Solubility of MgO in Single-Crystal Al_2O_3

Ken ANDO* and Masataka MOMODA

(Department of Nuclear Engineering, Faculty of Engineering, Kyushu University
6-10-1, Hakozaki, Higashi-ku, Fukuoka-shi 812)

* Present address : Metals and Ceramics Lab., Toshiba Res. and Dev. Center, Toshiba Corporation

単結晶 Al_2O_3 における MgO の固溶度

安藤 健*・百田正隆

(九州大学 工学部 応用原子核工学科)
* 現在 : (株) 東芝総合研究所

A new diffusion-couple method was developed to determine the solubility of MgO in Al_2O_3 . The solubility was determined by electron probe microanalysis. The solubilities determined in air using a diffusion-couple of a single crystal and a large grain-sized polycrystal are approximately 55 and 95 wt ppm at 1973 and 2073 K, respectively, much smaller than those previously determined by Roy and Coble. The cause of the large difference is attributed to the difference in the physical states of the samples. While single crystals and large grain-sized polycrystals were used in this work, powder was used in the previous work. When 400 wt ppm MgO-doped polycrystalline Al_2O_3 was annealed in air for 2.5 d at 2073 K, second phase particles of spinel precipitated at grain boundaries, especially at triple grain boundaries.

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1. Introduction

In order to elucidate self-diffusion mechanisms in pure oxides, it is helpful to clarify the defect structures in crystals in which aliovalent cations are dissolved. Ando et al. measured the oxygen self-diffusion coefficient in Fe^{3+} -doped MgO single crystals and clarified that the predominant defect on the oxygen ions was the vacancy pair ($V_{\text{O}}^{\bullet} V_{\text{Mg}}^{\bullet}$) and the oxygen ions diffused not by a mono-vacancy mechanism but by a vacancy pair mechanism.¹⁾ Analogously to the previous work, it is very informative to clarify the defect structures in crystals in which lower-valent cations are dissolved. The system MgO-doped Al_2O_3 was selected as an example for the purpose. During the progress of this experiment, however, we noticed that the solubility of MgO in Al_2O_3 was much smaller than those previously determined by Roy and Coble in 1968.²⁾ It seemed worth while, therefore, to redetermine the solubility of MgO in Al_2O_3 .

It is very important to clarify the roles of additives in sintering. Since the development of the transparent sintered- Al_2O_3 in which a small amount of MgO (≤ 0.25 wt%) was added,³⁾ many works have been performed to make clear the role of the MgO in the sintering of Al_2O_3 . Recently, Berry and Harmer reviewed and studied the role in the sintering.⁴⁾

It is expected that the most decisive knowledge

to clarify the role is to know whether the MgO effectively functions in the solid solution region or in the outer region of the solid solution. The most decisive study to solve the problem is to determine the solubility of MgO in Al_2O_3 . So far as the authors are aware, only one paper was published about the solubility by Roy and Coble.²⁾

According to their work the solubility in vacuum was too small to detect by the change of the lattice parameter. They have determined the solubility, therefore, using a unique technique as follows. A pre-equilibrated two-phase mixture of Al_2O_3 plus spinel was placed in a closed Mo crucible with a undoped powder of Al_2O_3 . The crucible was divided into two sections vertically with a spacer. The mixture was placed in the lower section and the undoped powder was placed on the spacer in the upper section. The crucible containing the mixture and the undoped- Al_2O_3 powder was annealed for 6 h at the same temperature at which the mixture was pre-equilibrated. The single-phase Al_2O_3 containing the MgO in equilibrium with spinel was removed and analyzed spectrochemically. The solubilities were obtained in the temperature range of 1803 to 2103 K. The solubilities obtained by them in vacuum, given as the atomic fraction Mg/Al at 1803 and 2103 K were 110×10^{-6} and 1400×10^{-6} , respectively.

It is expected that the solubility measured by Roy and Coble is larger than that which would be obtained using an Al_2O_3 single crystal by the following reasons. One reason is that the sample used by Roy and Coble was powder of an average particle size of $2\mu\text{m}$. The second reason is that the powder was already in a progress of sintering: It is supposed that the powder was in a condition of initial-stage sintering and some grain boundaries were introduced.

