

GROWTH OF UNIFORM SOLID SOLUTIONS OF NAPHTHALENE AND 2-NAPHTHOL BY REPEATED PASS ZONE-LEVELING

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Received 4 December 1974; revised manuscript received 9 May 1975

The construction of a zone-leveling apparatus is described. The apparatus was tested with the binary system naphthalene and 2-naphthol. The experimental concentration distribution profiles in the zone-leveled ingots are compared with profiles calculated by the theory of Kirgintsev and Kudrin. The concentration distribution measured in the polycrystalline zone-leveled ingots shows a variation of 0.01 mole fraction in the uniform part of the ingot. The isothermal initial melting behaviour of uniform solid solutions of naphthalene and 2-naphthol is described.

1. Introduction

For the study of thermodynamic properties of solid solutions data obtained from the phase diagrams of the system under consideration can be used. There are reasons to believe that many T, X phase diagrams in the literature – although they may give a reasonable picture of the qualitative behaviour of the underlying system – are quantitatively far from correct. The main source of the discrepancies lies in the fact that measurements were performed on solid solutions considered to be homogeneous, i.e., having a uniform concentration distribution, whereas it must now be accepted as highly probable that their composition varied over a wide range. We therefore decided to grow homogeneous solid solutions of organic material by means of the zone-leveling technique. Thermodynamical homogeneity is a macroscopic property of the solid phase. From a practical point of view, we define a homogeneous solid solution as a phase in which no concentration gradient is present and in which the variation in the concentration lies between narrow limits, say within 0.01 mole fraction. With the zone-leveling apparatus described in this article solid solutions having a concentration distribution which is uniform within this range can be prepared. Besides the concentration distribution in the zone-leveled ingots, the melting behaviour of samples taken from the uniform part of the

zone-leveled ingot was studied with regard to their homogeneity. This melting behaviour appeared to be quite different from the one observed for samples taken from a simply solidified liquid solution, which is a frequently used technique for growing organic solid solutions.

2. Experimental

A detailed description of the construction of the zone-leveling equipment is given elsewhere [1].

Macrosegregation, microsegregation and lateral segregation are governed by mass and heat transfer during zone-leveling. The degree of uniformity of the concentration distribution in the zone-leveled ingot is therefore governed by the accuracy with which the mass and heat transfer parameters are controlled. These parameters are the linear velocity of the zone through the ingot (the solidification rate) the speed of rotation of the ingot (rotation furthers the symmetry of the heat flow lines through the interfaces by which a flat freezing interface can be obtained) and the temperature of the heater, coolers and surroundings (to avoid constitutional supercooling).

Zone-leveling takes place in the ingot container (fig. 1). It consists of two concentric precision glass tubes closed off by Teflon plugs. The inner and outer

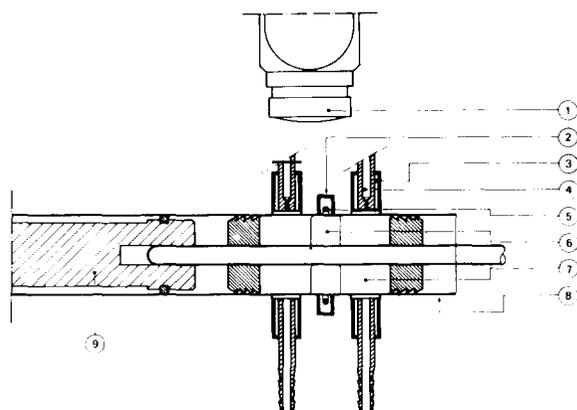


Fig. 1. Construction of the zone-level unit: (1) stereo-microscope, (2) radiation reflector, (3) rapid cooling, (4) slow cooling (liquid film), (5) heating wire, (6) zone, (7) ingot, (8) ingot container, (9) rotation shaft.

bore of the inner glass tube are 0.30 and 0.40 cm respectively. The tolerance in the wall thickness is less than 0.01 cm over a length of 15 cm. The outer glass tube has an outer and inner bore of 1.52 and 1.27 cm respectively and the same tolerance in the wall thickness as the inner glass tube. In the inner glass tube a thermopile, consisting of five copper–constantan thermocouples spaced 0.3 cm apart is inserted. During zone-leveling the zone formed in the rotating ingot moves along the thermopile so; the temperature distribution in the ingot and zone can be derived from the measured thermo EMF profile in the ingot and in the zone. The zone-level unit is mounted horizontally and rotated at an adjustable speed. The zone is formed by a heater and two coolers, fixed stationary with reference to the zone-level unit. The temperature of the heater, consisting of a single loop of Ni–Cr wire, is adjustable from 298 K until 500 K and is controlled within 0.06 K by a closed-loop circuit. The coolers combine two cooling techniques, namely a direct liquid film cooling on the rotating zone-level unit and a high speed cooling, which stabilizes the temperature of the liquid film. The temperature of the liquid film is adjustable from 250 K until 300 K and controlled within 0.04 K. The temperature of the surroundings is controlled within 0.5 K. By adjustment of the heater, coolers and the speed of rotation a zone with flat melting and, more important, freezing interface can be obtained in the ingot.

