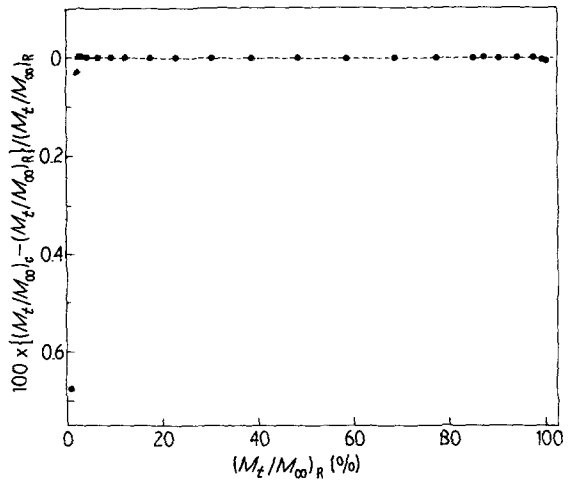


Figure 1 Estimated error of diffusion coefficient, when neglecting higher terms in Equation 2.  $M_t/M_\infty$ : the fractional exchange amount ( $\alpha = 0.1$ ,  $D = 10^{-12}$  cm<sup>2</sup> sec<sup>-1</sup>; C and R denote from Equations 2 and 1, respectively).

$$\begin{aligned} \frac{M_t}{M_\infty} = (1 + \alpha) & \left\{ 1 - \frac{\gamma_1}{\gamma_1 + \gamma_2} \operatorname{erfc} \left[ \frac{3\gamma_1}{\alpha} \left( \frac{Dt}{A^2} \right)^{1/2} \right] \right. \\ & \left. - \frac{\gamma_2}{\gamma_1 + \gamma_2} \operatorname{erfc} \left[ -\frac{3\gamma_2}{\alpha} \left( \frac{Dt}{A^2} \right)^{1/2} \right] \right\} \\ & + \text{higher terms} \end{aligned}$$

$$\gamma_1 = \frac{1}{2} \left[ (1 + \frac{4}{3}\alpha)^{1/2} + 1 \right] \quad \gamma_2 = \gamma_1 - 1 \quad (2)$$

The error of Equation 2 in neglecting the higher terms has been estimated. One can calculate the respective values  $(M_t/M_\infty)_C$  using Equation 2 and  $(M_t/M_\infty)_R$  using Equation 1 whose summation number was taken as 2000. These results are shown in Fig. 1. As seen, the values of  $[(M_t/M_\infty)_C - (M_t/M_\infty)_R] / (M_t/M_\infty)_R \times 100$  are less than 2% over wide values  $(M_t/M_\infty)_R$ . Calculations of the diffusion coefficients in the present study, therefore, were done using Equation 2.

## 3. Result and discussion

### 3.1. Material characterization

According to the phase relation of the Fe<sub>2</sub>O<sub>3</sub>–MgO system in air, as reported by Phillips *et al.* [9] (Fig. 2), magnesio-wüstite more or less forms with the host magnesio-ferrite at elevated temperatures, as long as the MgO/Fe<sub>2</sub>O<sub>3</sub> mole ratio is taken to be unity. If Fe<sub>2</sub>O<sub>3</sub> is taken to be in a slight excess, the magnesio-ferrite phase can be stable up to higher temperatures. A mole ratio of 0.95 was, therefore, chosen in the present study. At room temperature, X-ray diffraction showed that this polycrystalline material was a monophasic spinel compound.

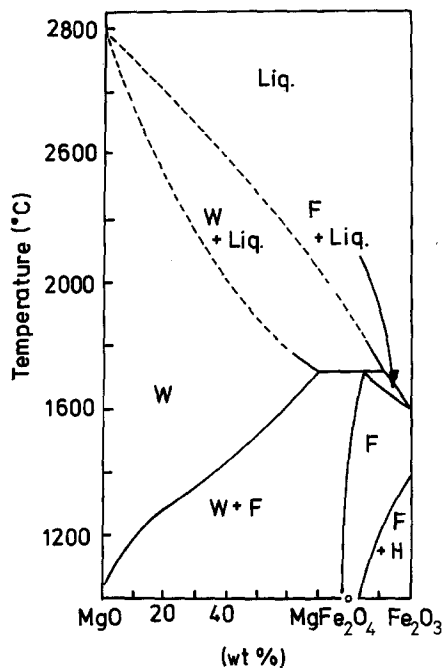


Figure 2 Phase relation of the MgO-Fe<sub>2</sub>O<sub>3</sub> system in air [9]. F, ferrite; W, wüstite; H, haematite.