Therefore, the main purpose of this work is to determine the solubility of MgO using single crystals of Al_2O_3 . In this work a new diffusion-couple method was used to determine the solubility. A pellet of an Al_2O_3 polycrystal doped with a little more excess MgO than the solubility was joined to a pellet of a pure single-crystal Al_2O_3 . The MgO concentration distributions in the couple after an annealing were detected by electron probe microanalysis (EPMA). Moreover, the distributions of the MgO concentration and the existence of spinel precipitates in the polycrystals were carefully searched.

2. Experimental procedure

2.1 Materials

High-purity Al_2O_3 powder* was used to prepare the polycrystalline samples. The purity of the powder was 99.99% and the main impurities were C, K, and Si in order of amount. The content of the Mg impurity was less than 1 ppm. The average particle size was $0.4\mu\text{m}$.

Magnesia doping was achieved by the addition of a specified quantity of a solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in ethanol to the powder. The alumina slurry was mixed in a water bath at about 330 K using an ultrasonic mixer until the most of the ethanol evaporated. The powder was crushed in a mortar made of polyamide resin to avoid contamination. After a calcination at 873 K for 7.2×10^3 s in air the powder was also crushed in the mortar. The powder was isostatically cold-pressed under a pressure of 1.96×10^2 MPa into pellets of about 0.015 m length and 0.010 m in diameter. The pellets were sintered in air at 1773 K. The firing times were 1.4×10^4 s for the standard samples used to make a calibration chart of EPMA and 3.6×10^4 s for the polycrystals used for the solubility measurements as an MgO source.

The single-crystal Al_2O_3 grown by the Verneuil method was the same rod of 0.0032 m in diameter as was previously used for the determinations of the oxygen self-diffusion coefficients.⁵⁾ The MgO content in the single crystal was less than 10 wt

ppm.

2.2 Diffusion couple

The diffusion couple was constructed with a pellet of the polycrystalline Al_2O_3 doped with 400 wt ppm MgO and a small pellet of a high-purity single-crystal Al_2O_3 . The polycrystal was used as a source of the MgO diffusing into the single crystal. The MgO amount 400 wt ppm was chosen after several experiments. The amount of the doping must be larger than the solubility so as to keep a constant activity of MgO at the interface during the annealing but the amount must be as small as possible so as to be able to detect the MgO concentration distributions both within the single crystal and the polycrystal at the same time with a high precision using EPMA.

A small pellet of the polished single-crystal Al_2O_3 was placed on the polished surface of the polycrystalline- Al_2O_3 pellet. The system was annealed at 1873 K to join the pellets each other. One couple was tightly wrapped with a platinum foil and mounted in the 400 wt ppm MgO-doped Al_2O_3 powder under a high pressure of isostatical cold-press to inhibit the preferential vaporization of the MgO from the couple. This couple was used for the determination of 1773 K. The another couple was directly mounted in the powder for the measurement of a high temperature 2073 K. The annealings were made in air in a high-purity Al_2O_3 tube heated in an Mo-wire wound furnace for 5.0 and 2.5 d at 1773 and 2073 K, respectively. The temperatures were measured using a thermocouple. After the annealing each couple was sawed into halves vertical to the interface. The one half was used for EPMA. Determinations of the chemical compositions were made from the relative intensities of Mg $K\alpha$ and Al $K\alpha$ lines using a calibration chart determined from the standard samples. The measurements were done under the conditions of an accelerating voltage of 30 kV and a sample absorption current of $0.25\mu\text{A}$. The counting time of the X-rays was 200 s.

3. Results and discussion

3.1 Calibration chart

Alumina polycrystals containing 0, 25, 50, 75, and 100 wt ppm MgO were used as the standard samples. The standard samples were obtained by sintering the Al_2O_3 powders doped with the specified amounts of MgO at 1773 K for 1.4×10^4 s. The densities of the standard samples were more than 99% of the theoretical. Despite the outer region of the solubility obtained in this work, which will be discussed later, it was difficult to find precipitates of spinel and the segregation of MgO in the 400 wt ppm MgO-

*AKP-HP, Sumitomo Chemical Co., Ltd., Osaka, Japan.

Fig. 1. The MgO-concentration dependence of the relative intensity of Mg $K\alpha$ and Al $K\alpha$ lines I_{Mg}/I_{Al} in the MgO-doped Al_2O_3 polycrystals.

