47. Effects of Additives (Fe$_2$O$_3$, Cr$_2$O$_3$ and CoO) on the Diffusion of Ni$^{2+}$ in MgO

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Diffusion coefficients of Ni$^{2+}$ in pure single crystal MgO and in the ones containing additives of Fe$_2$O$_3$, Cr$_2$O$_3$ and CoO were measured using an electron microprobe analyzer. It was found that addition of Cr$_2$O$_3$ and Fe$_2$O$_3$ enhanced the diffusion of Ni$^{2+}$ considerably but CoO did not have such an effect. It is inferred that the diffusion of Ni$^{2+}$ takes place solely via extra vacancies formed due to the substitution of 2 Fe$^{3+}$ (or 2 Cr$^{3+}$) for 3 Mg$^{2+}$ in MgO in the additions of Fe$_2$O$_3$ and Cr$_2$O$_3$. On the other hand, addition of CoO does not cause extra vacancies in MgO owing to the coincidence of the valence of Mg$^{2+}$ with that of Co$^{2+}$ and does not probably enhance the diffusion.

1. Introduction.

As for the effects of impurities or additives on the diffusion in ionic crystals, investigations were made in great detail concerning sodium chloride$^{1,2}$, in the first place, and it is understood that substitution for Na$^+$ of the ions having higher valences leads to formation of extra vacancies and consequently to enhancement of Na$^+$ diffusion in NaCl. In addition, this effect could be observed even when impurities were not added especially. Namely, it was seen that the Arrhenius plot of Na$^+$ diffusion coefficients consisted of two straight lines of different slopes, one for the higher temperature range and the other for the lower temperature range. This phenomenon is considered to be due to the fact that at the low temperature range lattice defects formed due to impurities predominate, while at the higher temperature range the thermally formed defects predominate.

As for oxides, ZrO$_2$ presents a most well-known example$^{3}$, namely it is stabilized in a cubic structure by the addition of a small amount of CaO, accompanied with the formation of anionic vacancies because of the valence difference between Zr$^{4+}$ and Ca$^{2+}$. These vacancies remarkably enhance the diffusivity of O$^{2-}$ and consequently increase the electric conductivity by ionic conduction. As a result, ZrO$_2$, as is well-known, is applied for a heating element quite often. On the other hand, such oxides as FeO, ZnO and CoO are liable to show structural non-stoichiometry depending on the atmosphere and result in lattice defects. These defects have been also shown to play an important role in the diffusion$^{4,5}$.

The extra vacancies resulting from impurities or additives and from structural nonstoichiometry seem very important to the diffusion phenomena, especially to reactions between oxides where reacted layers have almost invariably nonstoichiometric structures and contain extra defects.

In this consideration, diffusion coefficients of Ni$^{2+}$ in single crystal MgO containing additives of Fe$^{3+}$ and Cr$^{3+}$ which cause extra vacancies in MgO and those in MgO containing Co$^{2+}$ which does not have such an effect, were compared in the present investigation.

The diffusion of metal ions in MgO has been reported previously$^{6,7}$, but no report has dealt with the effects of impurities or additives on the diffusion particularly.

The term “extra vacancies” means the vacancies other than those thermally formed in a stoichiometric compound and includes extrinsic ones formed due to impurities and intrinsic ones due to nonstoichiometric structures.

2. Experimental.

2.1. Reagents.

MgO single crystal: selected from fused MgO (Ca, Al, Fe less than 300 ppm).
The other reagents: special grade chemically pure reagents.

2.2. Methods of doping MgO single crystal with impurities.

Thin sections of MgO single crystal (less than 0.3 mm thick) were held between polycrystalline MgO solid solution tablets containing various concentrations of additives as shown in Fig. 1 and heated. Table 1 lists the heating conditions.

Table 1. Conditions for adding impurities.

<table>
<thead>
<tr>
<th>Specimens for heat treatment</th>
<th>heating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>polycrystalline MgO</td>
<td>MgO single crystal</td>
</tr>
<tr>
<td></td>
<td>1 mol% Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>0.2 mol% Cr₂O₃</td>
</tr>
<tr>
<td></td>
<td>1 mol% NiO</td>
</tr>
<tr>
<td></td>
<td>2.5 mol% CoO</td>
</tr>
<tr>
<td></td>
<td>MgO single crystal</td>
</tr>
<tr>
<td></td>
<td>5 mol% NiO</td>
</tr>
</tbody>
</table>

To check the uniformity of adding, a doped thin section was tested by the electron microprobe analysis. It was found that in the cases of Fe₂O₃ and CoO, the uniformity was satisfactory, but that in the case of Cr₂O₃, the concentration of Cr decreased gradually beyond about 100 μ from the interface. However, the diffusion distance of Ni²⁺ being less than 100 μ, the uniformity of adding may be considered satisfactory enough in all the cases.

