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Solidification behaviour of binary organic monotectic alloys

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Abstract

The solid–liquid equilibrium data on a faceted-nonfaceted system involving diphenyl and succinonitrile show the formation of a eutectic (0.9679 mole fraction of succinonitrile) and a monotectic (0.0742 mole fraction of succinonitrile) with a liquid miscibility gap in the system. From the linear velocity of crystallization data on the pure components, the eutectic and the monotectic, determined by the capillary method at different undercoolings, it can be inferred that they obey the Hillig–Turnbull equation. The microstructural investigations show peculiar characteristic features in the eutectic and the monotectic.

Keywords: Monotectic crystallization; Monotectic phase diagram; Organic monotectic; Organic monotectic alloys

1. Introduction

Metallic eutectics and intermetallic compounds constitute an interesting area of investigation in metallurgy and materials science from the point of view of developing new materials of commercial and technical importance [1, 2]. Recent interest has been centred in both the fundamental understanding of the solidification [3, 4] and the properties of polyphase alloys, and in the technological developments of in situ composites for particular applications. While a high transformation temperature [5, 6] and opacity cause considerable inconvenience in experimentation of these systems, due to high density differences the density-driven convection effects give rise to erroneous results on solidification. Since transparent binary systems involving organic compounds permit visual observation of phase transformations and processes during solidification, they are being used as model systems for unravelling the mysteries of

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solidification. Low transformation temperatures, ease of purification, minimized convection effects and a wider choice of materials are the special features which have prompted a number of research groups [7–12] to undertake some physicochemical investigations on organic systems. In addition, the experimental technique used for organic systems are more easy and convenient in comparison to those adopted in metallic systems.

While a eutectic reaction is characterized by isothermal decomposition of one liquid phase into two solid phases, a monotectic reaction involves breaking of a liquid phase into one solid and one liquid phase. Because of the limited choice of materials and more extensive experimental difficulties associated with the miscibility gap, less attention has been focussed on the study of monotectic alloys. Diphenyl (DP) is a material of high enthalpy of fusion (16.8 kJ mol^{-1}) which simulates [9] non-metallic solidification, and succinonitrile (SCN) with a low enthalpy of fusion (3.9 kJ mol^{-1}) solidifies like a metal. As such, the SCN–DP system may be taken as a suitable analogue of the Al–Si (metal–non-metal) system for direct observation of solidification. In the last decade, several articles [13–16] explaining various interesting phenomena observed during the solidification of a monotectic alloy have been published. With a view to studying solidification behaviour of an organic eutectic and monotectic, the DP–SCN system was chosen and its phase diagram, growth kinetics and microstructure studied.

2. Experimental

2.1. *Materials and purification*

Succinonitrile obtained from Aldrich, Germany, was purified by repeated distillation under vacuum. Diphenyl (Sojuz Chem, Moscow) was purified by fractional crystallization with ethanol. The purity of each compound was found to be 99%.

2.2. *Phase diagram*

The phase diagram of the SCN–DP system was determined by the thaw-melt method [17–19]. In this method, mixtures of two components covering the entire range of composition were prepared in different long-necked test tubes. These mixtures were homogenized by melting followed by chilling in ice; and their thawing and melting temperatures were determined using a Toshniwal melting-point apparatus equipped with a precision thermometer.

2.3. *Linear velocity of growth front*

The linear velocity of crystallization of pure components, eutectic and monotectic was determined [20, 21] by measuring the movement of the growth front in a capillary. For this, the sample was placed in a pyrex glass tube (internal diameter 0.5 cm) with a 15-cm-long flat portion having right-angle bends. The tube was kept in an silicone oil thermostat maintained at a temperature slightly above the melting point of the compound under study. The temperature of the thermostat was lowered and maintained at a temperature at which the measurements were to be made. A seed crystal of the same substance was introduced in one of the arms and the rate of movement of the crystallization front in the horizontal portion was recorded using a stop-watch. The crystallization velocity was measured at various degrees of undercooling in this manner.

