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Interdiffusion in the TlCl–TlBr System

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In order to compare the observed interdiffusion coefficients with those calculated by theoretical formulae proposed for ionic crystals, self-diffusion coefficients of Tl, Cl, and Br in TlCl–TlBr solid solutions and interdiffusion coefficients of the TlCl–TlBr system were determined at 400°C over the whole composition range. It was found that $D^*_{\mathrm{Cl}}:D^*_{\mathrm{Br}}:D^*_{\mathrm{Tl}} \fallingdotseq 18:9:1$, and that the maximum difference between observed interdiffusion coefficients and those calculated by a formula originated by Lindström is 13%.

Introduction

A mass flow relative to the initial interface of a diffusion couple was first observed by Kirkendall (*1*) in 1940's. The phenomenological theory of such a situation has been developed by Darken (*2*) who treated a binary alloy from the standpoint that each component had its own diffusivity. Many diffusion experiments performed on metal systems have shown the validity of Darken's equation.

As to the interdiffusion of ionic crystals, Wagner (*3*) derived a rate equation for the spinel formation by assuming that two species of cations move in the opposite direction so that the electrical neutrality is preserved locally. Formulae expressing the interdiffusion coefficient of ionic solid solutions have been proposed by Cooper and Heasley (*4*), Müller and Schmalzried (*5*), and Lindström (*6*). According to these formulae, the interdiffusion coefficient, $\tilde{D}$, can be calculated by using the self-diffusion coefficient, D^*, of constituent ionic species and the chemical potential of a component single salt forming solid solutions.

Only a few experimental works have been carried out on the interdiffusion of ionic solid solutions for the examination of the proposed formulae (*5*, *7*).

Agreement between calculated and experimental values of interdiffusion coefficients was found to be unsatisfactory. The purpose of this work is to determine the self-diffusion coefficients of Tl, Cl, and Br and the interdiffusion coefficients in the TlCl–TlBr solid solutions over the whole composition range at 400°C, and to compare the observed $\tilde{D}$ values with those calculated by the proposed formulae. TlCl and TlBr form a homogeneous solid solution with purely ionic conduction (*8*, *9*). Radioisotopes suitable for the diffusion measurement are obtainable and the heat of mixing of TlCl–TlBr solid solutions are available (*10*).

Experimental

A. Measurement of Tracer Self-Diffusion Coefficients, D^*

Purification of TlCl and TlBr, preparation of single crystals and determination of self-diffusion coefficients by the serial sectioning technique, have been performed in a similar way as reported in a previous paper (*11*).

It has been shown by the emission spectroscopic analysis that purified TlCl and TlBr contain less than a few tens ppm impurities. Single crystals were prepared from mixtures of purified TlCl and TlBr by the Bridgman method. Radioisotopes and their chemical forms are shown in Table I. Since ^{36}Cl was supplied as an aqueous solution of NaCl and ^{204}Tl as that of $TlNO_3$ and HNO_3, a solution of radioactive TlCl was prepared from these original solutions. Use of radioactive TlCl resulted in a good linearity in the plot of log (activity) vs (distance)^2.

TABLE I

RADIOISOTOPES USED FOR THE SELF-DIFFUSION MEASUREMENTS

	Tl	Br	Cl
Radioisotope	^{204}Tl	^{82}Br	^{36}Cl
Type of decay	β^-,EC	β^-,γ	β^-,EC
Half-life time	3.8y	35.9h	3.1×10^5y
Chemical form	^{204}TlCl aqueous solution	Na^{82}Br aqueous solution	Tl^{36}Cl aqueous solution