The flat shape of the freezing interface and the zone-length are kept constant during the process. For this purpose, the interface is regularly checked with a stereo-microscope with a magnification of 100 \times . The minimum zone-length is 0.3 cm for a zone with flat interfaces and a cross-section radius of 0.63 cm. The zone is moved through the ingot by a slow motion mechanism and the direction of the linear velocity is automatically reversed by photo-switches if the zone reaches the end of the ingot. Close attention had to be paid to obtain a uniform linear velocity, for fluctuations in the linear velocity can cause severe variations in the concentration distribution in the ingot. The uniformity of the velocity is 5% at a speed of 0.04 cm hr⁻¹.

Vibration-free placement of the apparatus is extremely important as vibrations cause fluctuations in the speed of travel too. Our vibration-absorbing table on which the zone-leveling apparatus is placed, has an eigenfrequency of 4 Hz.

3. Experimental results

The zone-leveling apparatus was tested by zone-leveling initial ingots, consisting of mixtures of naphthalene and 2-naphthol. Both components were zone refined [1] and showed purities better than 99.99%. The melting point of naphthalene is 353.4 K and that of 2-naphthol 393.6 K.

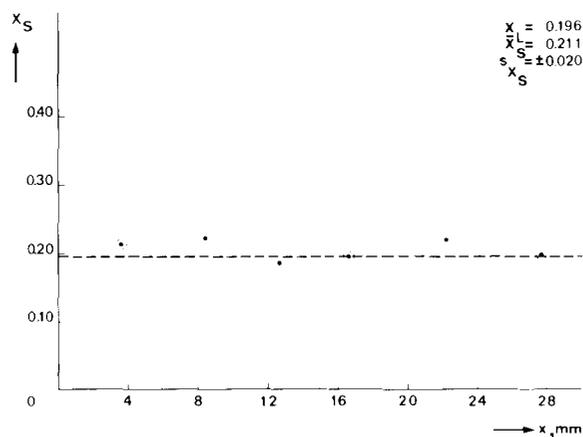


Fig. 2. Concentration distribution in the initial ingot: \bar{x}_S (2-naphthol) = 0.211; x_L = 0.196 (mole fraction of 2-naphthol in the initial liquid, dashed line); linear velocity during normal-freezing = 0.66 cm min⁻¹.

The initial ingot was prepared by normal-freezing [1] a well-stirred melt of the two components of composition X_L in the zone-level unit at a linear velocity of about 60.0 cm hr^{-1} . A typical concentration distribution profile in the initial ingot, determined by gas chromatography is given in fig. 2. The variation in the approximately uniform concentration distribution along the ingot is about 0.02 mole fraction. An "initial transient" in the concentration distribution was not detected in several initial ingots, suggesting a kind of quenching of the melt at this linear velocity.

To decrease the variations in the concentration distribution in the initial ingot, the latter is treated by repeated pass zone-leveling. If a terminal transient was present, that part of the ingot was first removed. Usually the length of the ingot is about 4 cm. Initially a zone of about 0.4 cm is formed. G , the temperature gradient in the zone ahead of the freezing interface and the rotation speed of the zone-level unit are adjusted in such a way that a flat freezing interface without microstructure is formed. G is kept in all cases bigger than the minimum value to avoid constitutional supercooling. The minimum values of G were calculated, using the familiar relationship to avoid constitutional supercooling for "partial-liquid mixing" in the zone [4]:

$$G \geq - \frac{mVX_{b,L}(1-k^0)}{D[k^0 + (1-k^0)\exp(-\delta V/D)]}, \quad (1)$$

where:

- G = temperature gradient in the zone, ahead of freezing interface;
- m = liquidus slope in K (mole fraction) $^{-1}$ at $X=X_L$ ($l=0$), i.e. mole fraction of the second component at freezing interface ($l=0$) in the liquid zone (L);
- V = solidification rate or linear velocity of the zone at negligible kinetical supercooling;
- D = diffusion coefficient of the second component in the zone;
- δ = thickness of the boundary layer ahead of freezing interface in the zone;
- k^0 = equilibrium distribution coefficient;
- $X_{b,L}$ = mole fraction of the second component in the bulk of the zone.