2.3. Heat treatment for diffusion.

A pile of pure and doped MgO pieces as shown in Fig. 2 was heated in a SiC-heating-element electric furnace. The temperature was controlled automatically (±5°C). On the pile was laid a protective tube for the thermocouple to make the temperature measurement more precise and the contact better. The heat treatment temperatures were 1450°C, 1480°C, 1510°C and 1550°C.

2.4. Analyzing method.

MgO pieces in the pile stuck together after the heat treatment and the whole system was applied to the specimen for analysis. The specimen was buried in resin after the heat treatment and cut perpendicular to the diffusion interface. The array of the specimen surface was such that a polycrystalline MgO piece containing 10 mol% NiO lay between doped and pure MgO single crystal pieces as shown in Fig. 3. The electron microprobe analysis was conducted perpendicular to the two interfaces, namely along the lines (1) and (2) as depicted in the figure. The specimen surfaces were polished thoroughly with SiC and diamond paste, and subsequently they were coated with carbon by separating in water a carbon film spattered on mica and scooping it, to afford them electric conductivity. To obtain the Ni concentration distribution across the interface, the Ni Kα intensity profile as drawn by the scanning was used, assuming that the intensity was linear with the concentration. To prove it, polycrystalline
MgO tablets containing 2, 4, 6, 8 and 10 mol% NiO were synthesized to be used for the standards. The Ni Kα intensities from the standards were plotted against the concentrations of NiO, as shown in Fig. 4. Obviously the plot was found to be almost linear. Another quantitative analysis, which is generally considered more precise, consists of making a calibration curve from the ratios of Mg Kα to Ni Kα intensity plotted against the concentration of Ni (or Mg) in the standards and obtaining the concentration for the spots to be analyzed by using this calibration curve. However, the Mg Kα intensity is so weak and easily influenced by the local state of surfaces. In addition, only the relative NiO concentration being necessary, the above-mentioned method was adopted in this investigation.

The recorded intensity profile was smoothed so as to average the local fluctuations. The variation of the diffusion coefficients accompanying this smoothing being less than 10%, it is considered negligible in view of the fairly large errors in the diffusion coefficient measurements.

### 3. Results

Diffusion coefficients were obtained by the methods shown in examples (a) and (b).

(a) MgO single crystal/polycrystalline MgO (10 mol% NiO) 1510°C, 45 hrs.

Fig. 5 shows the Ni Kα scanning profile as drawn perpendicular to the interface. It was smoothed as the figure shows and considered to indicate the concentration distribution. In obtaining diffusion coefficients, it was assumed that the diffusion followed the Fick’s law and that the concentration of NiO was held at a definite value all through the polycrystalline MgO because of a high diffusivity of Ni2+ ion in it. According to the Fick’s law, the concentration C at the distance x after time t is given by

\[
C = C_0 \left[1 - \text{erf} \left( \frac{x}{\sqrt{2Dt}} \right) \right] \quad \text{(1)}
\]

\[
\therefore \text{erf}^{-1}(1-C/C_0) = \frac{x}{2\sqrt{Dt}} \quad \text{(2)}
\]

The plot of \(x - \text{erf}^{-1}(1-C/C_0)\) against x gives a straight line, as shown in Fig. 6. From the slope of this, it follows that

\[
\frac{1}{\sqrt{2Dt}} = 0.015
\]

(b) MgO single crystal (0.5 mol% Cr2O3)/polycrystalline MgO (10 mol% NiO), 1450°C, 4 hrs.

Fig. 7 shows the Ni Kα scanning profile. Similarly to (a), the plot of x against \(\text{erf}^{-1}(1-C/C_0)\)
was conducted. From the slope of the straight line, it follows substituting \( t = 4 \times 60 \times 60 \) that

\[
D = 2.8 \times 10^{-10} \text{ cm}^2/\text{sec}.
\]

Fig. 7. Electron microprobe analysis scanning profile: single crystal MgO (0.5 mol% Cr\(_2\)O\(_3\))/polycrystalline MgO (10 mol% NiO) 1450°C, 4 hrs.