2.4. Microstructure

To record [20–22] microstructures of the pure components, eutectic and monotectic, a small amount of sample was taken on a well-washed, dried glass slide and placed in an oven maintained at a temperature slightly higher than the melting point of the sample. On complete melting a coverslip was glided over the melt and allowed to cool. After a few minutes, the supercooled melt was nucleated by a seed crystal of the same composition and care was taken to have unidirectional freezing. After complete freezing the solid was placed on the platform of a Lietz Labour lux D optical microscope and different regions of the solid were observed. Microphotographs of suitable magnification were taken with the help of a camera attached to the microscope.

3. Results and discussion

3.1. Phase diagram

The eutectic change is a three-phase reaction in which a liquid phase dissociates to give two solids

$$L \rightleftharpoons S_1 + S_2 \qquad (1)$$

Similar to this, the monotectic is another three-phase reaction in which a liquid phase gives a solid phase and another liquid phase

$$L_1 \rightleftharpoons S + L_2 \qquad (2)$$

The two liquids namely, L_1 and L_2, are mutually immiscible and they constitute individual phases. A typical monotectic-type phase diagram obtained for the SCN–DP system is given in Fig. 1. This clearly shows the formation of a monotectic (0.0742 mole fraction of SCN) and a eutectic (0.9679 mole fraction of SCN). The boundary of the $L_1 + L_2$ field is the limit of liquid immiscibility. This field may be regarded as being made up of an infinite number of tie lines which connect the two phases L_1 and L_2, the composition of each phase being varied with temperature. With increasing temperature, the tie-lines become progressively shorter until the ultimate tie-line, at the top of the area, has zero length. This is known as the critical point where the two liquid phases, having identical composition, become indistinguishable. The temperature corresponding to this point is known as the upper consolute temperature and it is found to be 53.5° C above the monotectic horizontal. Above this

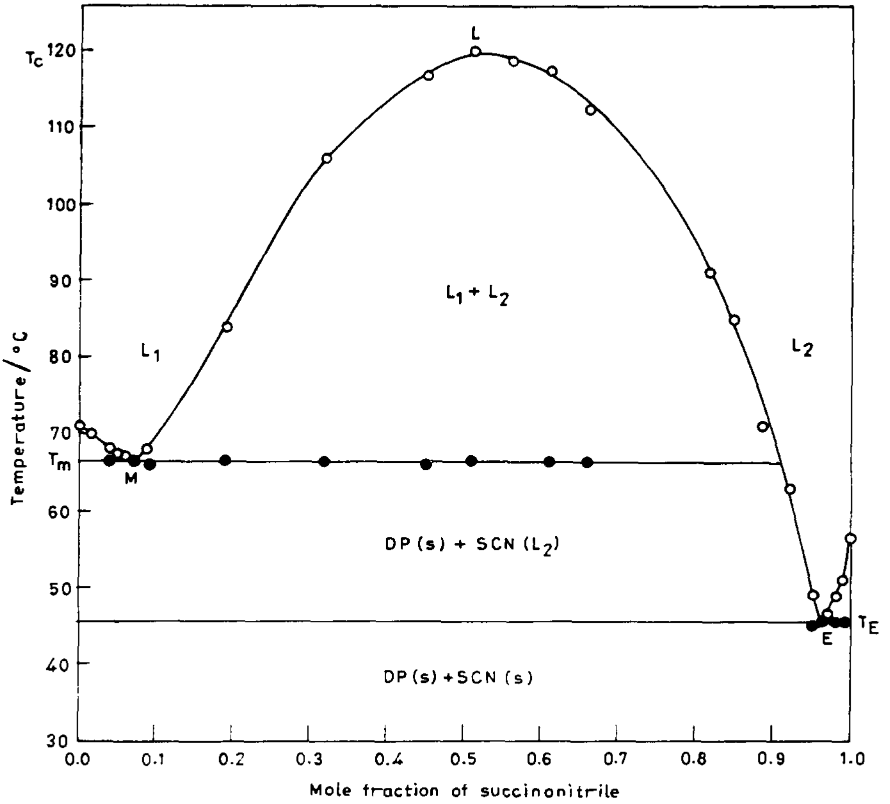

Fig. 1. Phase diagram of diphenyl–succinonitrile system; ○, melting temperature; ●, thaw temperature.

