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Interdiffusion of Zinc Ions in Aluminium Cobalt(II) Oxide and Aluminium Nickel(II) Oxide

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The interdiffusion coefficients $\tilde{D}$ of Zn^{2+} ions in aluminium cobalt(II) oxide (cobalt aluminate) and aluminium nickel(II) oxide (nickel aluminate) were measured. In the former $\tilde{D}$ is independent of the concentration of the composition-dependent cation vacancies, while in the latter it decreases with increase in the concentration of cation vacancies. The difference in the distribution of cations and cation vacancies in the spinel lattice has a great effect on the interdiffusion coefficients of Zn^{2+} ions. The results were interpreted by means of the vacancy mechanism for Co^{2+} and Ni^{2+} ions and the interstitial or interstitialcy mechanism for Zn^{2+} ions. The activation energy is independent of the concentration of Zn^{2+} ions or cation vacancies; 355 kJ mol^{-1} for cobalt aluminate and 364 kJ mol^{-1} for nickel aluminate.

The vaporization rate of ZnO from the spinel solid solution of the $ZnO–CoO–Al_2O_3$ system was more pronounced than from that of the $ZnO–NiO–Al_2O_3$ system above 1300 °C in air.[1] It was suggested that the diffusion of Zn^{2+} ions in the spinel phase might be a rate determining process during the course of vaporization of ZnO. Thus the measurements of the diffusivity of Zn^{2+} ions and its dependence on the concentration of the composition-dependent cation vacancies in aluminium cobalt(II) oxide (cobalt aluminate) and aluminium nickel(II) oxide (nickel aluminate) were undertaken in the present work.

When $(A_x^{2+}B_{1-x}^{2+})O\cdot M_2^{3+}O_3$ forms a solid solution of $(A_xB_{1-x})O\cdot nM_2O_3$ with M_2O_3, the concentration of the composition-dependent cation vacancies is $(n-1)/(9n+3)\times 100$ cation site percent, increasing with the increase of n up to the solubility limit.

Studies have been carried out on the ionic diffusion in spinels. However, most of them are concerned with perfect spinels having no composition-dependent cation vacancies. Only a few studies on the defective spinels have appeared. Ando and Oishi[2] reported that the self-diffusion coefficients of oxygen ions in $MgO\cdot 1.2Al_2O_3$ and $MgO\cdot 2.2Al_2O_3$ single crystal spinels are close to those in $MgO\cdot Al_2O_3$ spinel. Morkel and Schmalzried[3] found for various kinds of spinels that the self-diffusion coefficients of cations in perfect spinels differ from those in defective spinels. Dieckmann and Schmalzried[4] measured the dependence of self-diffusion coefficient of iron ions in magnetite on oxygen partial pressure and found that the diffusion mechanism changes with the change in P_{O_2}. Yamaguchi *et al.*[5] proposed a vacancy mechanism of Ni^{2+} ion diffusion in magnesium aluminate on the basis that the interdiffusion coefficient of Ni^{2+} ions increases in proportion to the increase in the concentration of the composition-dependent cation vacancies.

The dependence of interdiffusion coefficients of Zn^{2+} ions on the concentration of the composition-dependent cation vacancies was found to differ in the two systems investigated in the present study. The mechanism of cation diffusion is also discussed.

Experimental

Material. The spinel powders of compositions $(Zn_xCo_{1-x})O\cdot nAl_2O_3$ and $(Zn_xNi_{1-x})O\cdot nAl_2O_3$ ($x=0$, 0.2; $n=1.0$—1.2) were synthesized from basic zinc carbonate, basic cobalt carbonate, basic nickel carbonate, and gibbsite of reagent grade. The pellets, diam. 10 mm and thickness 2—4 mm, were obtained by hot-pressing the spinel powders in a carbon mold under the pressure 260 kg/cm^2 at 1000 °C for 2 h. The pellets were further sintered densely for 1—2 h at 1700 °C to give the relative density colse to that of a single crystal. They were polished with SiC abrasives and diamond paste, and the diameters and thicknesses were measured with a micrometer. The sintering degrees, apparent density/theoretical density, calculated for a cation vacancy model, were 80—85%.