Table I gives characteristic data such as the oxygen fraction with respect to the constituent cations and densities of this material. A close agreement was observed between oxygen fractions in the stoichiometric composition, AB<sub>2</sub>O<sub>4</sub> (0.5741) and those calculated on the basis of the chemically analysed contents of the three cations, Fe<sup>3+</sup>, Fe<sup>2+</sup> and Mg<sup>2+</sup>. The picnometrically determined density also agrees with the density calculated from the lattice constant assuming the sample to be a solid solution of MgFe<sub>2</sub>O<sub>4</sub>-Fe<sub>3</sub>O<sub>4</sub>. Hence, this material may contain less than 0.2 mol% cation vacancies.

### 3.2. Diffusion characteristics

Fig. 3 shows a typical time dependence of the dimensionless quantity,  $Dt/A^2$ , determined using Equation 2 in polycrystalline and single-crystal ferrites. No measurable weight change occurred during diffusion annealing in both materials. Both

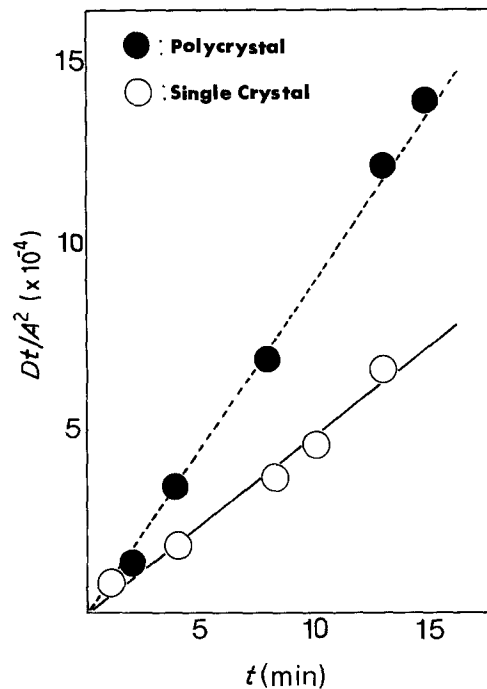


Figure 3 Plots of  $Dt/A^2$  against time,  $t$ , for single and polycrystalline magnesio-ferrites.

plots show straight lines passing through the origin, indicating that the surface exchange kinetics were not rate-controlling. Therefore,  $D_a$  (the apparent diffusion coefficient) may be calculated giving the particle radius for  $A$  in Equation 2.

Fig. 4a shows the temperature dependence of the diffusion coefficients thus estimated for single crystal particles with various sizes. No particle size dependence was found in these particles. This fact rules out the existence of sub-grain-boundaries. Accordingly, the values in Fig. 4a can all be regarded as the volume diffusion coefficients for the single crystal, and expressed by:

$$D = 1.24 \exp(-83\,500/RT) \text{ cm}^2 \text{ sec}^{-1} \quad (3)$$

In the polycrystalline material, on the other hand, the diffusivity varies with the size of particles used (see Fig. 4a), implying that the oxygen exchange is also influenced by grain-boundary

TABLE I Chemical analysis, oxygen fraction and density of the polycrystalline magnesio-ferrite

Content (wt %)*			Oxygen fraction from contents	Picnometric density (g cm <sup>-3</sup> )	Calculated density <sup>‡</sup> (g cm <sup>-3</sup> )
MgO	FeO	Fe <sub>2</sub> O <sub>3</sub> <sup>†</sup>			
19.5 ± 0.2	1.22 ± 0.04	79.3 ± 0.4	0.5712 ± 0.0003	4.50	4.52

\*Except ig. loss, and foreign ions.

<sup>†</sup>Subtracting ferrous oxide amount from total iron oxide.

<sup>‡</sup>Calculated from X-ray lattice constant, assuming Mg<sub>0.966</sub><sup>2+</sup>Fe<sub>0.034</sub><sup>2+</sup>Fe<sub>2.00</sub><sup>3+</sup>O<sub>4.00</sub>.