temperature there is complete miscibility in the liquid state (L). At the invariant monotectic temperature, L_1 (liquid rich in DP), L_2 (liquid rich in SCN) and solid DP are in equilibrium.

In the present system, when a liquid of monotectic composition is cooled below the montectic temperature (T_M) the monotectic reaction occurs and a liquid L_1 which is rich in DP decomposes into a solid phase S (rich in DP) and another liquid L_2 (rich in SCN) according to the reaction

$$L_1(\text{rich in DP}) \rightleftharpoons \text{DP(s)} + L_2(\text{rich in SCN}) \qquad (3)$$

However, when a liquid of the eutectic composition is allowed to cool below the eutectic temperature (T_E), the eutectic liquid decomposes to give two solids

$$L_2(\text{rich in SCN}) \rightleftharpoons \text{S}_1(\text{rich in DP}) + S_2(\text{rich in SCN}) \qquad (4)$$

Thus, the monotectic reaction is similar to the eutectic reaction except that one of the product phases of the monotectic reaction is a second liquid phase.

3.2. Growth kinetics

The data on linear velocity of crystallization of pure components, eutectic and monotectic, determined at different undercoolings by studying the rate of movement of the interface in a capillary, are given in Table 1 and Fig. 2. According to Hillig and

Table 1
The values of u and n

Material	$u/\mathrm{mm\ s^{-1}\ deg^{-1}}$	n
Diphenyl	1.3803×10^{-6}	7.8
Succinonitrile	2.7542×10^{-2}	2.3
DP-SCN monotectic	2.9512×10^{-4}	4.4
DP-SCN eutectic	1.9952×10^{-4}	3.7