Diffusion Measurements. Interdiffusion between pure polycrystalline cobalt aluminate (or nickel aluminate) ($x=0$) and the spinel solid solution containing Zn^{2+} ions ($x=0.2$) was studied, the concentration of the composition-dependent cation vacancies being the same in both compositions (n is equal). The diffusion couple, made by giving the polished surfaces an intimate contact, was interposed between alumina plates. Annealing was carried out in the air in a vertical tube furnace with a SiC heating element. Temperature was measured with a calibrated Pt–Pt 13% Rh thermocouple. Although ZnO vaporized from the diffusion couples during the course of annealing, its amount was almost negligible in the diffusional zone near the interface. Annealing was carried out at 1320—1540 °C over a period of 24—96 h. After annealing, the diffusion couple was embedded in epoxy resin and cut perpendicular to the diffusion interface with a diamond cutter. The cut surface was polished carefully with SiC grains and diamond paste and then coated with gold by vacuum sputtering. The specimens were mounted on the sample holder and analyzed by an electron probe microanalyzer. They were moved perpendicular to the diffusion interface at 50 μm/min while the electron beam was kept fixed; the intensity profile of Zn *Kα* radiation was then obtained. The microprobe was calibrated using standard samples having compositions $(Zn_xCo_{1-x})O\cdot Al_2O_3$ and $(Zn_xNi_{1-x})O\cdot Al_2O_3$, where $x=0.05$, 0.1, and 0.2. The standards were mounted and polished following the procedure for the diffusion couples. The relative intensity of Zn *Kα* radiation to that of Al *Kα* radiation showed good linearity as regards the concentration of Zn^{2+} ions in both cases.

Results and Discussion

The intensity profile of Zn $K\alpha$ radiation obtained by electron microprobe analysis was smoothed so as to average the statistical fluctuations. The curve thus obtained was considered to represent the concentration distribution of Zn^{2+} ions in the diffusion couple as the intensity of Al $K\alpha$ radiation was constant throughout the diffusional zone. A typical profile is shown in Fig. 1. The concentration curves were not apparently symmetrical as regards the original interface, and the Matano interface in all cases was determined graphically. The concentration-dependent diffusion coefficients were calculated by the Boltzmann-Matano solution:

$$D(c') = (-1/2t)(\mathrm{d}x/\mathrm{d}c)_{c=c'}\int_0^{c'} x\mathrm{d}c,$$

where t is the annealing time, x the distance, and c, c' the concentration of Zn^{2+} ions. When Matano's method is used, the molar volume change caused by diffusion should be taken into acount as pointed out by Prager[6] and Balluffi.[7] In the present diffusion couples, however, the maximum molar volume changes due to the diffusion of Zn^{2+} ions were 0.14 and 0.48% for cobalt aluminate and nickel aluminate, respectively, as calculated from the lattice constants reported by Romeijn.[8] The changes were not significant and the effect of the molar volume change on diffusion coefficients was negligible.

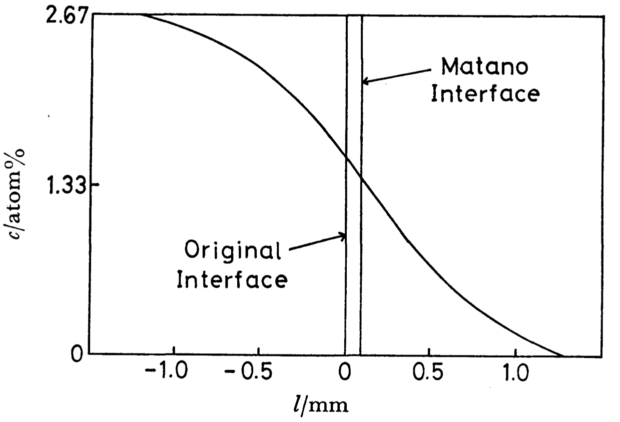

Fig. 1. Concentration profile of Zn^{2+} ions in $CoO\cdot 1.1Al_2O_3$ annealed at 1540 °C for 48 h.

Cobalt Aluminate. Interdiffusion coefficients $\tilde{D}$ of Zn^{2+} ions in cobalt aluminate are plotted against the concentration of Zn^{2+} ions in Fig. 2. The coefficient decreased with the increase in the concentration of Zn^{2+} ions in the perfect spinel which has no composition-dependent cation vacancies, while that of Zn^{2+} ions in the defective spinels turned out to be approximately independent of the concentration of Zn^{2+} ions. The value remained almost unchanged with the change in the concentration of cation vacancies.