B. Measurement of Interdiffusion Coefficient, $\tilde{D}$

Disks, 2 mm in thickness and 10 mm in diameter, were cut from single crystals of various compositions. Then, the disks were polished with #1000 to #4000 emery papers, rinsed with water and ether, and dried. After two disks of different compositions were coupled by contacting end to end, the diffusion couple was sandwiched between two stainless steel weights and placed in a pyrex tube, 10.5 mm in diameter. In order to secure the contact between sample disks, the couple was preheated for a few minutes at about 300°C under a pressure of about 7 kg/cm^2. After that the glass tube was evacuated and sealed. Diffusion couples used and the time of annealing are listed in Table II. After the diffusion annealing, the couple was taken out and cut into two pieces in a direction parallel to the cylindrical axis and the sectional surface was polished with diamond paste, rinsed, dried and then coated with an aluminum film by the vacuum deposition technique. Concentration–penetration curves of Cl and Br were determined by means of Shimazu-SM type Electron Probe Microanalyzer. From the curves, the interdiffusion coefficients were determined by Matano's method (*12*).

TABLE II

COUPLES USED FOR THE INTERDIFFUSION MEASUREMENTS

Couple	Time of annealing (min)	note
TlCl/TlBr	912	*a*
$TlCl_{0.4}Br_{0.6}$/TlBr	279	*a*
$TlCl_{0.1}Br_{0.9}$/$TlCl_{0.5}Br_{0.5}$	124	*a*
TlCl/TlBr	912	*a, b, c*
TlCl/TlBr	279	*b*
TlCl/TlBr	114	*b*

[a] Employed for the measurement of interdiffusion coefficient.

[b] Employed for the investigation of proportionality between x and $\sqrt{t}$.

[c] Concentration profile is shown in Fig. 3.

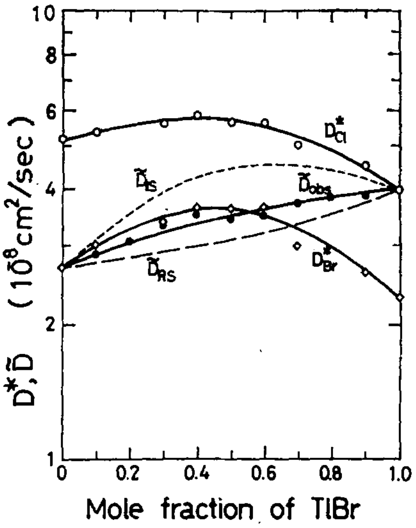

FIG. 1. Self-diffusion coefficients, D^*, and interdiffusion coefficients, $\tilde{D}$, at 400°C in the TlCl–TlBr system.

Results

Self-Diffusion Coefficients

The tracer self-diffusion coefficients of Cl, D^*_{Cl}, and those of Br, D^*_{Br} are shown in Fig. 1. By the open circles and the open squares respectively. The self-diffusion coefficients of Tl, D^*_{Tl} are shown in Fig. 2. by the open triangles.

It is seen from the figures that $D^*_{Cl} : D^*_{Br} : D^*_{Tl}$ is about 18:9:1.

It was found by Christy and Dobbs (*13*), and Jackson and Young (*14*) that point defects in pure TlCl are of the Schottky type and the concentration is about 1000 ppm at 400°C. From the similarity of crystal structure and comparison of self-diffusion data of TlCl and TlBr (*11*), the defect concentration in pure TlBr is estimated as nearly the same as TlCl. Since the impurity concentration in purified TlCl and TlBr was less than a few tens ppm, it seems that the impurities had a negligible effect on the self-diffusion coefficients.

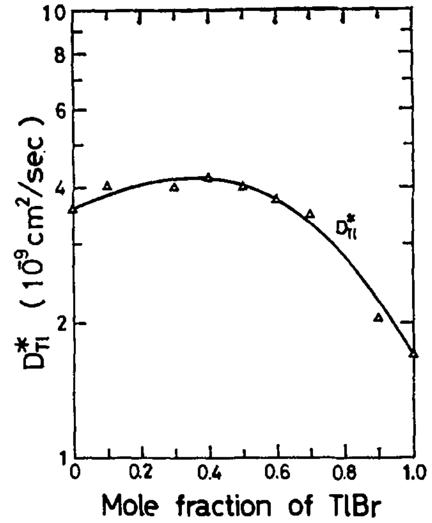

FIG. 2. Self-diffusion coefficients of Tl, D^*_{Tl}, at 400°C in the TlCl–TlBr system.