Fig. 2. The optical micrograph of 400 wt ppm MgO-doped polycrystalline Al_2O_3 annealed at 2073 K for 2.5 d in air.

Fig. 3. The second phase particles of spinel precipitates in the polycrystalline Al_2O_3 annealed at 2073 K for 2.5 d in air in which 400 wt ppm MgO was previously added.
(a) Scanning electron micrograph, (b) Characteristic X-ray image of Mg $K\alpha$ line

doped Al_2O_3 which was sintered at the same temperature and for the same period as the standard samples were. This indicates that even if the amount of MgO, 75 and 100 wt ppm, exceeds the solubility, all of the samples prepared can exactly be the standard samples for the calibration chart. The average grain size for the standard samples and for the 400 wt ppm MgO-doped samples were $10\mu\text{m}$.

The calibration chart is shown in Fig. 1. In this experiment the concentration of the MgO which has a confidence of 99.7% was 70 wt ppm. The confidence decreased to 95% at 50 wt ppm. The magnitude of the relative intensity $I_{\text{Mg}}/I_{\text{Al}}$ in Fig. 1 slightly changed day by day or on conditions of the analyzer, although the MgO concentration dependence of the relative intensities did not change. Therefore, the couples and the standard samples were mounted in a resin at the same time and the relative intensities for these samples were measured alternately.

3.2 Distribution of spinel precipitates

The microstructure of the polycrystal far from the interface which was used for the measurement at 2073 K is shown in Fig. 2. The grain size was increased to approximately $50\mu\text{m}$ during the annealing of 2.5 d. The etching was made in air at 1673 K for 1.8×10^3 s. When the microstructure was enlarged using scanning electron microscopy, small precipitates of spinel could be found at grain boundaries, especially at triple grain boundaries as shown in Fig. 3 (a). These precipitates were confirmed to be spinel by observing the intensities of the X-rays of Mg and Al $K\alpha$ lines for the same positions in Fig. 3 (a). The image of Mg X-rays is shown in Fig. 3 (b). The upper and lower images were taken before and after the etching, respectively. Each sample clearly showed the appearance of spinel precipitates.

Magnesia distributions across a grain boundary were searched by step-scanning method of EPMA along a line which was shown in Fig. 4 (a). The MgO concentration distributions are shown in Fig. 4 (b). This analysis was made before the etching and the searched line in Fig. 4 (a) was identified with the positions of as-grown pores as a guide after the analysis. The similar analyses were made at several positions across a grain boundary. All of the results were the same as that shown in Fig. 4. Any special high intensities of Mg $K\alpha$ line were not obtained across a grain boundary.

It is concluded, therefore, that when 400 wt ppm MgO-doped Al_2O_3 is well-sintered in air to be a large grain size of approximately $50\mu\text{m}$ at 2073 K, second phase particles of spinel (MgO·

(a) 20 μm

Fig. 4. The MgO-concentration distributions across a grain boundary for the polycrystalline Al_2O_3 annealed at 2073 K for 2.5 d in air in which 400 wt ppm MgO was previously added.

The line on the scanning electron micrograph of (a) indicates the trace along which the analysis of (b) was made.

$n\text{Al}_2\text{O}_3$; where the n is a small number more than unity) are precipitated preferentially at triple grain boundaries. Although it is not completely decisive because of the diffusion of electrons in the specimen to a width of several micrometers in the analysis of EPMA, it is also concluded that no precipitates of spinel and no segregation of the MgO can be found at the grain boundaries between the two grains.

3.3 Solubility of MgO in Al_2O_3

The MgO concentration distributions in the couple annealed at 1973 K are shown in Fig. 5. Magnesium ions diffused into the single-crystal Al_2O_3 . We can see the value of the MgO concentration in the single crystal is about 55 wt ppm in the vicinity of the interface. As shown in Fig. 5, this value is almost the same as those obtained in

the polycrystal in which previously 400 wt ppm MgO was doped. A high intensity of Mg $K\alpha$ line

Fig. 5. The MgO-concentration distributions in the diffusion couple of polycrystalline and single-crystal Al_2O_3 annealed at 1973 K for 5.0 d in air. 400 wt ppm MgO was previously doped in the polycrystalline Al_2O_3 .

