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Note

ZONE-MELTING STUDIES OF THE $ZnCl_2$–$CuCl_2$ EUTECTIC SYSTEM

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The zone-melting method has been used for many years for the preparation and purification of single crystals [1,2] and the determination of the composition of binary and ternary eutectics [3,4]. This technique is useful for determining the effective distribution coefficient and effects of various factors such as temperature, number of passes and concentration on the effective distribution coefficient. Such studies for eutectics where the parent phases are compounds have not been made in detail. In the present paper we report results of zone-melting studies on the $ZnCl_2$–$CuCl_2$ eutectic system.

EXPERIMENTAL

Materials and purification

Zinc chloride and cupric chloride (BDH grade) were repeatedly washed with alcohol and kept in an oven maintained at 120°C. Finally the purification was carried out by zone-melting technique as described earlier [5,6].

Determination of concentration

The concentration of cupric chloride was determined by taking the samples at different points in the zone-refined tube. A double-cell 102 Systronic colorimeter was used for determination of the $CuCl_2$ concentration.

RESULTS AND DISCUSSION

Various equations have been developed by Wilcox et al. [7] for the zone-melting of eutectic systems with an equilibrium coefficient of zero. For the planar interfaces,

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$$X = l(C_e/C_0)\rho_1/\rho_s \quad (1)$$

and

$$C = C_0\left[1 + \left(\frac{C_e}{C_0} - 1\right)\exp(-XV\rho_s/D\rho_l)\right] \quad (2)$$

Equation (1) is for the case of complete mixing; eqn. (2) applies to the non-mixing case. The terms used are given in ref. 7. In the present case, zone-melting studies were made with a mixture containing 1 wt.% $CuCl_2$ and the zone length was 3.0 cm. The zone velocity was 1.22 cm h^{-1}. The concentration of cupric chloride vs. distance indicates that cupric chloride moved in the direction of zone travel. Since the concentration varies with distance, it was concluded that the equation for complete mixing is not valid in the present case. Log$(1 - C/C_0)$ was plotted against distance X to test the validity of eqn. (2). A straight line is not obtained, indicating that the equation for the non-mixing is also not applicable. From the above it appears that cellular or dendritic growth is occurring at the interface.

Lord [8] derived an exact expression for the solute concentration as a function of distance in zone length from the beginning of an ingot, and the number n of passes. The expression is

$$C/C_0 = 1(1-k)\exp(-kx/1)(Z) \quad (3)$$

where

$$Z = \left(n - \sum_{i=1}^{n-1}\sum_{s=1}^{t} e^{-sk}k^{s-1}\sum_{r=1}^{s-1} \mathrm{fr}(s)\,(x/1)^r(r+1-kx/1)\right) \quad (4)$$

$$\mathrm{fr}(s) = s^{(s-r-2)/(s-r-1)!r!} \quad (5)$$

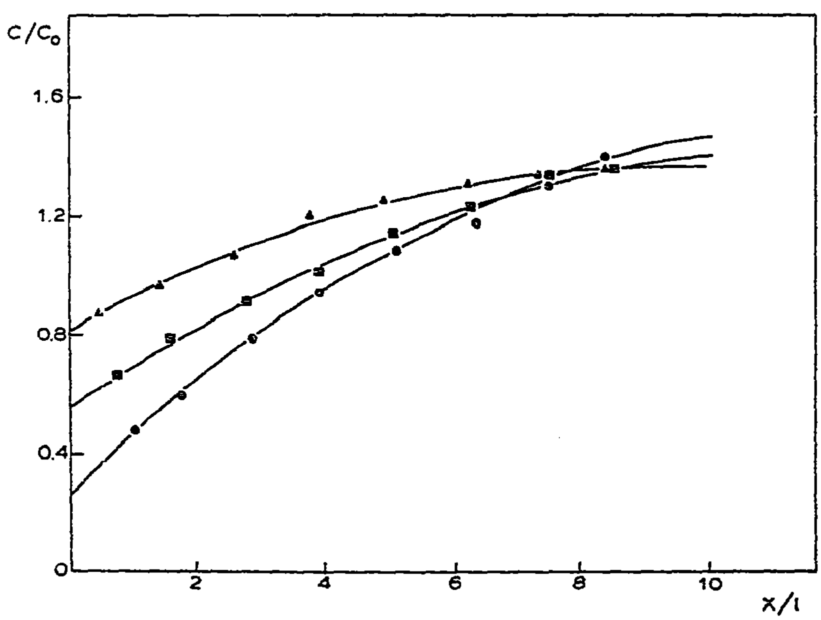

Fig. 1. Relative distribution of $CuCl_2$ in the mixture after one pas (▲), five passes (■), and 10 passes (●).

The terms are explained in ref. 1. For one pass, eqn. (3) reduces to

$$C/C_0 = 1 - (1-k)\exp - (kx/1) \quad (6)$$

Equation (6) was tested by plotting C/C_0 vs. $x/1$ (Fig. 1). The effective distribution coefficient was found to be 0.82. The value of separation factor $(1-k)$ is 0.18 for $CuCl_2$ in $ZnCl_2$.

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