Morkel and Schmalzried[3] found that the self-diffusion coefficient of Co^{2+} ions in $Co_{0.85}Al_{2.10}O_4$ ($\fallingdotseq CoO\cdot 1.235Al_2O_3$) is larger than that in $CoAl_2O_4$ ($=CoO\cdot Al_2O_3$). This suggests the vacancy mechanism for the diffusion of Co^{2+} ions in cobalt aluminate. If the diffusion of Zn^{2+} ions were also to occur by the vacancy mechanism in cobalt aluminate, the interdiffusion coefficients would increase with the increase in the concentration of the composition-dependent cation vacancies, but this was not the case.

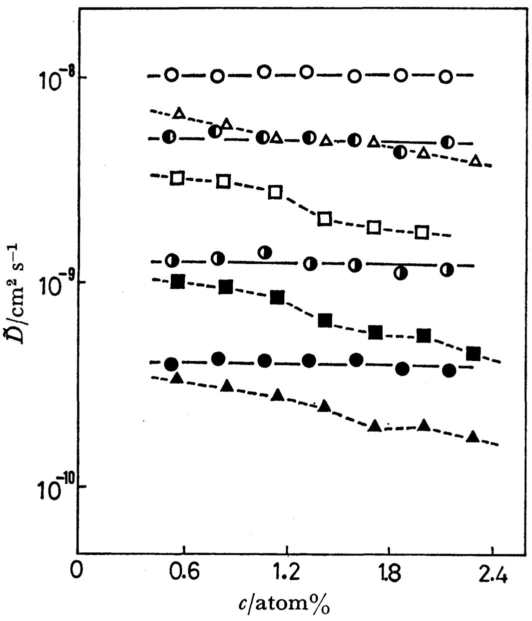

Fig. 2. Interdiffusion coefficients of Zn^{2+} ions in $CoO\cdot nAl_2O_3$ as a function of the concentration of Zn^{2+} ions. $n=1.0$: △ (1540 °C), □ (1470 °C), ■ (1400 °C), ▲ (1320 °C); $n=1.1$: ○ (1540 °C), ◐ (1470 °C), ◑ (1400 °C), ● (1320 °C).

According to Darken's binary diffusion equation, when two kinds of ions interdiffuse, the effect of diffusion of the first ions on the interdiffusion coefficient increases with the increase in the concentration of the second ions. Thus, the diffusion of Zn^{2+} ions comes to play an important role as the concentration of Zn^{2+} ions decreases

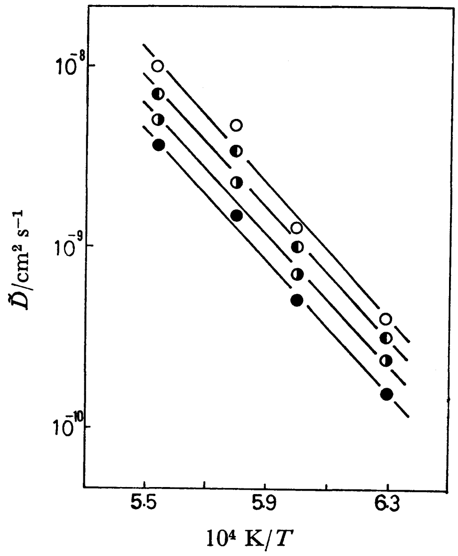

Fig. 3. Arrhenius plots of interdiffusion coefficients of Zn^{2+} ions for $CoO\cdot nAl_2O_3$.
○: $c_{Zn}<2.5$ ($n=1.1$, 1.2), ◐: $c_{Zn}=0.0$ ($n=1.0$), ◑: $c_{Zn}=1.0$ ($n=1.0$), ●: $c_{Zn}=2.0$ ($n=1,0$), where c_{Zn} is the concentration of Zn^{2+} ions in atomic percent.

(the concentration of Co^{2+} ions increases). The so-called impurity diffusion coefficients of Zn^{2+} ions for both perfect and defective spinels obtained by extrapolating interdiffusion coefficients to zero concentration of Zn^{2+} ions were the same within experimental errors. The Arrhenius plot shown in Fig. 3 is expressed as follows:

$$D_i = 2.1\times 10^2 \exp(-355000/RT) \quad (\mathrm{cm^2/s}),$$

where D_i is the impurity diffusion coefficient, R the molar gas constant, and T the absolute temperature. These results give no evidence for the vacancy mechanism of Zn^{2+} ion diffusion.