(E) distance from the interface

Electron microprobe analysis conditions.
same as in Fig. 5.

Fig. 8. Diffusion coefficients of Ni\(^{2+}\) in pure single crystal MgO and in doped single crystal MgO (cm\(^2/\text{sec}\)).

In the same manners, diffusion coefficients of Ni\(^{2+}\) in pure and doped single crystal MgO were measured at various temperatures as listed in Table 3 and shown in Fig. 8.

In the addition of Cr\(_2\)O\(_3\), chromium replaces Mg almost in the form of trivalent ions, as will be discussed later. Therefore, the number of vacancies formed due to substitution of Cr\(^{3+}\) for Mg\(^{2+}\) is one half number of Cr\(^{3+}\) substituted. In this consideration, the diffusion coefficients in the addition of various amounts of Cr\(_2\)O\(_3\) were measured and plotted against the amounts of Cr\(_2\)O\(_3\) added, as shown in Fig. 9. It is clearly seen here that the diffusion coefficient is linear with respect to the Cr\(_2\)O\(_3\) concentration. This seems to show that the diffusion of Ni\(^{2+}\) in the addition of Cr\(_2\)O\(_3\) proceeds solely via excessive vacancies formed due to the addition of Cr\(_2\)O\(_3\).

4. Discussions.

4.1. Valence of iron in MgO.

Many reports\(^8,9,10\) have dealt with the valence of iron in MgO and it has been understood that iron exists as a mixture of divalent and trivalent ions. The ratio of them differs according to the concentration of iron in MgO. Namely, as the concentration increases, those in the trivalence increase. In addition, the ratio depends on the oxygenpartial pressure and temperature. However, no detailed data of the ratio considering all these factors simultaneously have ever been obtained. Also in the present investigation, iron is considered to have existed as a mixture of divalent and trivalent ions, causing extra vacancies in MgO.

4.2. Valence of chromium in MgO.

R. Roy\(^11\) stated on the basis of the density of MgO containing Cr\(_2\)O\(_3\) in various concentrations that chromium existed as

\(\text{Ni}^{2+}\) in pure and doped single crystal MgO were measured at various temperatures as listed in Table 3 and shown in Fig. 8.

In the addition of Cr\(_2\)O\(_3\), chromium replaces Mg almost in the form of trivalent ions, as will be discussed later. Therefore, the number of vacancies formed due to substitution of Cr\(^{3+}\) for Mg\(^{2+}\) is one half number of Cr\(^{3+}\) substituted. In this consideration, the diffusion coefficients in the addition of various amounts of Cr\(_2\)O\(_3\) were measured and plotted against the amounts of Cr\(_2\)O\(_3\) added, as shown in Fig. 9. It is clearly seen here that the diffusion coefficient is linear with respect to the Cr\(_2\)O\(_3\) concentration. This seems to show that the diffusion of Ni\(^{2+}\) in the addition of Cr\(_2\)O\(_3\) proceeds solely via excessive vacancies formed due to the addition of Cr\(_2\)O\(_3\).
trivalent ions in MgO, causing extra vacancies. A. Cimino, M. LaJacono, P. Porta and M. Valigi found by the iodometry that Cr existed almost as trivalent ions with a small amount of hexavalent ones. The decrease of the lattice constant with increasing concentration of Cr$_2$O$_3$ in MgO also indicated that Cr existed as tri-or higher valent ions, because the lattice would expand if divalent chromium ion ($r=0.83$ Å) should replace Mg$^{2+}$ ($r=0.64$ Å).

4.3. Effects of extra Vacancies.

It is considered that the formation of extra vacancies leads to enhancement of diffusion as shown clearly in Fig. 8. In other words, the diffusion coefficients increased remarkably only in the additions of Cr$_2$O$_3$ and Fe$_2$O$_3$ which are considered to cause extra vacancies, more remarkably in the addition of Cr$_2$O$_3$. Since chromium exists almost as trivalent ions causing extra vacancies and iron as a mixture of divalent and trivalent ions, it seems reasonable that if the same molar amount of Fe$_2$O$_3$ and Cr$_2$O$_3$ is added, Cr$_2$O$_3$ is more effective. Comparing the diffusion coefficients in pure MgO with those in the ones containing the additives of Fe$_2$O$_3$ and Cr$_2$O$_3$, it is assumed that in the latter cases the diffusion occurred almost solely via extra vacancies. Under this assumption, the diffusion coefficient is proportional to the concentration of extra vacancies. To confirm this relationship, the diffusion coefficients were measured in the additions of various amounts of Cr$_2$O$_3$, as shown in Fig. 10. It shows clearly that the diffusion coefficients are proportional to the amount of Cr$_2$O$_3$ added.

