A New Method for Determination of Self-diffusion Coefficients in Solid Solutions

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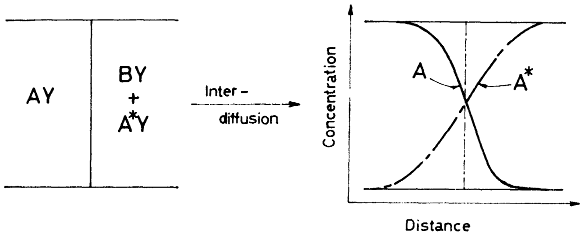
A new method for obtaining the self-diffusion coefficients of A in the AY–BY solid solution has been proposed. In this method, the tracer diffusion of A* and the interdiffusion between AY and BY are carried out simultaneously, and the self-diffusion coefficients are determined as a function of composition over the whole range of composition in a similar way as the Boltzmann-Matano analysis. Since this method employs a diffusion couple consisting of single crystals of AY and BY, one can avoid troubles and errors due to segregation and/or phase separation which are often encountered in experiments using solid solutions as specimens. In order to confirm the validity of the proposed method, D_{Cl}* in the TlCl–TlBr system and D_{Ag}* and D_{Na}* in the AgBr–NaBr system have been determined at 400 °C by this method and compared with the results obtained by the conventional method. A good agreement has been found between them.

Self-diffusion coefficients in solid solutions are usually determined as a function of composition by using single crystals of various compositions. However, segregation occurs during solidification of melts and segregated crystals cannot be easily homogenized by annealing. Sometimes, phase separation occurs with lowering temperature and the single crystal changes into a polycrystal. In such a case, it is difficult to obtain self-diffusion coefficients by the conventional method.

The purpose of this paper is to propose a new method for obtaining self-diffusion coefficients in solid solutions as a function of composition. In this method, the tracer diffusion of an element and the interdiffusion between the component salts are carried out simultaneously, and the concentration profiles are analysed in a similar way as the Boltzmann¹⁾-Matano²⁾ method which is usually used to obtain interdiffusion coefficients. Employment of this new method can avoid experimental difficulties due to the segregation and/or the phase separation.

Theoretical

1. Flux and Mass Balance Equations. Let us assume that ionic crystals AY and BY form a solid solution. If pure AY and BY containing a small amount of A*, a radioactive isotope of A, are in contact with each other and allowed to diffuse mutually, the concentration curve for A including both radioactive and stable isotopes and that for A* would be as shown in Fig. 1. Denoting the fluxes of A and A*, relative to one end of the specimen, by J'° and J'^{*} and those relative to the local lattice by J° and J^{*}, respectively, we obtain



(a) (b)

Fig. 1. Schematic diagram for interdiffusion in AY–(B,A*)Y system.

$$J'^{\circ} = J^{\circ} + c^{\circ}v \tag{1}$$

$$J'^{*} = J^{*} + c^{*}v, \tag{2}$$

where v is the velocity of the local lattice relative to one end of the specimen and c is the molar concentration. Symbols ° and * express the quantities with respect to A and A*, respectively. Neglecting cross terms, we have the following phenomenological equations,

$$J^{\circ} = -\frac{D^{*}c^{\circ}}{RT}\frac{\partial\tilde{\mu}^{\circ}}{\partial x} \tag{3}$$

$$J^{*} = -\frac{D^{*}c^{*}}{RT}\frac{\partial\tilde{\mu}^{*}}{\partial x}, \tag{4}$$

where x is the distance, D^{*} is the self-diffusion coefficient of A and $\tilde{\mu}$ is the electrochemical potential. $\tilde{\mu}^{\circ}$ and $\tilde{\mu}^{*}$ are written as follows:

$$\tilde{\mu}^{\circ} = \mu^{\circ} + ZF\phi \tag{5}$$

$$\tilde{\mu}^{*} = \mu^{*} + ZF\phi, \tag{6}$$

where μ, ZF and ϕ are the chemical potential, electric charge per mole and electric potential, respectively. μ° is the chemical potential of A in the system of (A, B)Y and μ^{*} is that of A* in the system of (radioactive A, stable A, B)Y which has the same concentration of B as the former system.