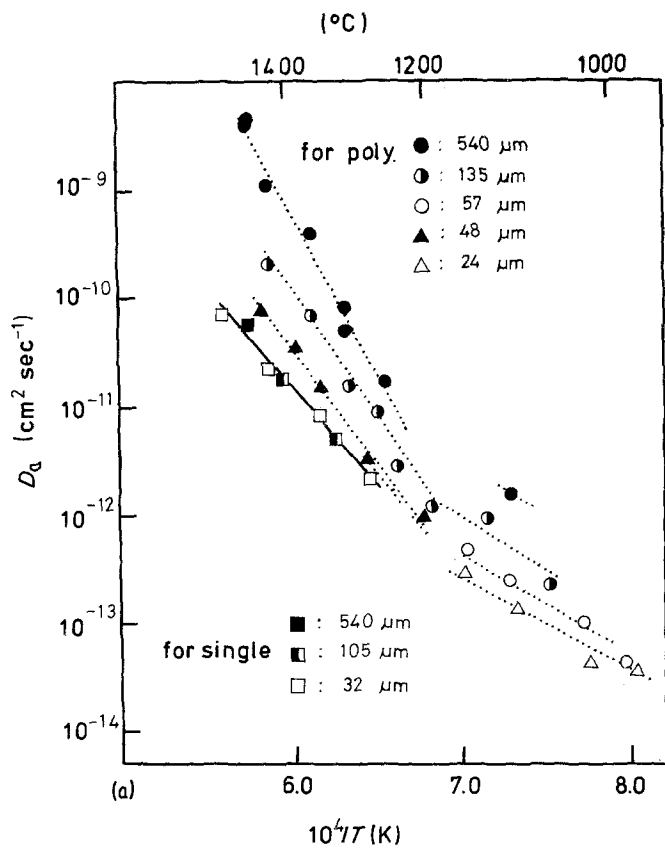
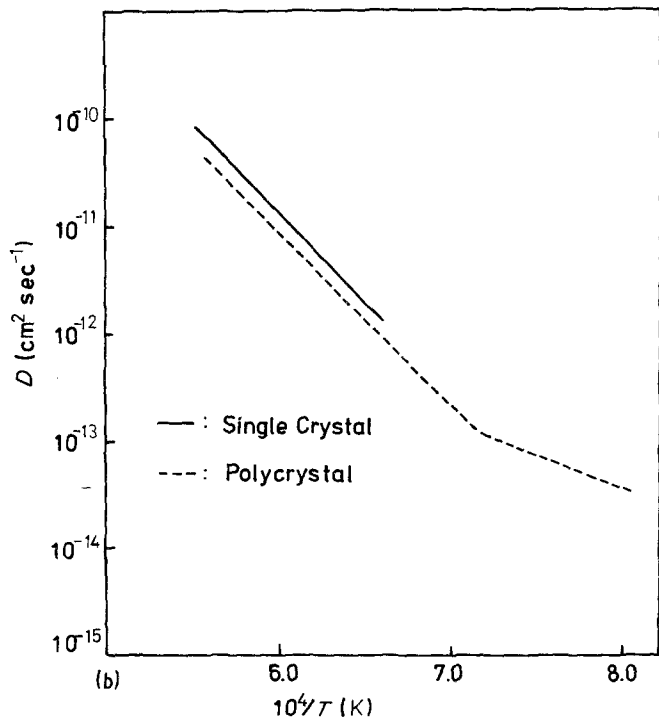


Figure 4 Temperature dependence of diffusion coefficients of magnesian ferrites. (a) Apparent diffusion coefficients of particles with a varying radius for the single crystal and polycrystal. (b) Volume diffusion coefficients in the single-crystal and polycrystalline magnesian ferrites. —, single crystal; ----, polycrystal.



