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NATURAL CONVECTION IN EVAPORATING SESSILE DROPS WITH CRYSTAL GROWTH

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ABSTRACT

Laser shadowgraphy is employed to study interfacial instability and natural convection inside a minute drop evaporating on a plate with internal crystal growth. Both pure and binary liquids are considered. Two methods of crystal growth are developed, one by the bulk-supercooling method and the other by the point-supercooling method. Interfacial instability is determined by the characteristics of periphery shape of the shadowgraph, while the shadowgraphic image describes the nature of flow behavior inside the drop. While internal crystallization plays no role in interfacial instability, it exerts a profound found influence on natural convection.

Introduction

Modern communication and computer electronics is affected by the manufacture of electronic semi-conductor devices of microscale (the dimensions of one micron or less). The performance reliability of these devices depends strongly upon the quality of the semi-conductor single crystals. One of the most important problems in the growth of large semi-conductor single crystals is the homogeneity of the electrical resistivity in the microscale. It has been disclosed that fluctuations of the electrical resistivity in such a crystal are caused by inhomogeneous

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dopant distribution which is due to the timewise variations in the growth rate. One factor leading to unsteady crystal growth is unsteady convection in the melt (or solution).

There are several basic types of isenthalpic solidification fronts such as planar, quasi-planar, scalloped (or cellular) and dendritic, depending on the degree of supercooling. The dendritic front is formed at low degrees of supercooling, ie., in undercooled melts. The solidification front becomes cellular as supercooling increases and takes a quasi-planar shape with further increased supercooling. Both the scalloped and quasi-planar forms occur in hypercooled melts. The planar-front solidification represents the limiting case of isenthalpic solidification. The type of specific solidification front to be formed is the problem of intraphase-interfacial (i.e. morphological) instability which is coupled with the hydrodynamic instability of the adjacent liquid. It is thus evident that fluid motions adjacent to a solid-liquid interface play an important role in crystal growth phenomena. The central issue of convection in melts and crystal growth has been treated in a large number of publications [for example, 1-6]. In addition, several reviews on the subject have appeared during the past decade [for example, 7-9]. Those reviews indicated that most attention has been focused on the influence of buoyancy and double-diffusive transport on flow and instability phenomena. Little effort has been devoted to investigate the effects of surface tension on the growth of crystals.

In a low-gravity environment, surface tension plays a dominant role in natural convection. Its effects become appreciable on earth, when the interface is curved or has thermal and/or concentration gradient. There are two basic modes of flow induced by surface tension gradients: One is called Marangoni instability with the gradients normal to the free surface. The other is named Marangoni convection with the gradients along the free surface. The two flow modes are referred to as Marangoni effects. Those induced by thermal and concentration gradients are called thermocapillary and diffusocapillary effects, respectively.

The Marangoni effects on interfacial stability of pure and binary liquid systems were studied by Castillo and Velarde [10-12]. Yang and his associates investigated the effects of surface tension on natural convection in sessile drops [13, 14] in rectangular tanks with interfacial temperature gradients [15] and in minute disk pools [16], all with phase change.

In the case of a pure liquid drop evaporating on a plate, evaporation induces a temperature gradient, resulting in the generation of thermocapillary force on the drop surface. As a result, the system is subjected to two types of convection: The Grashof convection due to gravitation buoyancy forces and the Marangoni convection induced by a gradient of the surface tension coefficient. The Rayleigh-Bernard instability, Marangoni instability, internal flow structures, free surface deformation and evaporation speed of sessile drops were studied in references [13, 17, 18].

For binary liquid drops, both thermocapillary and diffusocapillary forces are induced due to the presence of temperature gradients on the free surface. Double-diffusive convection takes place in the drop: Both thermally - and solutally - induced buoyance forces can cause the Grashof convection. Likewise, the Marangoni convection can be induced by both thermal and solutal gradients of the surface tension coefficient. A new disclosure of interest was the occurrence of the maximum or minimum speed of evaporation at the azeotropic point of binary liquid drops [19, 20].

In the present paper, a shadowgraphic method is employed to study flow and interfacial stability in evaporating sessile drops with crystal growth. Sessile drops with surface-tension controlled convection offer the possibility of understanding the origin, formation and eventual suppression of defects in crystal growth from melts or in fabricating new alloys in the absence of buoyancy-driven natural convection and sedimentation phenomena. The study can be useful to the enhancement of crystal quality by the low-gravity environment where thermo- and diffuso-capillary effects on crystal growth are dominant.

Experimental Apparatus

Figure 1 is a schematic diagram for the shadowgraphic study of convection in a sessile drop with crystal growth. It consists of a laser light, a test plate, two aluminized mirrors, a screen and a camera. A minute drop was placed on a flat plate for evaporation in open air. A helimum-neon laser was used as the light source. The two mirrors could reflect light with no refraction. They were mounted in parallel on a frame set at 45 degrees. The test plate was inserted into the vertical light beam between the two mirrors, which was arranged to obtain a horizontal view of the evaporating drop.