Because A* atoms have the same chemical properties as stable A atoms, A* atoms are expected to be distributed in stable A atoms with complete randomness and to interact with others in a quite same manner as stable A atoms. Therefore, μ^{*} is expressed as

$$\mu^{*} = \mu^{\circ} - T\bar{S}_c, \tag{7}$$

where $\bar{S}_c$ is the partial molal configurational entropy of A* in both radioactive and stable A atoms. $\bar{S}_c$ is written as

$$\bar{S}_c = R\ln(c^{\circ}/c^{*}). \tag{8}$$

Combination of Eqs. (7) and (8) gives

$$\mu^{*} = \mu^{\circ} + RT\ln(c^{*}/c^{\circ}). \tag{9}$$

Combination of Eqs. (5), (6), and (9) yields

$$\tilde{\mu}^* = \tilde{\mu}^\circ + RT\ln(c^*/c^\circ). \tag{10}$$

Substituting Eq. (10) into Eq. (4) and comparing Eq. (4) with Eq. (3), we obtain

$$J^* = \frac{c^*}{c^\circ}J^\circ + D^*\left(\frac{c^*}{c^\circ}\frac{\partial c^\circ}{\partial x} - \frac{\partial c^*}{\partial x}\right). \tag{11}$$

Substitution of Eq. (11) into Eq. (2) and comparison of Eq. (2) with Eq. (1) results in

$$J'^* = \frac{c^*}{c^\circ}J'^\circ + D^*\left(\frac{c^*}{c^\circ}\frac{\partial c^\circ}{\partial x} - \frac{\partial c^*}{\partial x}\right). \tag{12}$$

Assuming that the molal volume of the AY–BY solid solution is independent of the composition, we obtain

$$J'^\circ = -\tilde{D}\frac{\partial c^\circ}{\partial x} \tag{13}$$

where $\tilde{D}$ is the interdiffusion coefficient of the AY–BY system. Equation (13) gives the mass balance equation,

$$\frac{\partial c^\circ}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial c^\circ}{\partial x}\right). \tag{14}$$

Substituting Eq. (13) into Eq. (12) we obtain the flux equation of A* as follows:

$$J'^* = -\frac{c^*}{c^\circ}\tilde{D}\frac{\partial c^\circ}{\partial x} + \tilde{D}^*\left(\frac{c^*}{c^\circ}\frac{\partial c^\circ}{\partial x} - \frac{\partial c^*}{\partial x}\right). \tag{15}$$

The mass balance equation of A* is

$$\frac{\partial c^*}{\partial t} = \frac{\partial}{\partial x}\left\{\frac{c^*}{c^\circ}\tilde{D}\frac{\partial c^\circ}{\partial x} - \tilde{D}^*\left(\frac{c^*}{c^\circ}\frac{\partial c^\circ}{\partial x} - \frac{\partial c^*}{\partial x}\right)\right\}. \tag{16}$$

Equations (14) and (16) give the concentration curves in such a system where the interdiffusion and the tracer diffusion proceed simultaneously.

2. *Equation for Determination of D^*.* The concentration of A obtained experimentally is not c° but the mole fraction N. Also, the normalized A* concentration n^* which is defined as the ratio of $c^*(x,t)$ to the initial value of c^* in BY, is obtained experimentally as the concentration of A*. Therefore, equations for N and n^* are required for the purpose of application, instead of Eqs. (14) and (16). Since Eqs. (14) and (16) are linear with respect to c° and c^* and the molar volume of the solid solution is assumed to be independent of composition, they are rewritten in the following forms:

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial N}{\partial x}\right) \tag{17}$$

$$\frac{\partial n^*}{\partial t} = \frac{\partial}{\partial x}\left\{\frac{n^*}{N}\tilde{D}\frac{\partial N}{\partial x} - D^*\left(\frac{n^*}{N}\frac{\partial N}{\partial x} - \frac{\partial n^*}{\partial x}\right)\right\}. \tag{18}$$

If the initial conditions for Eq. (17) are described in terms of the Boltzmann variable $\eta \equiv x/(2\sqrt{t})$, N is a function of η only and Eq. (17) can be transformed into an ordinary differential equation,

$$-2\eta\frac{\mathrm{d}N}{\mathrm{d}\eta} = \frac{\mathrm{d}}{\mathrm{d}\eta}\left(\tilde{D}\frac{\mathrm{d}N}{\mathrm{d}\eta}\right). \tag{19}$$

Similarly, if the initial conditions for n^* in addition to those of N are described as a function of η, Eq. (18) is rewritten as

$$-2\eta\frac{\mathrm{d}n^*}{\mathrm{d}\eta} = \frac{\mathrm{d}}{\mathrm{d}\eta}\left\{\frac{n^*}{N}\tilde{D}\frac{\mathrm{d}N}{\mathrm{d}\eta} - D^*\left(\frac{n^*}{N}\frac{\mathrm{d}N}{\mathrm{d}\eta} - \frac{\mathrm{d}n^*}{\mathrm{d}\eta}\right)\right\}. \tag{20}$$

