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Fractional Solidification Phenomena

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Summary

Zone melting of organic compounds was observed under the microscope. A host of phenomena were noted that can greatly affect the separation attained in a fractional-solidification operation. Liquid and gaseous inclusions moved toward the melt in some systems and farther into the solid in other situations. Sometimes impure melt was sucked into the frozen solid through cracks. Insoluble foreign particles were both bounced and incorporated by freezing interfaces of camphor and anthracene. Oscillations in interface position were caused by irregular free connection both inside and outside the sample cells. Bubbles in the melt sometimes caused agitation of the melt and other times selective growth of a volatile component. Bulk drainage and falling crystals from horizontal melting interfaces were observed. During melting of camphor–anthracene mixtures some anthracene platelets grew larger.

The separation attained in a fractional-solidification operation is ascertained by measurement of composition before and after treatment (*1*). Many phenomena influence the separation, but their individual effects cannot be determined by simple bulk analysis. To determine these phenomena it is necessary to observe the actual process under a microscope. In the present research, mixtures of organic compounds were observed under the microscope during zone melting. Some of the observed phenomena were expected, whereas many were surprises. Time-lapse photography was required to see the slower phenomena. Where pertinent, mention is also made of observations from related experiments.

One must keep in mind throughout that there are two ways in which impurities can be incorporated in a solid growing from a melt. Most theoretical treatments consider the incorporation of impurities only as solid solutions with a smooth solid–liquid interface. However, it is common for impurities also to be carried along as second-phase material—as gases, solids, or trapped melt. It should similarly be noted that the interface may be rough for a variety of reasons, e.g., constitutional supercooling, strong faceting of the growing solid, the presence of second-phase material in the melt, etc.

EXPERIMENTAL

A special zone melting apparatus (Fig. 1) was constructed for operation under the microscope. It was similar in function to the directional solidification apparatus of Hunt et al. (*2*), except that both a melting and freezing interface were generated in the present experiments. The cell or tube A containing the material was placed on the carriage B that moved slowly past the hot wire C or other heat source. Since the heat

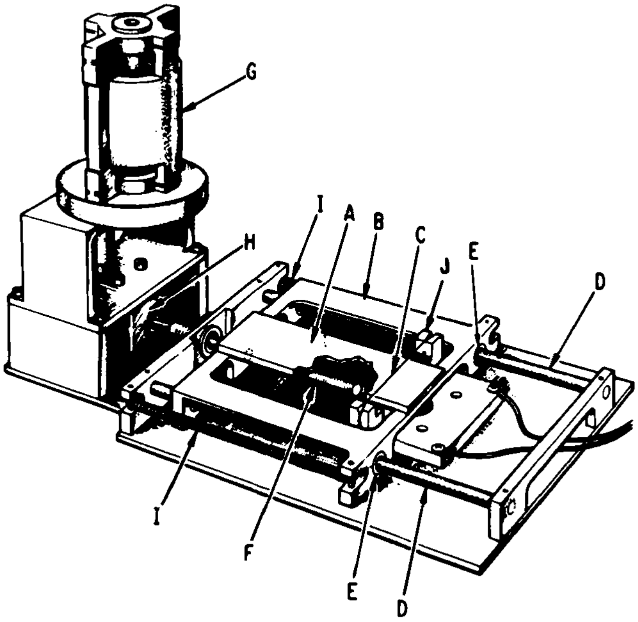

FIG. 1. Microscope-stage zone-melting apparatus. Overall length is 20.3 cm. This diagram shows a thick cell with one heating wire above and one below the cell. Letters are keyed to the text.

source was stationary, the microscope could be focused onto the freezing interface and other features which then remained relatively stationary with respect to the viewer. The carriage B slid along the guide rods D on Teflon bearings E and was driven by the lead screw F. Drive power was provided by a dc servo motor G (Electro-Craft Corp.) that was stepped down by the worm gear H. The entire gear train had a low backlash, and tension was maintained by the springs I. Linear travel rates ranging between 0.01 and 5.4 cm/hr were produced by varying the power to the motor with a stepless speed controller.