Reliable data for k^0 and m were derived from the T, X phase diagram of naphthalene plus 2-naphthol.

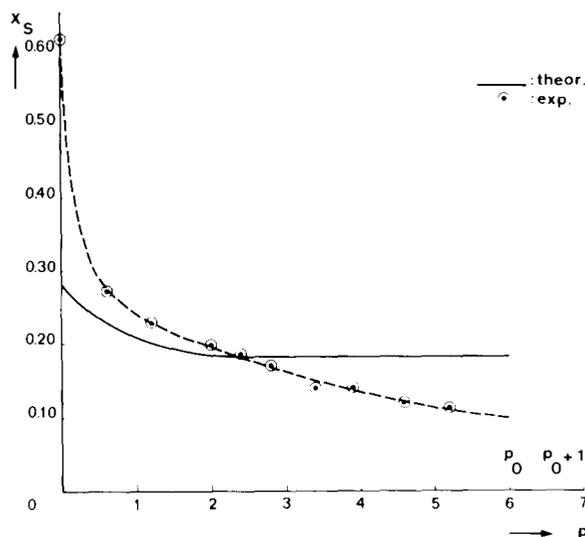


Fig. 3. Concentration distribution in the zone-leveled ingot after the first zone pass. Linear velocity during normal-freezing = 1.32 cm min^{-1} , initial liquid composition $X_L = 0.182$ (2-naphthol); linear velocity during zone-leveling = $(4.2 \pm 0.3) \times 10^{-5} \text{ cm sec}^{-1}$, zone length = 0.50 cm, ingot length (l_0) = 3.50 cm, $p_0 = 6.0$, $G = 60.0 \text{ K cm}^{-1}$, rotation speed = 6.9 rpm.

This diagram was calculated with the help of the "Equal G Curve" method [2] starting with the experimental phase diagram of Vetter et al. [3]. G was calculated by eq. (1) and with $V = 0.30 \text{ cm hr}^{-1}$, $\delta = 0.01 \text{ cm}$ [1], $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ and the data derived from the calculated phase diagram (see table 1).

During the first passage of the zone an air bubble was observed to form in the zone. Its volume increases because of the disappearing porosity of the solid material in the initial ingot. The concentration distribution profile in the ingot after the first zone pass is given in fig. 3 [a list of symbols is given in the legend of eq. (2)]. The exponentially decreasing concentration along the ingot is probably caused by the decreasing contact surface between liquid and solid during the first zone pass, by which mass transfer between both phases is diminished. After the first zone pass, the volume of the air bubble in the zone reaches a minimum. During the second zone pass in the reverse direction the very small volume of air left does not change in size. The same goes for the zone length. The concentration distribution profile after the second zone pass is given in fig. 4. At the end of this pass the direction of travel is again automatically reversed. It can be

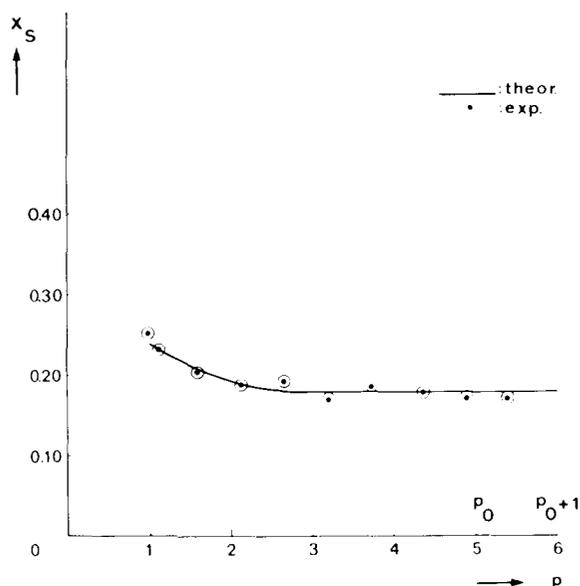


Fig. 4. Concentration distribution in the zone-leveled ingot after the second zone pass. Linear velocity during normal-freezing = 1.32 cm min^{-1} , initial liquid composition $X_L = 0.178$ (2-naphthol); linear velocity during zone-leveling = $(2.3 \pm 0.2) \times 10^{-5} \text{ cm sec}^{-1}$, zone length = 0.50 cm , ingot length (l_0) = 3.00 cm , $p_0 = 5.0$, $G = 50.0 \text{ K cm}^{-1}$, rotation speed = 6.9 rpm .

seen from fig. 4 that after two zone passes there is a uniform concentration distribution within 0.01 mole fraction in the major part of the zone-leveled ingot.