Assuming that the mole fraction of A*Y is very small, we can describe the initial conditions in Fig. 1 as follows:

$$N = 0,\quad n^* = 1 \quad \text{for } \eta = +\infty$$
$$N = 1,\quad n^* = 0 \quad \text{for } \eta = -\infty.$$

Integrating Eqs. (19) and (20) with respect to η and rearranging them, we obtain the following expressions for D^*,

$$-D^*(N_\mathrm{m}) = \frac{2N_\mathrm{m}\int_0^{n_\mathrm{m}^*}\eta\,\mathrm{d}n^* - 2n_\mathrm{m}^*\int_0^{N_\mathrm{m}}\eta\,\mathrm{d}N}{N_\mathrm{m}\left(\frac{\mathrm{d}n^*}{\mathrm{d}\eta}\right)_{\eta=\eta_\mathrm{m}} - n_\mathrm{m}^*\left(\frac{\mathrm{d}N}{\mathrm{d}\eta}\right)_{\eta=\eta_\mathrm{m}}}$$
$$= \frac{N_\mathrm{m}\int_0^{n_\mathrm{m}^*}x\,\mathrm{d}n^* - n_\mathrm{m}^*\int_0^{N_\mathrm{m}}x\,\mathrm{d}N}{2t\left\{N_\mathrm{m}\left(\frac{\partial n^*}{\partial x}\right)_{x=x_\mathrm{m}} - n_\mathrm{m}^*\left(\frac{\partial N}{\partial x}\right)_{x=x_\mathrm{m}}\right\}}, \tag{21}$$

where N_m and $n_\mathrm{m}{}^*$ are N and n^* at $\eta_\mathrm{m}\{=x_\mathrm{m}/(2\sqrt{t})\}$, respectively and $D^*(N_\mathrm{m})$ is the self-diffusion coefficient of A in a homogeneous solid solution of composition N_m. The so-called Matano interface is taken as the origin of η or x. If the concentration profiles of both interdiffusion and tracer diffusion are obtained experimentally, we can determine the self-diffusion coefficients of A and B in the AY–BY solid solution by means of Eq. (21).

Experimental

In order to confirm the results of the aforementioned theory experimentally, the self-diffusion coefficients of Cl in the TlCl–TlBr system and those of Ag and Na in the AgBr–NaBr system were determined by the new method and compared with the results obtained by the conventional method.

1. *TlCl–TlBr System.* Single crystals of TlCl and TlBr were prepared in a similar way as reported previously.[3] Disks, 2 mm in thickness and 10 mm in diameter, were cut from these crystals. A few drops of aqueous TlCl*(^{36}Cl) solution were applied to both ends of the disk. After the drying, the disk was sealed in an evacuated Pyrex-glass ampoule and annealed at about 400 °C for several days to distribute Cl* uniformly in the disk. Then, the disk was finished to obtain flat end surfaces. The doped disk was coupled with an undoped one as follows:

Couple A: TlCl(Cl*)/TlBr

Couple B: TlCl/TlBr(Cl*)

where TlCl(Cl*) and TlBr(Cl*) are ^{36}Cl-doped disks, and TlCl and TlBr are undoped disks. Couple A was used for obtaining the interdiffusion profile, because the concentration of Cl* is proportional to the concentration of Cl. Couple B was employed for determining the profile of tracer diffusion accompanied by interdiffusion. The couple was sealed in a Pyrex-glass ampoule evacuated to 10^{-3} Torr and annealed at 400 °C. Then, the couple was taken out and sectioned serially from one end. The procedures of diffusion annealing and sectioning are described elsewhere.[3,4] The weight and radioactivity of each sectioned layer were measured. Mole fraction of TlCl of each layer was determined from the radioactivity. Density of the layer was calculated from the mole fraction and lattice constant of this system.[5] The thickness of each layer was determined from the weight, the cross sectional area and the density. As the interface between the disks acts as a natural marker during the interdiffusion, it was taken as the standard plane for determining the distance. In this way, the mole fraction of TlCl was determined as a function of distance from the interface.

The relation between radioactivity and weight per cross sectional area was also obtained for couple B. As the annealing time required for couple A was different from that for couple B, the weight per cross sectional area for couple A was multiplied by the square root of the ratio of the annealing time for couple B to that for couple A, to obtain the corresponding profiles of self-diffusion and interdiffusion. The mole fraction of TlCl in couple B was determined from the corresponding profiles with the same origin of distance, and the normalized concentration of Cl* was calculated as a function of distance from the interface.