Our experiments were performed with resistance-heated nichrome wire as the heat source. For these experiments, the design of the wire support J (Fig. 2) proved to be especially crucial. It was necessary to construct the support of electrically insulating material, and yet a high thermal conductivity was required to prevent overheating of the wire in the vicinity of the binding posts K. Boron nitride proved to be the ideal material. In order to keep the wire taut when the temperature was raised, a spring-loaded pin I was provided to take up the slack caused by thermal expansion.

With very thin cells, it was desirable to locate the wire above the cell to ensure complete visibility of the interfaces and to prevent sublimation and possible crystallization of volatile components in the bubbles that frequently formed in the zone. Heating wires both above and below thicker cells proved advantageous. Initial operation showed irregular

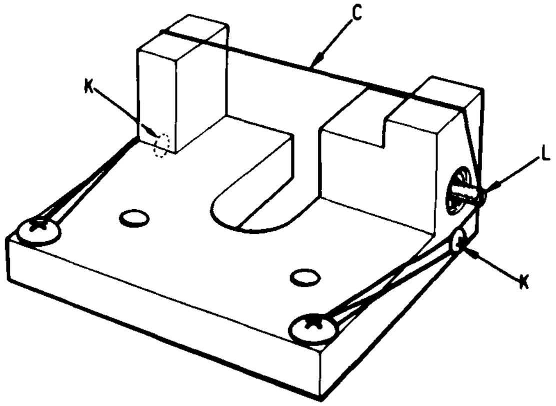

FIG. 2. Heating-wire support for microscope-stage zone-melting apparatus. Shown is a single-wire heater normally positioned above the thin cells.

cooling caused by drafts, and therefore a plastic heat shield (not shown) was placed around the apparatus. To eliminate thermal irregularities due to a chimney effect, the light port under the cell and the viewing port above the cell were blocked with microscope cover glasses, except when a microscope objective was inserted in the top port.

Mixtures of organic compounds were employed for the experiments because they are low melting and transparent. Concentrated mixtures were used for most of the experiments in order to accentuate certain of the phenomena. These may be regarded as possessing simple eutectic phase diagrams. The mixtures were usually in thin cells, which were produced by immersing two large cover glasses in the organic melt. The cover glasses were then pressed tightly together and withdrawn from the melt. After this sandwich was cooled to room temperature, its edges were sealed with epoxy to prevent volatilization. During zoning the melt was prevented from reaching the epoxy by the cooling effect of small pieces of aluminum that were laid over the end sections of the heating wire, thus producing lens-shaped zones. Thick cells were also prepared by placing strips of glass between two microscope slides or cover glasses and sealing with epoxy or solder glass. The melt was poured into these cells after preheating them.

TRANSPORT PHENOMENA

In the usual picture of zone melting it is imagined that a single-phase solid both exits from the molten zone and feeds the zone. Impurities are imagined to be present only as solid solution. However, this is frequently—perhaps usually—not true. The amount of impurity often exceeds its solid solubility, and so the impurity is present as a second phase. Breakdown of the interface to a rough or cellular condition can lead to trapping of melt to produce second-phase material in the product (*3*, *4*). Bubbles and impurities are also often present as inclusions in the cast solid before zone melting is initiated.

Such second-phase material was observed to move out of the solid and into the zone in various organic mixtures. For example, inclusions of melt in zoned 70% anthracene–30% camphor moved at rates on the order of 2 mm/hr in gradients of 465°C/cm in the thin cells. Similar rates were observed for inclusions in naphthalene originally containing 0.1% methyl violet. The grain boundaries in camphor were found to melt (because of the impurities concentrated there) near the zone and migrate into it at about 1 cm/hr. The mechanism for such behavior involves formation of a low-melting mixture between impurity and the solid. Since the solubility of the solid in the molten inclusion increases with temperature, the inclusion migrates toward the heat source (*5*). The process is essentially temperature-gradient zone melting (*1*, *6*). Rates of movement can be estimated theoretically, as discussed in Ref. (*5*). It may be seen that increasing the temperature gradient increases the travel rate but decreases the distance in the solid over which the inclusion is molten. Decreasing the impurity content has the same qualitative effects.