4. Experimental and theoretical concentration distribution in the zone-leveled ingot

With the theory of zone-leveling developed by Kirgintsev and Kudrin [5] the number of zone passes, n , to obtain a uniform concentration distribution between certain limits and the distribution profile after each zone pass were calculated [1] using different types of concentration distribution in the initial ingot. The concentration dependence on the effective segregation coefficient was also used in these calculations.

The equation for macrosegregation during zone-leveling, in differential form, using a number of commonly used assumptions [1] is:

$$\frac{dX_S^n(p)}{dp} = \frac{1}{\lambda_{\text{eff}}} [\lambda_{\text{eff}} - X_S^n(p)(\lambda_{\text{eff}} - 1)]^2 \times [X_S^{n-1}(p+1) - X_S^n(p)], \quad (2)$$

where:

p = dimensionless position in the ingot, $p = x/b$ with x being the distance down the ingot in cm and b being the zone length in cm;

p_0 = dimensionless length of the solid part of the ingot, $p_0 = l_0/b$ with l_0 being the length in cm of the solid part of the ingot, so, the total dimensionless length of the ingot is $p_0 + 1$;

$X_S^n(p)$ = concentration X , mole fraction of 2-naphthol, in the solid S at position p in the ingot for the n^{th} zone pass;

λ_{eff} = effective segregation coefficient defined as $k_{\text{eff},2}/k_{\text{eff},1}$ with $k_{\text{eff},2}$ and $k_{\text{eff},1}$ being the effective distribution coefficient of the second and the first component respectively;

$X_S^{n=\infty}$ = uniform concentration distribution in the ingot after infinite number of zone passes.

The boundary conditions are for $n = 1$, the first zone pass:

$$X_S^{n=1}(p=0) = \lambda_{\text{eff}} \int_0^1 X_S^{n=0}(p) dp \times \left[1 - (1 - \lambda_{\text{eff}}) \int_0^1 X_S^{n=0}(p) dp \right]^{-1}; \quad (3)$$

and for $n > 1$:

$$X_S^n(p=0) = X_S^{n-1}(p=p_0). \quad (4)$$

Differential eq. (2) was solved by computer using the Nordsieck method. The calculation of $X_S^n(p)$ was terminated for that value of n for which the zone-level criterion Δ is reached. Here, Δ is defined by the equations:

$$\frac{1}{p_0} \int_0^{p_0} |X_S^{n-1}(p) - X_S^{n=\infty}| dp > \Delta, \quad (5a)$$

$$\frac{1}{p_0} \int_0^{p_0} |X_S^n(p) - X_S^{n=\infty}| dp \leq \Delta; \quad (5b)$$

$X_S^{n=\infty}$ is calculated with the equations:

$$X_S^{n=\infty}/(1 - X_S^{n=\infty}) = \lambda_{\text{eff}} [X_L^{n=\infty}/(1 - X_L^{n=\infty})], \quad (6a)$$

$$X^{n=0}(p_0 + 1) = X_S^{n=\infty} p_0 + X_L^{n=\infty}, \quad (6b)$$

if $X^{n=0}$, the concentration distribution in the initial ingot and zone is approximately uniform. λ_{eff} was calculated as a function of X_S for “partial-liquid mixing” in the zone:

$$\lambda_{\text{eff}} = k_{\text{eff},2}/k_{\text{eff},1} = \frac{k_2^0 [k_1^0 + (1 - k_1^0) \exp(\delta V/D)]}{k_1^0 [k_2^0 + (1 - k_2^0) \exp(\delta V/D)]}. \quad (7)$$

The values of k_2^0 and k_1^0 in eq. (7), defined as X_S^0/X_L^0 and $(1 - X_S^0)/(1 - X_L^0)$ respectively, were derived from the calculated phase diagram of naphthalene and 2-naphthol for each X_S value. With $D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, $V = 0.3 \text{ cm hr}^{-1}$ and $\delta = 0.01 \text{ cm}$, λ_{eff} was calculated for each X_S value, giving the relation:

$$\lambda_{\text{eff}}(X_S) = 0.76 X_S + 1.59. \quad (8)$$

This expression for $\lambda_{\text{eff}}(X_S)$ was used for the calculation of the concentration distribution profile $X_S^n(p)$ in the zone-leveled ingot after each zone pass and for the calculation of the number of zone passes, n , to reach the zone-level criterion Δ .