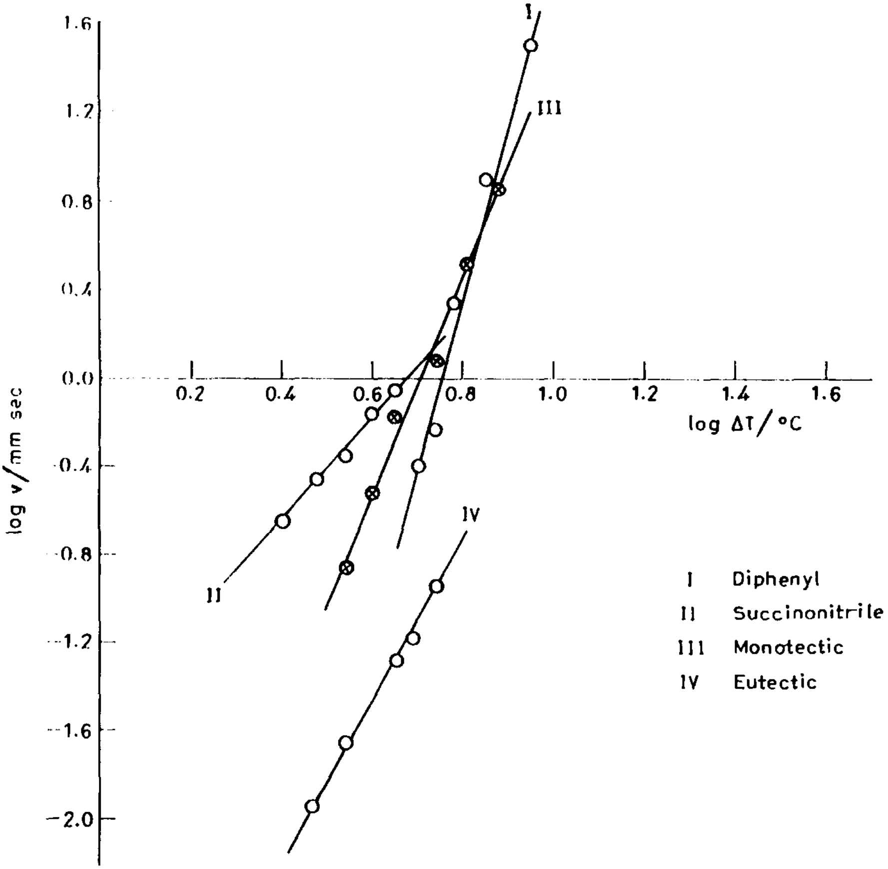

Fig. 2. Linear velocity of crystallization of diphenyl, succinonitrile and their monotectic and eutectic.

Turnbull [23], the linear velocity of crystallization (v) is related to undercooling (ΔT) by the reaction

$$v = u(\Delta T)^n \tag{5}$$

where u and n are constants depending on the nature of materials under investigation.

Eq. (5) can also be represented as

$$\log v = \log u + n \log(\Delta T) \tag{6}$$

When a graph is plotted between log v on the y-axis and $\log(\Delta T)$ on the x-axis, a straight line should be obtained. The value of the constants u and n can be determined from the intercept of the line on the y-axis and the slope of the line, respectively. The values of u and n, evaluated for the present system are given in Table 1. While the value of n of DP is a maximum (7.8), that of SCN is a minimum (2.3), and the values of n of the eutectics and monotectics lie between these two limits. The higher [24] value of n of of DP is due to its high enthalpy of fusion which makes the temperature of the growing interface higher in comparison to the bath temperature. However, SCN, being a material of low enthalpy of fusion, does not appreciably affect the temperature of the interface. As expected, the eutectic and monotectic show intermediate behaviour.

It is well known that the value of u gives a measure of the rate of crystallization. It may be inferred from Table 1 that the value of u of SCN is higher than that of DP. This suggests that the growth velocity of DP is very much smaller than that of SCN. It seems that the large amount of heat released in the solidification of DP inhibits its solidification. The growth rate of eutectic and monotectic lies between these two limits. These results may be explained by the mechanism proposed by Winegard et al. [25]. According to them the eutectic solidification starts with the nucleation of one of the phases. This would grow till the surrounding liquid becomes rich in the other component and a stage is reached when the second component also nucleates. Now there are two possibilities. If the growth velocity of the eutectic is less than that of both components, the crystallization of the eutectic takes place by the alternate nucleation mechanism. However, if the growth velocity of the eutectic is more than that of either component, its crystallization takes place by the side-by-side growth mechanism. In the present investigation, the melting point of DP being higher than that of SCN, it nucleates first followed by the nucleation of SCN. Now the two phases grow by the side-by-side growth mechanism.

While eutectic solidification is well known and verified by many experiments, only a small number of experiments have been performed on the monotectic system due to difficulties raised by the miscibility gap. In the absence of any special theory for monotectic systems, Derby and Favier [26] have extended the Jackson–Hunt [9] model for monotectic systems as well. However, the interfacial energy [27] between two liquid phases in monotectic systems plays a very important role in their solidification.