Air bubbles were also observed to move rapidly (several centimeters per hour) into the zone in camphor and many of its mixtures. The mechanism is essentially the same as above with camphor vapor moving through the air bubbles. Similar behavior would be expected for bubbles in any volatile solid.

In contrast to the above, inclusions containing both melt and a bubble were observed to move farther into the solid in 88% anthracene–12% camphor mixtures (Fig. 3). The bubbles vibrated. Furthermore, a particle

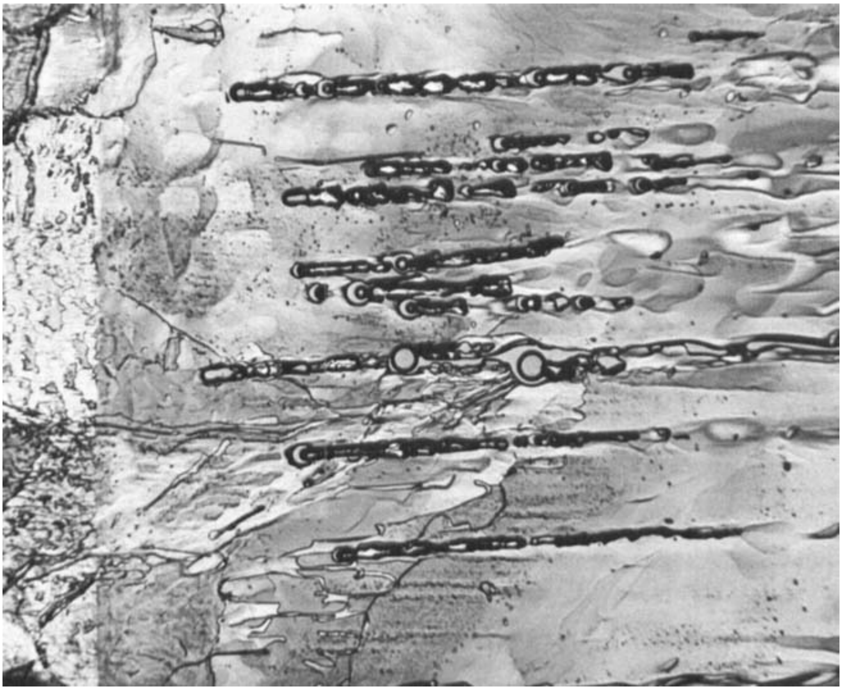

FIG. 3. Bubble-containing melt inclusions moving to the left away from the molten zone in an 88% anthracene–12% camphor mixture. The vertical line on the left is at the eutectic temperature. 307×.

on one of the bubbles showed them to be rapidly spinning. The bubble–melt inclusions continued to move into the solid until they reached the eutectic temperature and then flattened out. The bubbles then moved back and forth erratically. It is hypothesized that camphor evaporated from the hot side of each bubble and condensed on the cold side, thus lowering the melting point there and causing further dissolution. It is believed that the subsequent circulation of the melt to the hot side was caused by the variation of surface tension along the bubble surface due to the variation in composition [see Refs. (*7*) and (*8*) for discussions of similar phenomena].

Such phenomena influence the separation. If melt inclusions move into the product solid then the separation is reduced, while the separation is increased when they move out into the molten zone. The reverse is true for inclusions in the solid that feeds the zone at the melting interface.

FREEZING PHENOMENA

The freezing interface is the location of the segregation action that produces the basic separation in any fractional solidification process. Thus phenomena occurring there have an immediate effect on the separation.