From the calculations it appeared that zone-leveling requires the smallest number of zone passes if the concentration distribution in the initial ingot is approximately uniform. The dependence of repeated pass zone-leveling on other parameters is shown elsewhere [1].

Figs. 3 and 4 also show the calculated concentration distribution profiles. In a qualitative sense the agreement is rather good after two zone passes (fig. 4).

5. Melting behaviour of uniform solid solutions of naphthalene and 2-naphthol

The influence of a non-uniform concentration distribution on thermodynamical properties was studied by measuring the melting behaviour of solid solutions prepared with different solidification techniques. It is often assumed [6] that a uniform organic solid solution can be obtained by simply cooling a well-stirred melt. Let us examine the solidification of an organic liquid solution of composition X_L . By cooling the liquid a solid phase originates consisting of a collection of crystals showing a non-uniform concentration distribution, unless there is complete diffusion in both solid and

liquid and both are sufficiently high [7]. However, diffusion of organic molecules of low symmetry in the solid is negligible since diffusion coefficients are less than $10^{-10} \text{ cm}^2 \text{ sec}^{-1}$. The composition of the first crystals formed in the liquid solution of composition X_L will be in equilibrium with the liquid solution. During further crystallization the shape of the concentration distribution profile in the crystallizing solid is decided by the type of mixing in the liquid.

There can be “complete liquid mixing”, “partial liquid mixing” or “no liquid mixing”, but in all cases a non-uniform concentration distribution is formed in the separated solid. Besides a concentration gradient in the solid, the concentration fluctuates randomly, caused by the lack of control of process parameters during solidification.

The last liquid always solidifies at a temperature below the solidus for the original liquid of composition X_L [7]. Melting of such a solid solution gives a melting temperature interval. This interval is often assumed to be caused by the fact that the solid solution – assumed to be uniform – “walks” along the solidus of the system during melting. However, this can only be true if, throughout the whole melting process, the solid and liquid solution are in equilibrium with each other. This implies that during “equilibrium” melting, there has to be a rearrangement of molecules in the solid solution as the composition of the solid has to change during the “walk” along the solidus. Moreover, during “equilibrium” melting the solid solution must be uniform at each composition, as thermodynamics says. As already indicated, with organic molecules of low symmetry diffusion in the solid phase is negligible. So, during melting at a finite melting rate of a really uniform organic solid solution the above-mentioned rearrangement of molecules will not occur and the solid phase will keep its original composition and uniformity.

This means that the initial melting behaviour of a uniform organic solid solution, composed of molecules of low symmetry, is expected to be *isothermal*, just like pure material. The liquid solution, the bulk of which has the same composition as the solid solution, will then be supercooled with respect to its liquidus temperature. Recrystallization in this supercooled melt will occur and the initial composition of the recrystallized part of the melt will be in equilibrium

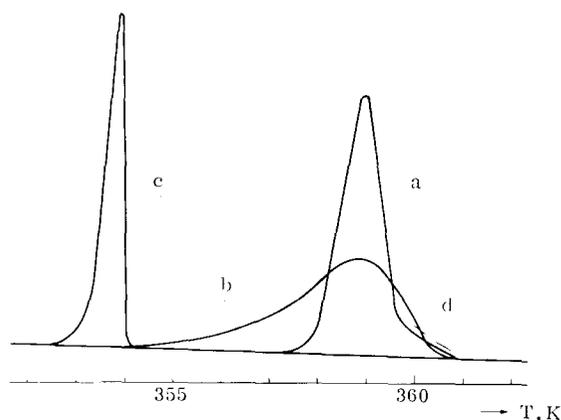


Fig. 5. Melting curves obtained by Differential Scanning Calorimetry for: (a) uniform solid solutions of naphthalene and 2-naphthol; (b) solid solutions, prepared by simply cooling a melt, formed by melting the solid solution used for the determination of curve (a); (c) zone-refined naphthalene.

with the composition of the original melt (which in turn is equal to the composition of the uniform solid solution from which the melt was formed). The final melting point observed after melting the uniform solid solution will be the liquidus temperature of the system under consideration at the composition of the uniform solid solution.