Fig. 6. The MgO-concentration distributions in the diffusion couple of polycrystalline and single-crystal Al_2O_3 annealed at 2073 K for 2.5 d in air. 400 wt ppm MgO was previously doped in the polycrystal.

Table 1. Comparison of the solubilities of MgO in Al_2O_3 obtained in this work and in the previous work of Roy and Coble.

Temperature (K)	This work		Roy & Coble	
	atomic fraction $\text{Mg}/\text{Al} \times 10^6$	MgO (wt ppm)	atomic fraction $\text{Mg}/\text{Al} \times 10^6$	MgO (wt ppm)
1973	70	55	513	406
2073	120	95	1126	890

due to a precipitate of spinel were observed in several places in the polycrystal. That value was not plotted in Fig. 5. The agreement of the MgO concentration in the single crystal and in the polycrystal indicates that the value about 55 wt ppm is the equilibrium value of the solubility in Al_2O_3 at 1973 K. These values are much smaller than those previously reported.²⁾

The MgO concentration distributions in the couple annealed at 2073 K are shown in Fig. 6. The feature of the concentration distributions is similar to that of 1973 K except the increase of the solubility to about 95 wt ppm. Precipitates of spinel were also observed at several places on the polycrystal as already discussed. According to the results of Roy and Coble, the solubilities were expressed as $\ln X = a - b/T$. Where X is the solubility of atomic fraction Mg/Al , T is the absolute temperature, and a and b are the constants. Using the two solubilities obtained in this work, the temperature dependence of the solubilities can be expressed by the next equation.

$$\ln X = 1.61 - 2.20 \times 10^4/T.$$

As compared in Table 1, the solubilities obtained in this work are much smaller than those obtained by Roy and Coble. These new solubilities obtained in this work are about 1/7 and 1/9 of those obtained by Roy and Coble at 1973 and 2073 K, respectively. The cause of this difference of the solubilities is thought to be due to the difference in the physical states of the samples of Al_2O_3 used in this work and the work of Roy and Coble. Our measurements were done using single crystals and large grain-sized polycrystals. On the other hand Roy and Coble used powder or loosely-sintered polycrystals. This facts suggest that the solubility of MgO in Al_2O_3 are larger at surfaces (including grain boundaries) than in the bulk. But the magnitude of the solubility is too small as clarified in this work and it is difficult to make clear the magnitude of the difference of the solubilities between in the bulk and at the surfaces. This interpretation is consistent with our result: It was difficult to find some precipitates of spinel and the segregation of MgO in the small grain-sized 400 wt ppm MgO-doped Al_2O_3 polycrystal.

3.4 The role of MgO in the sintering of Al_2O_3

It is clarified in this work that the solubility of MgO in Al_2O_3 is much

smaller than those previously reported. This is an important knowledge to clarify the role of the MgO in the sintering. Berry and Harmer studied the role as a solid-solution additive using 198 wt ppm MgO-doped Al_2O_3 at 1873 K in air.⁴⁾ But according to the results of this work, the value of the 198 wt ppm already exceeds the solubility at the temperature 1873 K. The work which have studied the effect of the MgO additive in the new solid-solution range obtained in this work can be found in the work of Peelen although his work has been done in a humid H_2 -atmosphere.⁶⁾ According to his result at 1903 K the addition of the MgO in the new solid-solution range was not so effective. The most effective result was obtained by the addition of 300 ppm. This value also exceeds the new solubility. Peelen pointed out himself that the second phase particles were precipitated in the 300 ppm MgO-doped Al_2O_3 in a humid H_2 -atmosphere at 1903 K. It is concluded, therefore, that the most effective amount of the MgO for the sintering is larger than the solubility: The MgO can effectively function in the outer region of the solubility. The high solubility of the MgO during the initial-stage sintering or at the interfaces which were proved by the difference of the solubilities between this work and the work of

Roy and Coble may be the most important clue to clarify the sintering mechanism. The precipitation theory or the MgO segregation theory must be considered once again.

As mentioned in the introduction of this paper, our main purpose is to clarify the defect structures in Al_2O_3 . Then we are going to determine the magnesium impurity-diffusion coefficients using these results obtained in this work and discuss the defect structures in Al_2O_3 .

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