Suck-back of impure melt into the frozen solid was often observed when organics were treated in glass tubes. In one experiment, naphthalene–0.1% methyl violet was contained in a horizontal 3-mm o.d. pyrex tube heated from below by the nichrome wire. At zone-travel rates of 5.4 cm/hr, the naphthalene cracked and sucked back melt for distances as large as 1 cm. When examined later, the heat from the microscope light caused the dark blue inclusions to melt and to flow through the channels in the solid. Cracking and suck-back were rare at zoning rates of 1 mm/hr and below. Apparently at such low travel rates the solid was able to relieve its thermal stresses sufficiently to avoid cracking.

In a related experiment on a different apparatus, a eutectic mixture of benzoic acid and naphthalene was subjected to the vertical Bridgman process (*1*) in a 31-mm i.d. pyrex tube. Sudden removal of the tube from the furnace caused the melt to suck back between the solid product and the glass tube for a distance of approximately 15 cm! Apparently the thermal expansion coefficient was larger for the organic than for the glass, thus allowing a gap to open between them.

Insoluble foreign particles are a very common impurity in organic reagents. Fractional solidification can be very useful for elimination of these defects (*1*, *9*). Foreign particles were pushed by the freezing interfaces of both camphor and anthracene in thin cells. However, the particles did not remain stationary at one location on the interface. Some moved sideways along the interface, while others were repeatedly bounced a considerable distance back into the melt. It is hypothesized that some of the particles tended to stick to the glass walls of the cell. Thus a greater force was necessary to free them than was necessary to merely push them at the freezing rate (*9*). This extra force would cause them to bounce into the melt when freed. Trapping of the particles occurred

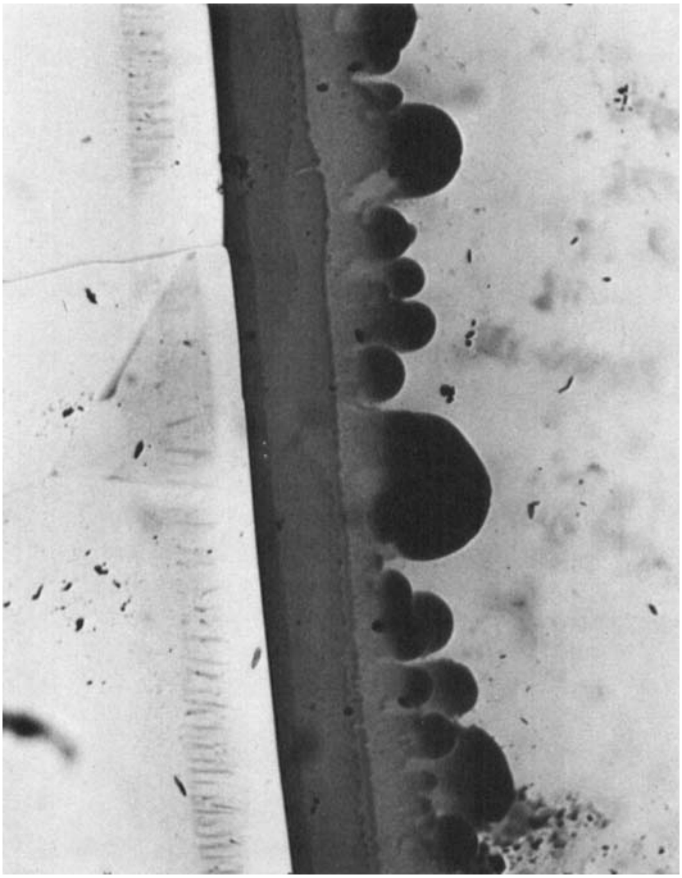

FIG. 4. Dye globules and concentration waves in naphthalene–0.1% methyl violet undergoing zone refining. Solid on left, melt on right. 153×.

at random times. Although trapping occurred preferentially at the grooves that formed at grain boundaries, it also took place on flat regions of the interface.