In general, the spinel structure consists of cubic close-packed oxygen ions with 1/8 of tetrahedral and 1/2 of octahedral interstices occupied by cations. The rest of the interstices are vacant as no-cation sites or interstitial sites. The structural formula for $(Zn_{0.5}Co_{0.5})O\cdot 2Al_2O_3$ spinel can be written as[1]

$$[Zn_{0.28}Co_{0.28}Al_{0.44}](Al_{1.86}\square_{0.14})O_4,$$

where $\square$ denotes cation vacancies, and [ ] and ( ) tetrahedral and octahedral sites, respectively. Thus, even though the concentration of the composition-dependent cation vacancies increases as $n>1.0$, the cation vacancies tend to occupy octahedral sites having little influence on the diffusion of Zn^{2+} ions on tetrahedral sites. The above formula represents only approximate distribution of cations and cation vacancies in the spinel lattice. There still remains the possibility of the existence of interstitial cations (especially Zn^{2+} ions) and octahedral Co^{2+} ions which could not be detected by the X-ray diffraction method. Consequently, the present result in which the interdiffusion coefficient is essentially independent of the concentration of the composition-dependent cation vacancies in cobalt aluminate could be explained on the assumption that Zn^{2+} ions diffuse through the spinel lattice *via* interstitial sites and not *via* octahedral sites.

Nickel Aluminate. Interdiffusion coefficients $\tilde{D}$ of Zn^{2+} ions in nickel aluminate obtained at 1470 °C are plotted as a function of the concentration of Zn^{2+} ions in Fig. 4. The interdiffusion coefficient is strongly dependent on the concentration of Zn^{2+} ions in each spinel with different concentration of cation vacancies. This is also the case for other annealing temperatures.

As is clear from Fig. 4, the interdiffusion coefficient decreases with increase in the concentration of the composition-dependent cation vacancies within the range of at least 1.45 cation site percent (corresponding to $n=1.2$) at low concentration of Zn^{2+} ions. It should be considered, as Yamaguchi *et al.*[5] reported, that the diffusion of Ni^{2+} ions in nickel aluminate occurs by the vacancy mechanism. The fact that $\tilde{D}$ increases with the increase in the concentration of Zn^{2+} ions in the cases of $n=1.15$ and 1.2 may support this suggestion. However, the present results deny the vacancy mechanism for the diffusion of Zn^{2+} ions in nickel aluminate.

The approximate structural formula of $(Zn_{0.5}Ni_{0.5})O\cdot 2Al_2O_3$ spinel is given by[1]

$$[Zn_{0.28}Ni_{0.14}Al_{0.44}\square_{0.14}](Ni_{0.14}Al_{1.86})O_4.$$

This indicates that both Zn^{2+} ions and cation vacancies prefer tetrahedral sites in nickel aluminate. Thus, when the concentration of the composition-dependent cation vacancies increases in nickel aluminate, they predominantly occupy tetrahedral sites causing the decrease in the interdiffusion coefficient of Zn^{2+} ions on tetrahedral sites. The decrease in the interdiffusion coefficient of Zn^{2+} ions should correspond to the decrease in the concentration of interstitial Zn^{2+} ions which are considered to be mobile as compared to those at normal cation sites, if the interstitial or interstitialcy mechanism for the diffusion of Zn^{2+} ions is assumed.

The activation energy obtained from the Arrhenius plots in Fig. 5 is nearly independent of the concentration of Zn^{2+} ions and the composition-dependent cation