That a temperature interval is observed for melting of a solid solution formed by simply cooling a melt of composition X_L is caused by the presence of the non-uniform concentration distribution as outlined at the beginning of this section. It is not caused by the fact that this solid solution, assumed to be uniform, “walks” along the solidus of the system. Melting of the non-uniform solid starts at a temperature below the solidus temperature for the original liquid of composition X_L from which the solid is grown. So, the initial melting point of this type of melting behaviour is certainly not the solidus temperature for the original liquid solution from which the solid has been grown, no matter if the liquid is well-stirred or not. This is one of the main causes of wrongly situated solidi in many published phase diagrams.

All this is illustrated in fig. 5. This figure shows three curves (heat flow rate dissipated by the sample versus temperature) measured by Differential Scanning Calorimetry (Perkin Elmer, DSC 2) at a heating rate of 0.62 K min^{-1} . Samples were either powdered or in one lump and about 1 mg in mass. Using different heating

Table 1

X_L^0	X_S^0	k^0	$X_{b,L}$	m (K)	G (K cm^{-1})
0.00	0.00	1.62	0.00	39.04	0.00
0.10	0.17	1.67	0.11	41.22	23.70
0.20	0.37	1.68	0.21	42.71	47.60
0.30	0.49	1.63	0.31	43.51	67.10
0.40	0.59	1.47	0.42	43.63	68.30
0.50	0.68	1.37	0.52	43.07	67.00
0.60	0.77	1.28	0.61	41.82	57.80
0.70	0.84	1.20	0.71	39.88	46.40
0.80	0.89	1.12	0.81	37.25	29.80
0.90	0.95	1.06	0.91	33.95	15.20
1.00	1.00	1.00	1.00	29.95	0.00

X_L^0 = mole fraction of 2-naphthol in the zone at the freezing interface;

X_S^0 = mole fraction of 2-naphthol in the solid at the freezing interface, $X_S^0/X_L^0 = k^0$;

m = liquidus slope at X (2-naphthol) = X_L^0 .

rates (0.3 until 10 K min^{-1}) did not change the shape of the curves.

Curve a was obtained using samples taken from the uniform part of a zone-leveled ingot ($X_{2\text{-naphthol}} = 0.180 \pm 0.004$ mole fraction). Curve b was obtained using solid solutions formed by simply cooling a melt obtained by melting the uniform sample, used for curve a, in the cell of the DSC apparatus. Mass transfer in the melt will be mainly by diffusion in this case, but solidification of the last liquid occurs below the solidus temperature of the melt as outlined above. The same goes for a well-stirred melt in which “partial liquid mixing” is present.

Curve c shows the melting behaviour of zone-refined naphthalene (purity better than 99.99%).

Comparing curves a and b shows a wide melting temperature interval for the latter. The final melting temperatures in both cases are the same as expected. The final melting temperature for the uniform solid solution of composition X_S is the solidus temperature corresponding to the initial composition of the recrystallized part of the supercooled melt of composition $X_L = X_S$. The final melting temperature for the non-uniform solid solution (curve b) is the solidus temperature corresponding to the initial composition of the solidified melt of composition X_L .

Curves a and c show the isothermal initial melting behaviour for the uniform solid solution.

The melting behaviour of samples taken from an

ingot, quenched from the melt of a naphthalene and 2-naphthol mixture ($X_{2\text{-naphthol}} = 0.2$ mole fraction) was studied too, as this method is frequently used for the preparation of uniform solid solutions of organic material [8]. The melting behaviour was measured by DSC as indicated above. Melting of these samples — after annealing just below the solidus for hours — started in the vicinity of the lowest stationary point (melting point of naphthalene). Although smaller than the melting temperature interval shown in curve b, the interval observed for these samples was about 3 K bigger than that shown in curve a. The heat flow rate dissipated increased exponential and not directly proportional with temperature as is shown by samples taken from the uniform part of a zone-leveled ingot.

Annealed samples taken from a quenched ingot containing molecules of low symmetry are, therefore, not as uniform as samples taken from the uniform part of a zone-leveled ingot.

6. Conclusions

Repeated pass operation with the constructed zone-leveling apparatus resulted in polycrystalline solid solutions with a concentration distribution which is uniform within 0.01 mole fraction. The ex-

perimental and theoretical concentration distribution profiles in the zone-leveled ingot agree qualitatively after two and more zone passes. The observed isothermal initial melting behaviour confirms not only the uniformity of the grown solid solutions but also is a strong indication of their thermodynamical homogeneity. The relation between homogeneity and the degree of uniformity of the concentration distribution in the solid phase is studied now.

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