3.3. Microstructure

When the monotectic liquid L_1 (rich in DP) is undercooled below the monotectic temperature T_M, solid S_1 rich in DP is deposited and the liquid at the interface is enriched in component SCN. When enriched liquid becomes supersaturated, droplets of L_2 (rich in SCN) nucleate to relieve the supersaturation. The nucleation problem [28] depends on the relative magnitudes of the three interfacial energies. $\gamma_{L_1L_2}$, $\gamma_{S_1L_1}$ and $\gamma_{S_1L_2}$, the interfacial energies per unit area between two liquid phases L_1 and L_2, the solid and L_1, and the solid and L_2, respectively, and the resulting microstructures depend on the interplay between these energies, the density difference between the two liquids and the rate of advance of the solid–liquid interface. If the magnitudes of the interfacial energies are such that

$$\gamma_{SL_2} < \gamma_{SL_1} + \gamma_{L_1L_2}$$

then the DP–SCN liquid wets the solidified DP perfectly and SCN-rich droplets will be surrounded by SCN–DP liquid. In this situation, there is the possibility of capillary instability of the type described by Schafer et al. [27]. As explained by the figures in Ref. [14], if the cell depths are greater than the droplet circumference, capillary instabilities will lead to development of SCN droplets and they will pinch off into spheres. DP-rich liquid solidifies behind these spheres afterwards. Repetition of this process produces a very well-arranged array of spheres as shown in the optical microphotographs of monotectic given in Fig. 3. At low growth rates, droplets are not long enough to develop capillary instabilities. These SCN droplets get surrounded by solidified DP in such a way that cylindrical rods of SCN freeze as the solidification proceeds further, as shown in Fig. 4.

The optical microphotograph of the eutectic given in Fig. 5 shows a cellular dendrite type [28] of microstructure which results from extensive constitutional supercooling extending to a few centimetres from the solid–liquid interface.

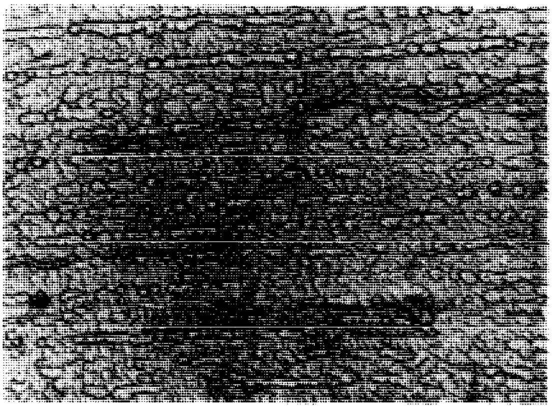

Fig. 3. Microstructure of diphenyl-succinonitrile monotectic, × 600.

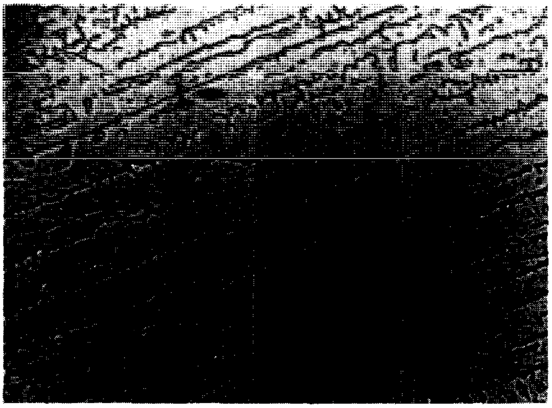

Fig. 4. Microstructure of diphenyl-succinonitrile monotectic, × 600.

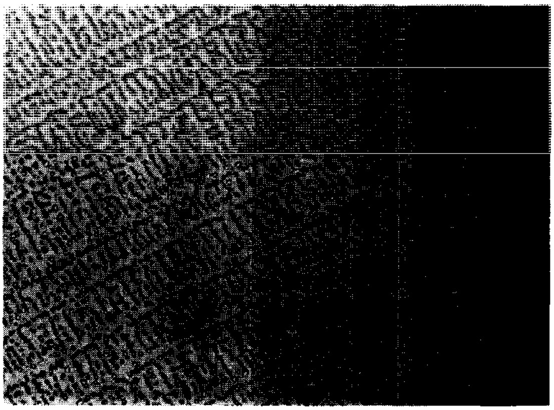

Fig. 5. Microstructure of diphenyl-succinonitrile eutectic, × 600.

Acknowledgements

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