2. *AgBr–NaBr System.* According to the results by previous investigators, the self-diffusion coefficients of this system depend on the purity of crystals in a composition range rich in NaBr.[6] Therefore, in the present study the experiment was carried out in a composition range from $N_{\mathrm{AgBr}}=0.4$ to 1.0. Commercially obtained AgBr of G. R. grade was further purified in an evacuated and sealed Pyrex-glass tube by the zone refining technique. The refining operation was repeated 30 times so that the concentration of impurity might decrease to the order of 10 ppm. NaBr of Merck's Suprapur grade (99.9995% pure) was used.

Single crystals were prepared by the Bridgeman method, and cut into disks, 2 mm in thickness. Radioisotope $^{110\mathrm{m}}$Ag or ^{22}Na was applied to the disks of $\mathrm{Ag_{0.4}Na_{0.6}Br}$, which were then annealed at about 410 °C for 20 days in an evacuated ampoule in order to homogenize the composition and distribute the radioisotopes uniformly in them. Concentration profiles were obtained by using the following couples,

Couple C: $\mathrm{AgBr/Ag_{0.4}Na_{0.6}Br(Na^*)}$
Couple D: $\mathrm{AgBr/Ag_{0.4}Na_{0.6}Br(Ag^*)}$
Couple E: $\mathrm{AgBr(Na^*)/Ag_{0.4}Na_{0.6}Br}$.

Couples C, D and E were used for obtaining the concentration profiles of interdiffusion, tracer diffusion of Ag* and tracer diffusion of Na*, respectively. Annealing was carried out at 400 °C, and the determination of concentration profile was performed in a similar way as the TlCl–TlBr system.

Results and Discussion

1. *TlCl–TlBr System.* The profile of the interdiffusion obtained by using couple A, is given in Fig. 2 as a plot of N_{TlCl} *vs.* distance. The diffusion profile of tracer Cl* is shown in Fig. 3, as a plot of n_{Cl}^* *vs.* distance. In both figures, the interface between the crystals was taken as the origin of the distance and are shown by symbol B. Figure 4 shows the profiles of self-diffusion and interdiffusion, expressed as a plot of concentration *vs.* η. Plane A in the figure indicates the Matano interface and it was taken as the origin of the distance.

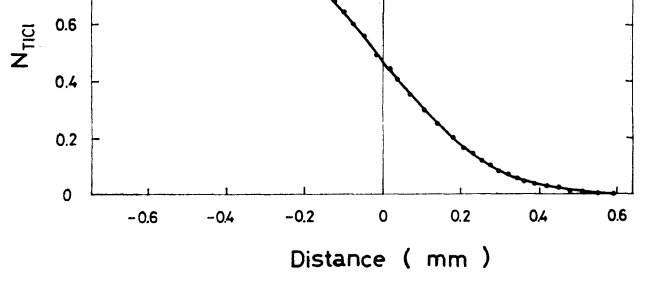


Fig. 2. Interdiffusion profile for TlCl–TlBr system.

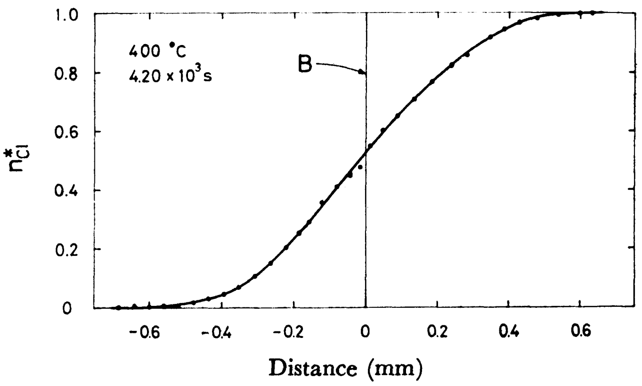


Fig. 3. Tracer diffusion profile of Cl* in TlCl/TlBr interdiffusion couple.

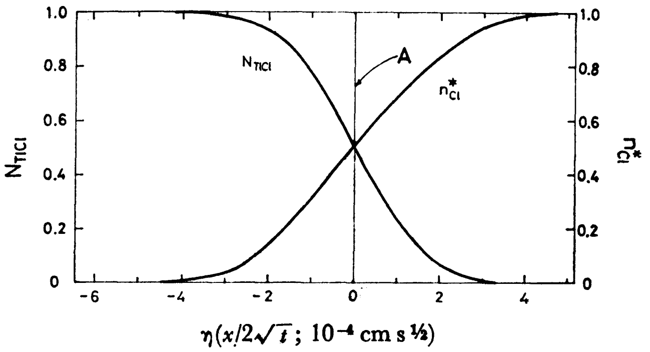


Fig. 4. Concentration profiles of TlCl and Cl* at 400 °C.