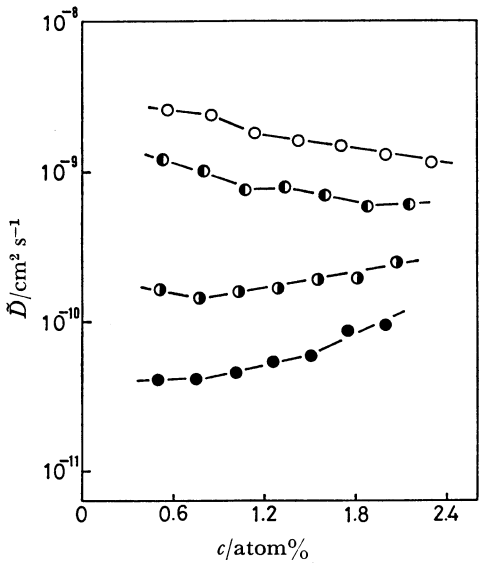

Fig. 4. Interdiffusion coefficients of Zn^{2+} ions in $NiO\cdot nAl_2O_3$ at 1470 °C as a function of the concentration of Zn^{2+} ions.
○: $n=1.0$, ◐: $n=1.1$, ◑: $n=1.15$, ●: $n=1.2$.

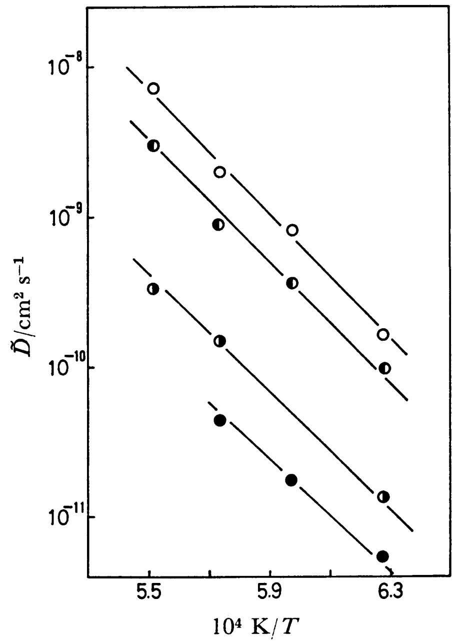

Fig. 5. Arrhenius plots of interdiffusion coefficients of Zn^{2+} ions for $NiO\cdot nAl_2O_3$.
○: $n=1.0$, ◐: $n=1.1$, ◑: $n=1.15$, ●: $n=1.2$.

vacancies, the average value calculated being 364 kJ mol^{-1}.

Contribution of Grain Boundary Diffusion. The contribution of grain boundary diffusion to the diffusion coefficients should be considered when polycrystalline specimens are used for diffusion measurements. The contribution can be detected by measuring the difference in diffusion coefficients between a single crystal and a polycrystal in an experiment on the coupling of two crystals. By this method, Yamaguchi *et al.*5) found no contribution for the diffusion of Ni^{2+} ions in magnesium aluminate. In the present work, it was difficult to obtain single crystals of aluminates containing Zn^{2+} ions because of the high vapor pressure of ZnO at high temperatures, so that the contribution of grain boundary diffusion could not be made clear.

Enhancement of anion diffusion at grain boundaries has been reported for Al_2O_3,9) MgO,10) and alkali halides.11) However, no evidence has been found for grain boundary enhancement of cation diffusion in spinels. The contribution of grain boundary diffusion was not taken into consideration in interpreting the present results.

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1) K. Koumoto and H. Yanagida, *Yogyo Kyokai Shi*, **85**, 193 (1977).

2) K. Ando and Y. Oishi, *J. Chem. Phys.*, **61**, 625 (1974).

3) A. Morkel and H. Schmalzried, *Z. Phys. Chem. (Frankfurt am Main)*, **Bd. 32**, S. 76 (1962).

4) R. Dieckmann and H. Schmalzried, *Ber. Bunsenges. Phys. Chem.*, **81**, 344 (1977).

5) G. Yamaguchi, M. Nakano, and M. Tosaki, *Bull. Chem. Soc. Jpn.*, **42**, 2801 (1969).

6) S. Prager, *J. Chem. Phys.*, **21**, 1344 (1953).

7) R. W. Balluffi, *Acta Metall.*, **8**, 871 (1960).

8) F. C. Romeijn, *Philips Res. Rep.*, **8**, 321 (1953).

9) Y. Oishi and W. D. Kingery, *J. Chem. Phys.*, **33**, 480 (1960).

10) H. Hashimoto, M. Hama, and S. Shirasaki, *J. Appl. Phys.*, **43**, 4828 (1972).

11) J. F. Laurent and Jacques Benard, *C. R. Acad. Sci. (Paris)*, **241**, 1204 (1955).