In this consideration, the ratio of trivalent iron in the total amount of iron was determined assuming that the diffusion coefficient is proportional to the number of trivalent ions. Namely, chromium being considered to exist totally as trivalent ions in MgO, the ratio of the trivalent iron in the total iron is expressed as the ratio between the diffusion coefficients in the additions of Fe$_2$O$_3$ and Cr$_2$O$_3$ in a same molar amount. Table 4 lists the results obtained in this manner. It is seen that about 20-30% of the total iron is trivalent and the rest is divalent in the temperature range used in the present investigation. Owing to a fairly great error (20-30%) of the diffusion coefficients more precise discussion will be refrained from here.

Table 4. Ratio of trivalent iron to the total iron dissolved in MgO as determined from the ratio $D_{Ni^{2+}}$ in Fe$_2$O$_3$-doped MgO/$D_{Ni^{2+}}$ in Cr$_2$O$_3$-doped MgO

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1450°C</th>
<th>1480°C</th>
<th>1510°C</th>
<th>1550°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$/total Fe</td>
<td>0.25</td>
<td>0.27</td>
<td>0.31</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8 shows the Arrhenius plots of the diffusion coefficients for various cases. From the slopes of the plots, the so-called activation energy for each case was calculated, as listed in Table 5. It is seen that the activation energy for the case of pure MgO single crystal is not so different from those for the cases of doped MgO single crystals. Only in the case of Cr$_2$O$_3$-doped MgO, the activation energy was smaller by 10 kcal, but the difference is not so much if the activation energy is decreased as much as the energy to form vacancies in adding impurities which cause extra vacancies. It is considered from these results that also with respect to diffusion in pure MgO single crystal, the extra vacancies formed due to impurities play a dominant role. There is a possibility that trivalent impurities, such as Al and Fe, in MgO result in extra vacancies.

The cation vacancy concentration in pure MgO single crystal at 1450°C was calculated to be about 2×10$^{-2}$ cation %, considering that the diffusion coefficient in 0.5 mol% Cr$_2$O$_3$-doped MgO single crystal was about 12 times as much as that in pure MgO single crystal. As described above, addition of 0.5 mol% Cr$_2$O$_3$ forms 0.25 cation % vacancy and the diffusion coefficient is proportional to the vacancy concentration. The calculated value of vacancy concentration in pure MgO is in a fairly good agreement with the impurity concentration (about 300 ppm) determined spectrographically. Although it is not concluded definitely, because of a relatively large error in determining the diffusion coefficient, that the diffusion in pure MgO single crystal takes place solely via extra vacancies formed due to impurities, it seems reasonable to think that the extra vacancies play an important role also in the diffusion in ordinarily pure MgO single crystal, in view of the little difference in activation energy between the cases of pure MgO single crystal and doped ones. In the previous papers$^{1,7}$ the activation energy for the Ni$^{2+}$ diffusion in MgO single crystal was approximately 80 kcal, as in the present investigation. It is possible that this value does not include the energy to form vacancies, if the extra vacancies due to impurities play a dominant role also in the diffusion in the ordinarily pure MgO single crystal as stated above.

Table 5. Activation energies for Ni$^{2+}$ diffusion.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>80 kcal/mol</th>
<th>78 kcal/mol</th>
<th>70 kcal/mol</th>
</tr>
</thead>
</table>

References.

3) W.D. Kingery, J. Am. Ceram. Soc. 42, 293

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SiC crystals grown in the cavity of a Lely furnace have been studied experimentally at 2500°C. In this study, special attention was called to the initial stage of recrystallization.

The results obtained are summarized as follows:

1) At the initial stage of recrystallization, β-SiC often crystallizes out. These crystals of β-SiC disappear with the progress of the subsequent recrystallization.

2) Two dimensional growth layers having no growth spiral are often observed on the basal surfaces of the initial platelets. Most of these crystals show one-dimensional disorder.

3) The transition from β- to α-SiC at about 2500°C seems to occur mainly through a vapour phase.

4) When the growth cavity is poorly supersaturated, β-SiC fails to appear. In this case, however, α-SiC initially formed often shows one dimensional disorder.

5) From these experimental results, it is concluded that the thermal stability gap between SiC polytypes has a certain relation to the kind of polypeptide to occur.

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