Irregular growth rates can drastically reduce the separation in a fractional-solidification process. In spite of all possible precautions, the interface position was observed to fluctuate on a microscopic scale in all experimental zone-melting arrangements. Variations in convective heating and cooling outside the cell or tube caused much of the problem. In addition, irregular free convection inside many of the cells and tubes was also observed. For example, stable oscillations occurred in naph-

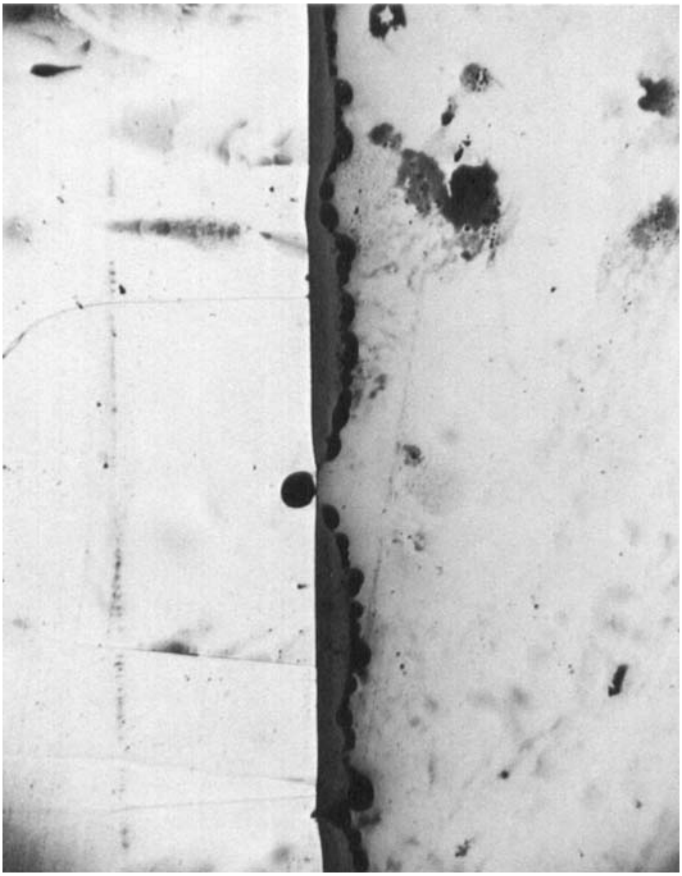

FIG. 5. Recently captured dye globule in naphthalene–0.1% methyl violet. 54×.

thalene contained in horizontal 3-mm o.d. tubes heated from below. Bubbles and insoluble particles served to mark the fluid behavior. Sometimes the bubbles oscillated or jerked in the axial direction and sometimes normal to the axis. Particles moving with the melt sometimes showed intermittent motion. The fluid between the bubble and the interface would turn over rapidly and then practically stop, only to repeat the circulation an instant later.

The freezing interface of naphthalene–0.1% methyl violet fluctuated during a zone-melting experiment using a thin cell. Concentration waves of the dye in front of the interface were clearly visible (Fig. 4). The surprising feature was the dark violet globules which remained a short distance from the interface, moving at the same average rate as the interface, only with no fluctuations. The concentration waves ended at