Interdiffusion Coefficients

Figure 3 shows a typical concentration curve of Br.

In order to examine the effect of the contact between the disks on the interdiffusion, penetration–concentration curves were obtained for different annealing times, and x, the distance between a plane of a specified concentration and the Matano interface, was plotted against $\sqrt{t}$, the square root of annealing time. Since a good proportionality was found in the plot, it was concluded that a sufficiently good contact had been effected by the treatment mentioned above.

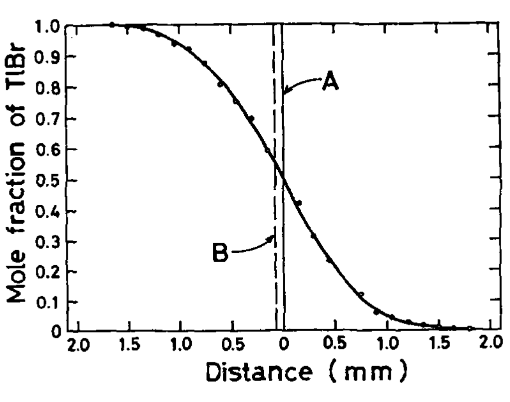

FIG. 3. Concentration profile of Br for a TlCl/TlBr interdiffusion couple annealed at 400°C for 912 min; A: Matano interface, B: original interface.

According to Matano's method, the interdiffusion coefficient can be obtained as a function of concentration from a single concentration–penetration curve. The interdiffusion coefficients at a specified concentration, obtained from different concentration–penetration curves, were averaged. The average values, $\tilde{D}_{obs}$, are represented by the solid circles in Fig. 1. The standard deviation of $\tilde{D}_{obs}$ was 8%.

Discussions

Relationships Between Formulae Proposed for the Calculation of Interdiffusion Coefficient

Three formulae for computing $\tilde{D}$ values from self-diffusion coefficients have been proposed for ionic crystals (*4–6*). Therefore, we shall discuss relationships between these formulae first.

Lindström's theory (*6*) is based on the kinetic theory by Manning (*15*), and vacancy flow is taken into consideration. The other theories do not do this. Therefore, the theory is most general of the three. Although Lindström's equation has been derived for AY–BY ionic crystals of fcc structure in which ions migrate via vacancies, it can be extended to ionic crystals of structures other than fcc as follows:

$$\tilde{D}_1 = \left(1 + \frac{\partial \ln \gamma_{AY}}{\partial \ln x_{AY}}\right)\left\{x_B D_A{}^* + x_A D_B{}^* + \left(\frac{1}{f} - 1\right) x_A x_B \frac{(D_A{}^* - D_B{}^*)^2}{x_A D_A{}^* + x_B D_B{}^*} - \frac{1}{f} x_A x_B \frac{(D_A{}^* - D_B{}^*)^2}{x_A D_A{}^* + x_B D_B{}^* + D_Y{}^*}\right\}, \tag{1}$$

where x and γ represent the mole fraction and activity coefficient, respectively, and f is the correlation factor. When the diffusion proceeds by the vacancy mechanism, f is 0.653, 0.727 and 0.781 for simple cubic, bcc and fcc structures, respectively (*16*).

If the vacancy flow is sufficiently small so that it can be neglected, Eq. (1) is reduced to

$$\tilde{D}_2 = \left(1 + \frac{\partial \ln \gamma_{AY}}{\partial \ln x_{AY}}\right)\left\{x_B D_A{}^* + x_A D_B{}^* - x_A x_B \frac{(D_A{}^* - D_B{}^*)^2}{x_A D_A{}^* + x_B D_B{}^* + D_Y{}^*}\right\}. \tag{2}$$

The same expression can be obtained by putting $z_A = z_B = -z_Y$ in the formula derived by Cooper and Heasley (*4*). $\tilde{D}_1$ is dependent on the crystal structure but $\tilde{D}_2$ is not.