The self-diffusion coefficients of Cl, D_{Cl}^*, at 400 °C were calculated from the curves given in Fig. 4 by using Eq. (21). The results are shown by solid circles in Fig. 5. For comparison, the values of D_{Cl}^* obtained by the conventional method[4] are shown by open circles in the same figure. Agreement between them is fairly good. The maximum difference is only 15% of D_{Cl}^*.

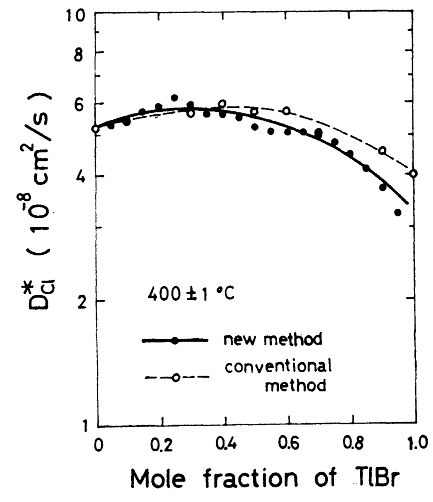


Fig. 5. D_{Cl}^* in TlCl-TlBr system.

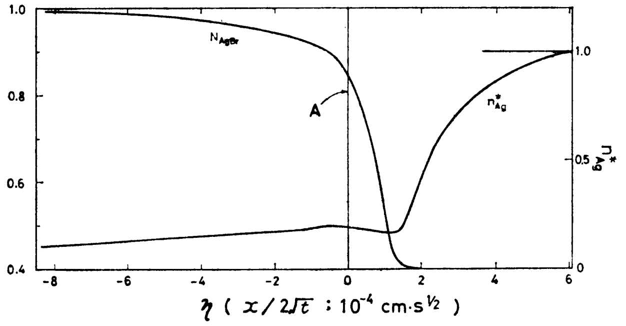


Fig. 6. Concentration profiles of AgBr and Ag* at 400 °C.

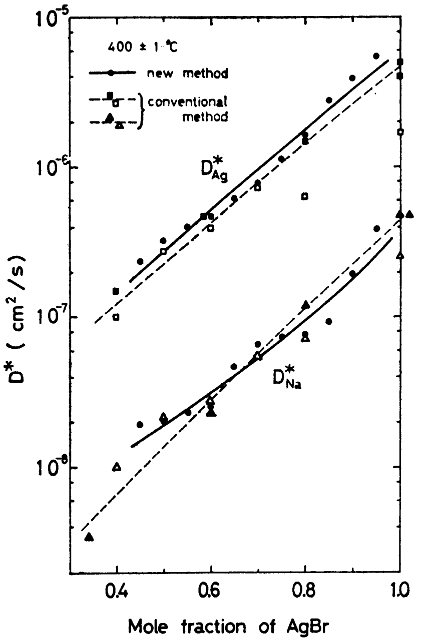


Fig. 7. D_{Ag}* and D_{Na}* in AgBr–NaBr system.
□, △: Tsuji *et al.*[6] ■, ▲: the authors
▨: Friauf[7] ▨, ◬: Wynnyckyj *et al.*[8]

2. *AgBr–NaBr System.* Figure 6 shows N_{AgBr} and n_{Ag}* as functions of η. These profiles were obtained from couples C and D, by assuming that Vegard's law holds for molar volume of the solid solution. D_{Ag}* at 400 °C were calculated from the curves shown in Fig. 6 by using Eq. (21). The results are shown by solid circles in the upper part of Fig. 7. D_{Na}* at 400 °C was calculated from the results for couples C and E. They are given by solid circles in the lower part of Fig. 7. The values of D_{Ag}* and D_{Na}* obtained by the conventional method are also shown in Fig. 7. Self-diffusion coefficients obtained by the new method well agree with those by the conventional method.

It is concluded that self-diffusion coefficients in solid solutions can be obtained by the method proposed in this paper.

Summary

(1) A new method has been proposed to obtain self-diffusion coefficients of A in AY–BY solid solution as a function of composition.

(2) D_{Cl}* in TlCl–TlBr system and D_{Ag}* and D_{Na}* in AgBr–NaBr system at 400 °C have been obtained by the new method and compared with the values obtained by the conventional method. A good agreement was found between them.

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