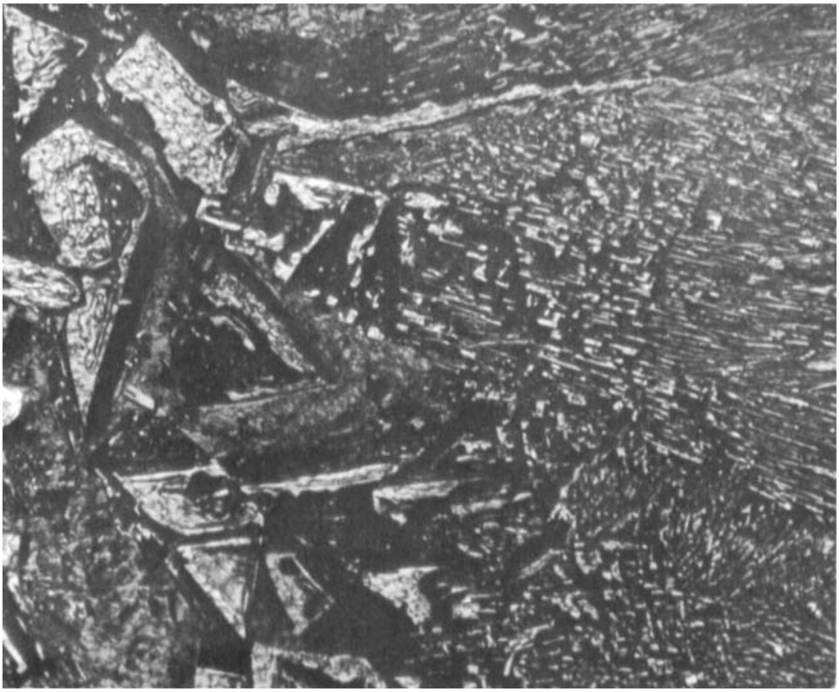

FIG. 6. Initially zoned portion of 73% camphor–27% anthracene mixture as carried out in a vertical 2 × 9 mm (inside) glass tube at 8.07 mm/hr. On the left are the original randomly oriented anthracene plates; on the right they are beginning to become aligned and were observed to extend into the melt during growth. 86×.

these globules. Occasionally one globule would fall behind and be overtaken and captured by the interface to form a liquid inclusion (Fig. 5). The explanation for this behavior is unknown, and further investigation is needed.

Several types of predicted behavior were also observed at the freezing interface. Rapid growth led to breakdown of the interface to a rough or dendritic structure, the exact shape depending on the compound and the conditions. For example, anthracene mixtures in large vertical tubes tended to produce platelets of anthracene protruding into the melt. Figure 6 shows the initially zoned portion of a 73% camphor–27% anthracene mixture. The visible material is anthracene. On the left are the original randomly oriented anthracene platelets, and on the right the developing structure is visible. Mixtures containing large amounts of *N*,*N*-dimethyl,*p*-nitroaniline invariably produced rods of this dye protruding into the melt (*10*). Figure 7 shows trapped melt freezing

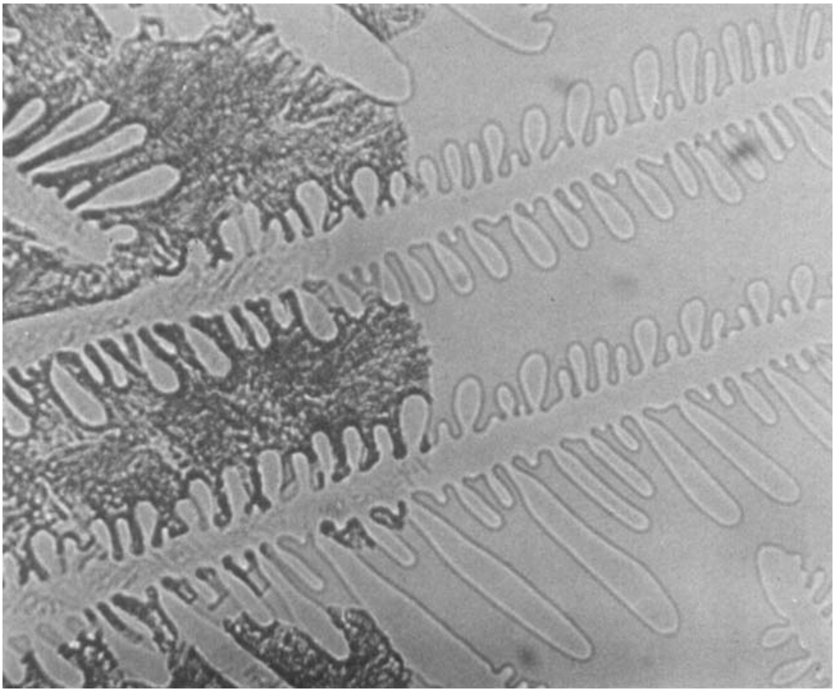

FIG. 7. Trapped melt freezing behind camphor dendrites while zoning at 5.4 cm/hr in mixture containing 12% anthracene. 153×.

among camphor dendrites propagating at 5.4 cm/hr in a mixture containing 12% anthracene. [Camphor is a nonfaceted metal analog (*11*)]. All such structures trap impurities to a much greater extent than does a smooth interface, and may reduce the separation to nil. In concentrated mixtures simultaneous growth of two solid phases may even occur and in some cases is desirable from a structural standpoint (*12*, *13*).