If it is assumed that solid solutions are ideal and Einstein's relation holds, Eq. (2) is further reduced to the formula derived by Müller and Schmalzried (*5*).

$$\tilde{D}_3 = x_B D_A^* + x_A D_B^* - x_A x_B (F^2/RTV\kappa)(D_A^* - D_B^*)^2, \qquad (3)$$

where A, B, and x_A are substituted for K, Rb and Z in the original equation by Müller and Schmalzried and F, V, and κ represent Faraday constant, molar volume and electrical conductivity, respectively.

The contribution of vacancy flow to the interdiffusion is evaluated by

$$\tilde{D}_1/\tilde{D}_2 = 1 + \frac{(1/f - 1)\, x_A x_B (\alpha - 1)^2}{(x_A \alpha + x_B)(x_A + x_B \alpha + \alpha\beta)}, \qquad (4)$$

where $\alpha = D_A^*/D_B^*$ and $\beta = D_B^*/D_Y^*$. It is evident that $\tilde{D}_1/\tilde{D}_2$ approaches unity as x_A or x_B decreases to zero, regardless of α, β, and f. $\tilde{D}_1/\tilde{D}_2$ is nearly equal to unity when $D_A^* \simeq D_B^* \geqslant D_Y^*$ and $\tilde{D}_1/\tilde{D}_2$ is a few tens % larger than unity when $D_A^* \gg D_B^* \gg D_Y^*$.

In the TlCl–TlBr system, A, B, and Y correspond to Cl, Br and Tl, respectively. Since α is about 2, β is about 10, and f is 0.653, the maximum difference between $\tilde{D}_1$ and $\tilde{D}_2$ is only 0.4% of $\tilde{D}_2$.

Comparison of Observed $\tilde{D}$ with Calculated $\tilde{D}$

For the calculation of $\tilde{D}$ by Eq. (1), the activity coefficient of component AY are necessary. If the TlCl–TlBr solid solution is assumed to be a regular solution, the activity coefficient of TlCl, γ_{TlCl}, can be calculated by the equation

$$\ln \gamma_{\mathrm{TlCl}} = x^2_{\mathrm{TlBr}}\, \Omega/RT. \qquad (5)$$

From the heat of mixing of the system reported by Hovi (*10*), Ω is estimated as 780 cal/mole.

The values of $\tilde{D}$ can be calculated by inserting the γ_{TlCl} values obtained by Eq. (5) and the observed self-diffusion coefficients of respective ionic species into Eq. (1) and substituting 0.653 for f.

The interdiffusion coefficients calculated with the regular solution approximation, $\tilde{D}_{RS}$, are shown by the broken line in Fig. 1. Agreement between observed and calculated values is fairly good. The maximum difference is 13% of $\tilde{D}$.

In order to show the contribution of deviation from ideal solution to the $\tilde{D}$ values, the $\tilde{D}$ values calculated by Eq. (1) with the ideal solution approximation, $\tilde{D}_{IS}$, are also plotted in Fig. 1 by the dotted line. The values are larger than the observed ones. If Ω is taken as 500 cal/mole, the calculated $\tilde{D}_{RS}$ values well agree with the observed ones.

It is noteworthy that $\tilde{D}_{\mathrm{obs}}$ approaches D^*_{Br} in TlCl as x_{TlBr} decreases to zero and approaches D^*_{Cl} in TlBr as X_{TlBr} increases to unity. Such a tendency is expected by Eqs. (1–3).

Conclusion

(1) The self-diffusion coefficients of Tl, Cl and Br in the TlCl–TlBr system were determined at 400°C over the whole composition range by the serial sectioning technique. It was found that $D^*_{\mathrm{Cl}} : D^*_{\mathrm{Br}} : D^*_{\mathrm{Tl}}$ is about 18:9:1.

(2) The interdiffusion coefficient was determined at 400°C by means of Electron Probe Microanalyzer.

(3) The relationships between the theories of interdiffusion proposed by Lindström, by Cooper and Heasley and by Schmalzried and Holt were discussed.

(4) The interdiffusion coefficient was calculated by extended Lindström's formula. The maximum difference in interdiffusion coefficients between observed and calculated was 13%.

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