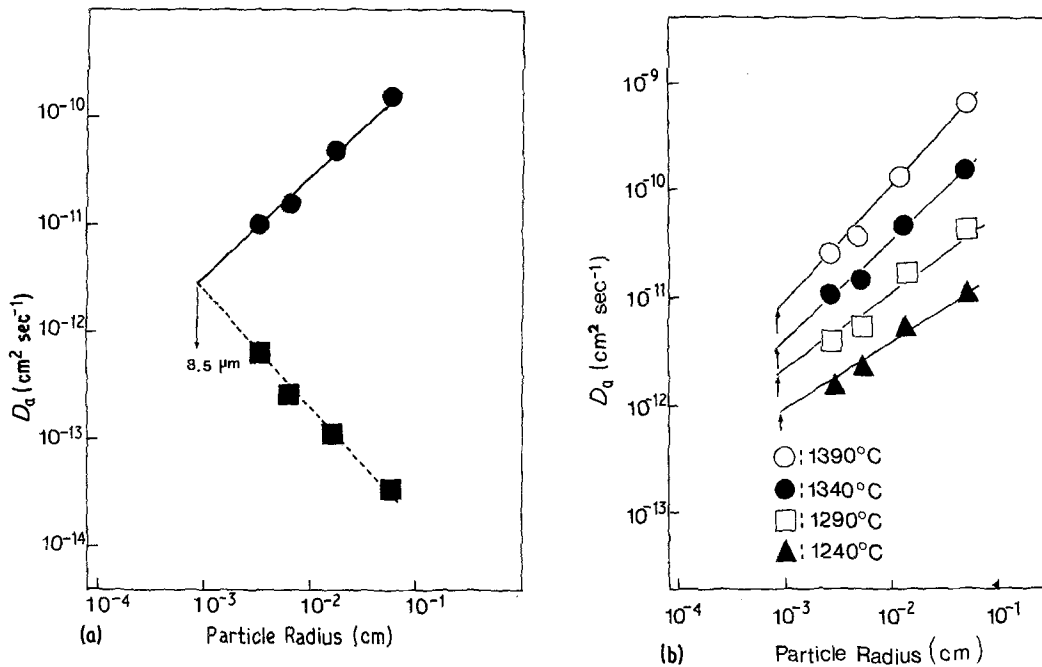


Figure 5 Particle size dependence of the apparent diffusion coefficients in polycrystalline magnesio-ferrite. (a) Calculated as  $A = \text{grain radius}$  (---■---) and  $A = \text{particle radius}$  (—●—) ( $1340^\circ\text{C}$ ). (b) Calculated as  $A = \text{particle radius}$  ( $1240$  to  $1390^\circ\text{C}$ ).

oxygen diffusion in addition to volume diffusion. In this case the resultant  $D_a$  is apparent.

The particle size dependence characteristics of  $D_a$  in general polycrystals are divided into three cases:

1. volume diffusion,  $D_1 \ll D_b$  (grain-boundary diffusion coefficient) where  $D_b$  is so fast that the concentration of  $^{18}\text{O}$  along the grain-boundary region is nearly equal to that in the gaseous phase through a diffusion anneal. In this case, calculation of  $D_a$  should be independent of particle size and is equal to  $D_1$ , taking the grain radius for  $A$ . This case was found in oxygen diffusion in polycrystalline  $\text{MgO}$  [10], and  $\text{Al}_2\text{O}_3$  [11], and nitrogen diffusion in  $\text{Si}_3\text{N}_4$  [12];

2.  $D_b = D_1$ . No preferential grain-boundary diffusion occurs in this case. A polycrystalline particle can be treated as a single-crystal particle as far as diffusion is concerned, and  $D_1$  can, therefore, be calculated by using the particle radius for  $A$ . This was reported for oxygen diffusion in calcia-stabilized zirconia [13].

3.  $D_1 < D_b$ . The relation between  $D_1$  and  $D_b$  lies between the foregoing two extreme cases 1 and 2. In this case, one cannot obtain  $D_1$  by using either the particle radius or grain radius for  $A$  in Equation 2.

Fig. 5a shows a plot of  $\log(\text{particle radius})$  against  $\log(D_a)$  which was calculated for the two cases of  $A = \text{grain radius}$  and  $A = \text{particle radius}$ . As seen there, both calculations give straight lines. The establishment of such straight lines was proved at least for the two extreme cases 1 and 2 [3]. When  $A = \text{particle radius}$ , a positive slope is obtained, and for  $A = \text{grain radius}$ , a negative one is obtained. Such diffusion characteristics correspond to case 3. If the two straight lines can be extrapolated to the point of intersection,  $D_a$  at this point should correspond to  $D_1$  [2].