Unexpected transient phenomena have also been observed during

FIG. 8. Pure camphor growing by vapor transport from bubble in eutectic mixture with anthracene. (Camphor-phase boundaries are very faint and extend between the dark solid on the left and the bubble on the upper right.) 38×.

dendritic growth. A camphor–anthracene mixture with excess camphor produced anthracene platelets when the growth rate was suddenly increased [see Ref. (*12*)]. This increased the camphor content in the melt, and eventually camphor nucleated on foreign particles in the melt. Camphor dendrites soon dominated the interface to produce the steady-state structure shown in Fig. 7.

PHENOMENA DUE TO BUBBLES IN THE MELT

The solubility of gases in solids is normally much lower than in the corresponding melts. As a result, gas bubbles tend to accumulate in the melt during fractional-solidification operations. These gas bubbles can have a large influence on the separation, particularly if one of the components is volatile. We have already seen how bubbles in some mixtures cause movement of impure melt into the solid. In addition violent movement of bubbles and vigorous movement of melt around bubbles

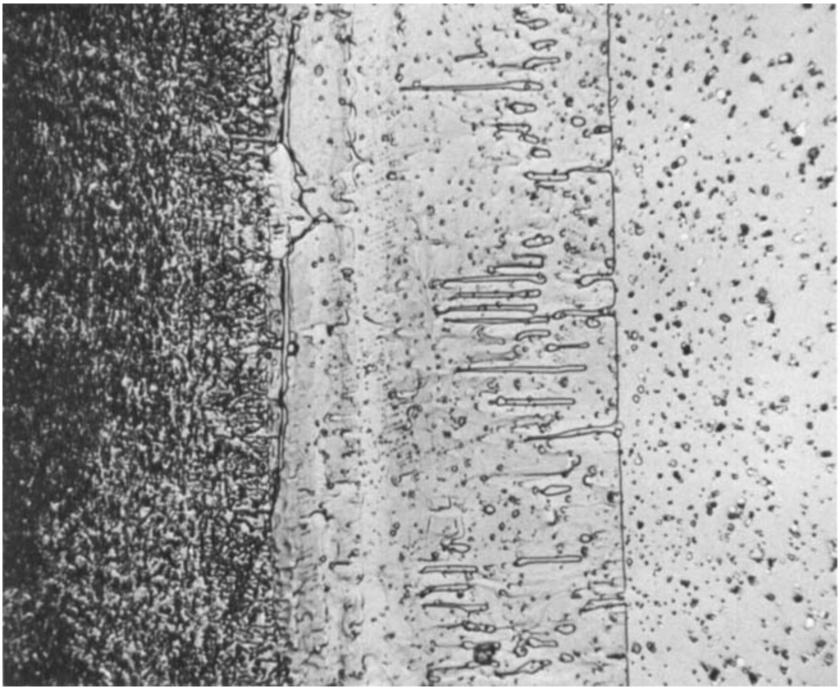

FIG. 9. Melting interface in anthracene-rich mixture with camphor. Note the line in the solid at the eutectic temperature, melt inclusions moving into the zone, and anthracene platelets in the melt. 54×.

were observed in various camphor–anthracene mixtures in both thin and thick cells. This is believed to result from volatilization combined with the dependence of surface tension on composition.

Great alterations in segregation can result from the bubble moving by or residing at the freezing interface. Mass transfer may be drastically reduced. Since the bubble reduces heat transport, it can also roughen the interface by altering the growth rate near it. In camphor mixtures it was also observed that the camphor preferentially volatilized from the melt side of bubbles and increased the camphor content on interface side sufficiently to cause growth of pure camphor there (Fig. 8). This occurred even in mixtures that lay on the camphor-poor side of the eutectic composition.

