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Note

ANALYSIS OF CRYSTALLIZATION DATA: THE α-NAPHTHOL–CATECHOL AND PICRIC ACID–CATECHOL SYSTEMS

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ABSTRACT

Experimental values of diffusion coefficient have been compared with the values computed by eutectic growth models of Chalmers and Jackson, Jackson and Hunt, Nash and Glicksman, and Sato and Sayama for the α-naphthol–catechol and picric acid–catechol systems. Dependence of $\lambda^2 \nu$ on concentration is also discused.

INTRODUCTION

Rastogi and co-workers [1–4] have studied several organic eutectics for solidification behavior, diffusion coefficient, thermochemistry and thermodynamics. In spite of high values of entropy of fusion for the parent components, diffusion coefficient measurements showed that values are in close agreement with those calculated by Jackson–Hunt [5] models. This raises a doubt because roughness parameters for the parent phases were greater than 2. In the present paper various recent models of eutectic growth are examined for α-maphthol–catechol and picric acid–cathechol eutectics. Finally, the dependence of $\lambda^2 \nu$ on the composition is also summarized.

THEORETICAL BACKGROUND

The first systematic attempt to solve the lamellar growth problem was due to Tiller [6]. He used the optimizing principle: at a given growth velocity resultant lamellar spacing is that characterized by the minimum interface undercooling.

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The minimization of interface undercooling leads to the relation

$$\lambda^2 \nu = \text{const.} \tag{1}$$

$$\frac{\Delta T^2}{\nu} = \text{const.} \tag{2}$$

Where ν is the freezing rate and λ is the lamellar spacing. However, this calculation was complex and incomplete because of an arbitrary criterion of minimum entropy factor and unknown shape factors involved in the calculation. Jackson and Chalmers [7] avoided the arbitrary condition of Tiller and found that

$$\lambda^2 \nu = \frac{32 \sigma_{\alpha\beta} T_1 e D}{m_\alpha (1 - k_\alpha) C_E L} \tag{3}$$

The terms are explained in ref. 7. The shape factor was eliminated by Jackson and Hunt [5] who solved the diffusion equation for a planar solid–liquid interface. They consider that solidification occurs with an isothermal interface undercooled by an amount ΔT given by

$$\frac{\Delta T}{m} = \nu \lambda C\alpha^L + \frac{a^L}{\lambda} \tag{4}$$

where

$$\frac{1}{m} = \frac{1}{m_\alpha} + \frac{1}{m_\beta} \tag{5}$$

m_α and m_β are the liquidus slopes, and $C\alpha^L$ and a^L are functions of alloy composition. The solution of eqn. (4) is

$$D = \frac{2P(1+\xi)^2 C_0 m \lambda \nu}{\Delta T \xi} \tag{6}$$

The parameters in eqn. (6) are D diffusion coefficient and phasial volume fraction ratio ξ and P. Although this theory explained a variety of observations, it was not entirely successful in remedying the unknown shape factor problem involved in Tiller's analysis. Secondly, the solid–liquid interface is not planar. A more realistic approach was made by Nash and Glicksman [8] in the manner described below—the assumption that freezing proceeds in a steady-state manner, i.e., the solid–liquid interface moves with constant velocity ν. They put the diffusion equation as

$$\nabla^2 C_L + \frac{\nu}{D} \frac{\partial C_L}{\partial y} = 0 \tag{7}$$

This equation was written in moving coordinate (x, y). Solution of eqn. (7)

indicates that operating point ψ for the growth is given as

$$\psi_{\mathrm{op}}=m_\alpha\left(\frac{\nu\lambda^2}{2D}\right)\left(\frac{\Delta S_{f\alpha}}{\gamma_{\alpha L}}\right)\left(\frac{C_{\beta E}\rho_\beta-C_{\alpha E}\rho_\alpha}{\delta^*\rho_\alpha+(L-\gamma^*)\rho_\beta}\right) \tag{8}$$

where δ^* is volume fraction. On substituting the value of ψ_{op}, eqn. (8) changes to

$$\lambda^2\nu=\left(\frac{a_0}{a_1}\right)\left(\frac{2D}{m_\alpha\,\Delta C_{f\alpha}}\gamma_{\alpha L}\right)\left(\frac{C_{\beta E}\rho_\beta-C_{\alpha E}\rho_\alpha}{\delta^*\rho_\alpha+(1-\gamma^*)\rho_\beta}\right) \tag{9}$$

The method of calculation of a_0 and a_1 is described in ref. 9.

Sato and Sayama [10] analyzed the eutectic growth under the minimum undercooling condition of partial eutectic interface. Their analysis was totally based on Jackson and Hunt's method. They assumed that outer slopes of α and β phases are isothermal on the average while in earlier analyses, the whole interface was assumed to be isothermal. Analysis indicates that lammellar spacing and undercooling are given as

$$\lambda^2\nu=\frac{2\bar{\Lambda}D}{C_0^\alpha+C_0^\beta}\left(\frac{1+\xi}{\xi}\right)^2\left(\frac{m_\alpha}{a_\alpha}\right)^{1/5}\left(\frac{a_\beta}{m_\beta}\right)^{6/5} \tag{10}$$

and

$$\left(\frac{1}{m_\alpha}+\frac{1}{m_\beta}\right)\Delta T=\frac{2}{\lambda}\left(\frac{1+\xi}{\xi}\right)\frac{a_\beta}{m_\beta}\left[\left(\frac{a_\alpha}{m_\alpha}\frac{m_\beta}{a_\beta}\right)^{1/5}+2\right] \tag{11}$$

This analysis indicates that if ξ_0 is small, the eutectic tends to grow partially co-operatively.

RESULTS AND DISCUSSION

The diffusion coefficient values calculated by various models, together with experimental values, are given in Table 1. Incidentally, values computed by all theories are of the same order of magnitude. Good agreement was achieved in spite of large differences in the methods of predicting the interfacial solute concentration. Secondly, each theory was developed for nonfaceted–nonfaceted eutectic growth; perhaps this is why experimental values are always higher than theoretical values.

Recently some theories have been developed [11], for the non-faceted–faceted system, but differences between diffusivities can only be resolved after development of a theory which includes interfacial molecular attachment kinetics and faceting. In the picric acid–catechol system lamellar

TABLE I

Calculated and experimental diffusion coefficient values [(cm^2 s^{-1})$\times 10^5$]

System	Jackson–Chalmers theory [7]	Jackson–Hunt theory [5]	Nash–Glicksman theory [8]	Sato–Sayama theory [10]	Experimental
α-Naphthol–catechol	6.71	6.69	7.20	6.67	9.93
Picric acid–catechol 0.126 mole fraction of picric acid (e_1)	1.34	3.60	4.81	5.32	6.00[a]
0.807 mole fraction of picric acid (e_2)	8.62	7.30	8.33	6.47	9.20[a]

[a] Ref. 2.

TABLE 2

Values of $\lambda^2 \nu$ for the picric acid–catechol system

Composition of the picric acid–catechol mixture (mole fraction of picric acid)	$\lambda^2 \nu$ (cm^3 s^{-1})$\times 10^8$
0.126	7.93
0.500	7.08
0.807	7.69

morphology was oberved for both eutectics as well as the 1 : 1 mixture. Values of $\lambda^2 \nu$ for all the mixtures are given in Table 2. It is clear that the $\lambda^2 \nu$ parameter is constant and independent of composition.

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