The Arrhenius plot of  $D_1$  thus calculated is shown in Fig. 4b. Two regions may be seen, which may be formulated as follows:

$$D = 1.52 \times 10^{-1} \exp(-78\,600/RT) \text{ cm}^2 \text{ sec}^{-1} \quad (> 1100^\circ\text{C}) \quad (4)$$

$$D = 1.20 \times 10^{-7} \exp(-38\,000/RT) \text{ cm}^2 \text{ sec}^{-1} \quad (< 1100^\circ\text{C}) \quad (5)$$

It is likely that the higher and lower temperature regions in Fig. 4b are due to intrinsic and extrinsic diffusion, respectively. Spinel has an oxygen closed packed structure and the vacancy mechanism is probable in oxygen diffusion.

The oxygen diffusion coefficient in single-crystal magnesio-ferrite, on the other hand, can be expressed only by Equation 3. As seen clearly in Fig. 4b, the data from the polycrystal are very close to those of the single crystal, at least at the high-temperature region. This indicates that the present method of calculation of  $D_1$  using polycrystalline materials is valid. Such agreement of  $D_1$  between single crystals and corresponding polycrystals has been encountered in several cases [2, 14].

Oxygen diffusion data have been reported in several materials with spinel structure such as  $MgAl_2O_4$ ,  $Mg_2TiO_4$  [2, 15]. The activation energies of  $MgAl_2O_4$  and  $Mg_2TiO_4$  were found to be 105 and 94 kcal mol<sup>-1</sup>, respectively. In metal systems, there is a pronounced relationship between the activation energy in diffusion and the melting point [16]. Although the melting points of  $Mg_2TiO_4$  and  $MgFe_2O_4$  are not exactly clear, because of the occurrence of incongruent melting, they may lie around 1760 and 1700°C [9, 17], respectively. Thus for at least three,  $MgAl_2O_4$  (m.p. 2105°C [18]),  $Mg_2TiO_4$ , and the present magnesio-ferrite, the order of magnitude of the activation energies qualitatively fits the order of their melting points. Among these three, two Debye temperatures, for the present ferrite (500 K) and  $MgAl_2O_4$  (700 K) [19, 20], are available. The activation energy can also be seen in relation to the Debye temperature in these two materials.

### 3.3. Grain-boundary diffusion

As seen in Fig. 4a, the apparent activation energies of  $D_a$  of magnesio-ferrite with different particle sizes are more or less higher than that of  $D_1$  (Table II), and the difference between  $D_a$  and  $D_1$  increases with increasing temperature. To determine this tendency more clearly, the particle size dependencies of  $D_a$  at several temperatures are illustrated in Fig. 5b in which  $D_a$  was calculated as  $A = \text{particle radius}$ . Fig. 5b shows that the relative magnitude of  $D_b$  with respect to  $D_1$  is greater with

TABLE II Apparent activation energy of each particle radius in magnesio-ferrite and magnesio-titanate polycrystal

Activation energy (kcal mol <sup>-1</sup> )	Particle radius (μm)			
	31.8	57.0	118.	540.
Present ferrite	87	96	114	142
Titanate	92	87	85	79

increasing temperature. This strongly suggests that the activation energy of grain-boundary diffusion is larger than that of volume diffusion in this temperature region. This tendency is contrary to oxygen diffusion in  $Mg_2TiO_4$  [2] and diffusion in many other oxides in which grain-boundary diffusion is less important at elevated temperatures [21].

Such anomalous behaviour in magnesio-ferrite may be caused by either an increase in oxygen defects along a grain-boundary or an increase in grain-boundary width at elevated temperatures. An important fact was that such an anomaly was also seen in iron-doped magnesia [22]. These two materials have iron ions in common, in which ferrous ion may increase with increasing temperature. Auger measurements of Mn-Zn-ferrite [23] have clarified the preferential formation of oxygen deficiencies along the grain boundary. Poulus also claimed the occurrence of a preferential reduction in the grain-boundary region with respect to the bulk with increasing temperature in Mn-Zn-ferrite [24]. For the present ferrite, the reduction and formation of oxygen vacancies may occur preferentially along grain boundaries at elevated temperatures, as a result of which oxygen diffusion becomes considerable.

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