MELTING PHENOMENA

In zone melting, the composition of the solid freezing out depends on the composition of the melt, which in turn depends on the composition

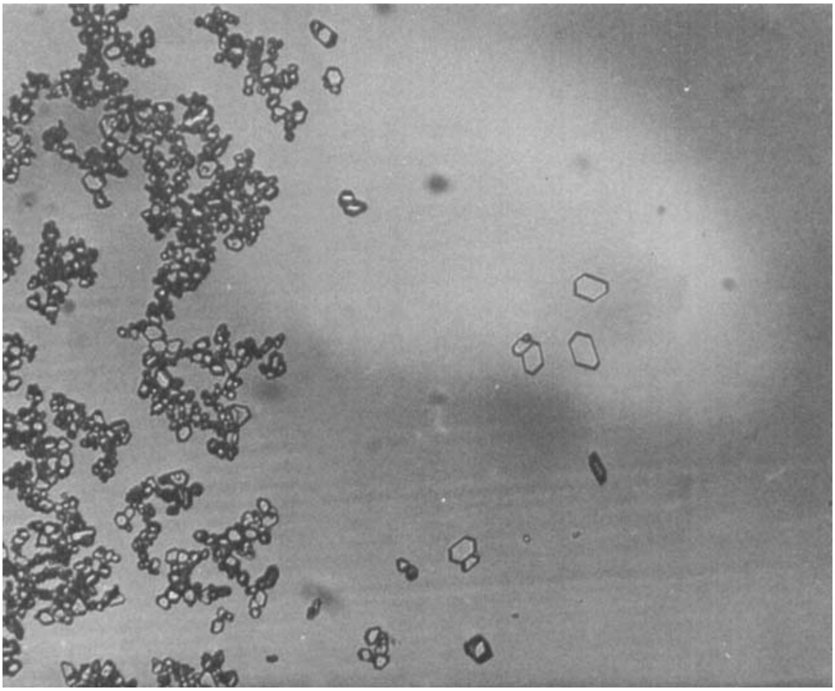

FIG. 10. Anthracene platelets growing during melt-down of mixture with camphor. 86×.

of material being fed into it. In theoretical treatments of zone melting, it is assumed that the feed composition equals the average composition of the solid. However, this is not true if the impurity concentration is very nonuniform—which is often the case (and especially so for cast ingots). Regions of higher impurity content will normally melt first (see Fig. 9 for an example of this). We have already seen that this impurity-enriched melt can migrate into the zone by means of the temperature gradient. If channels are present, bulk drainage can also occur. Drainage is particularly easy if the melting solid lies above the molten zone with a bubble separating them. This behavior was observed experimentally in several organics. Pieces of solid also fell off the melting surface and either melted in the bulk zone or were trapped at the freezing interface.

During the melt-down of camphor–anthracene mixtures prior to zoning, an interesting phenomenon was observed. Some of the anthracene crystallites grew to sizeable platelets (Fig. 10) and then later melted. This also occurred at the melting interface during zoning both in the thick and the thin cells. Surprisingly, such behavior took place even with mixtures containing slightly less anthracene than the reported eutectic composition! Perhaps surface energies and strain energies sufficiently altered the melting points of the various crystallites to cause this behavior.

CONCLUSIONS

We have seen that fractional solidification is usually not the elementary segregation process that is typically pictured. A host of phenomena can occur in the melt and in the solid that have major influences on the separation. The behavior depends strongly on the composition of the mixture, so it may change drastically during purification. Thus it is not surprising that macroscopic experimental results on fractional solidification so often deviate from the simple theoretical predictions.

Acknowledgments

Gloria Anthony designed the microscope-stage zone-melting apparatus and supervised its construction. J. R. Teviotdale prepared many of the cells used in the experiments.

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