The optical path from the lower mirror was horizontal and intercepted by a vertical screen. The image on the screen was recorded by a polaroid camera using the type 57, ASA 3000 films. A drop was carefully placed on the test plate by means of a micro syringe. Two cooling methods were employed for crystal growth:

a. Point-Supercooling Method

Only a point in the base surface of a drop was cooled to produce the seed for crystallization. In this method, a hole of 0.813-mm diameter was drilled on the test plate. A silver wire of equal diameter was inserted through the hole with its tip flush with the upper surface of the test plate. Cyanoacrylate was used to seal the hole. In performing a crystallization experiment, a drop was placed on the test plate with its base center located at the wire end. Then, the loose end of the silver wire was inserted in between two small pieces of dry ice which were encased in a styrofoam enclosure. The dry ice was not allowed to come near the test plate to prevent cooling.

b. Bulk Supercooling Method

A second method was devised which was to cool the entire base of the drop. The plate was precooled by dry ice. A drop was then placed on the plate. When an appropriate degree of supercooling was achieved, the drop surface was lightly touched by the tip of a fine needle. It triggered the destruction of a metastable state in the drop, initiating dendritic solidification in the bulk volume of the drop.

Results and Discussion

Two liquids of suitable freezing points and their mixtures were studied by means of laser shadowgraphy: Dimethyl sulfoxide (DMSO) and cyclohexane. Table 1 lists some properties of the liquids.

Table 1. Some properties of DMSO and cyclohexane [21]

	Cyclohexane	DMSO
Chemical Formula	C_6H_{12}	$(CH_3)_2SO$
Melting Point, °C	6.5	18.4
Boiling Point, °C	80.7	189
Specific Density at 20 °C	0.7785	1.1014
Molecular Weight	84.16	78.13
Refractive Index	1.4266	1.4770

Both methods of crystal growth by point-cooling and bulk-supercooling were utilized. Additional test series were conducted on each pure liquid and binary mixture for drop evaporation without cooling such that no crystallization occurred. The purpose is to compare the difference in flow phenomena between drops with crystal growth and those without crystallization. The drops tested had the initial base diameter of approximately 8 mm. Some representative shadowgraphs are presented in figs. 2 through 5. The time history of crystal growth in an evaporating drop may be divided into three stages: initial, intermediate and final stages.

The periphery of the drop image on the photographs portrays the interfacial flow structure which is called interfacial instability or interfacial turbulence [17]. Three types of interfacial instability exist: Stable, unstable and substable.

(1) The stable type refers to a drop forming a spherical segment with a very smooth surface. The periphery exhibits a perfect circle; (2) When a drop surface is rippled as in the unstable type, the periphery forms irregular radiant stripes with a saw-tooth-like circle; and (3) The substable type interface is in-between the two limits.

a. Dimethyl Sulfoxide

Figure 2 are the shadowgraphs of dimethyl sulfoxide drops with crystal growth by bulk-supercooling (series A) and without crystallization (series B). Figure 2-A-a reveals the formation of dendritic crystals in suspension and around the drop periphery which were formed by disruption of the supercooled drop under metastable conditions. In the intermediate stage Fig. 2-A-b, the dendritic crystals grew and merged, forming radial branches. The crystallization was near its completion at the final stage, Fig. 2-A-c.

No distinct wave front was detected in the flow field inside the drop. The photos in Fig. 2-B were taken at 3, 5 and 10 seconds, respectively. It is realized that the interface of the evaporating DMSO drop belongs to the substable type as evidenced by the shape of the image periphery being distorted from a circle and spiked. Since the shadowgraphs of the drop with crystal growth in Fig. 2-A exhibit a similar periphery shape, one may conclude that crystallization does not affect the interfacial instability of the drop. Because DMSO has a slow vaporization rate due to its high boiling point, Table 1, little change was noted in the size and shape of the DMSO image over a long period of time.

Figure 3 illustrates the flow patterns in a DMSO drop with crystal growth induced by the point-supercooling method. Photo a shows the drop on the plate before the point cooling was initiated. Photos b and c (of a different drop) exhibit the change in flow structures as time elapses after the initiation of point cooling. There exists three distinct regions. The inner region corresponds to the crystal in growth, while the outer one is the stagnant liquid. The middle region is the flow induced by the advancing solid-liquid interface. The difference in densities of the three distinct structures results in three regions of different darkness. As the solid-liquid interface advances outward with crystal growth, the flow field is pushed toward the drop periphery. The stagnant liquid region shrinks accordingly.

b. Cyclohexane

The crystallization of cyclohexane by the point-supercooling method is shown in Figure 4. The evaporation study of cyclohexane drops [17] revealed that their interface belongs to the stable type as evidenced by the image shape being a perfect circle. The image shape remains perfectly circular (nearly one half of the circular image failed to appear due to the selected illuminating direction). The solid-liquid interface is nearly circular and so is the wave front of the flow which is faintly visible in photo b. When the process is completed, the crystals display a form of sunburst.

c. Dimethyl Sulfoxide-Cyclohexane Mixtures

Several binary mixtures of DMSO and cyclohexane were studied. In the interest of brevity, only the results of one mixture with DMSO = 25% and cyclohexane = 75% by volume are presented here. Figures 5-A and - B depict the evaporating drop with and without crystal growth, respectively. The crystallization was achieved by means of the point-supercooling method. Photos a, b and c correspond to the initial, intermediate and final stages, respectively. Due to the simultaneous occurrence of temperature and concentration gradients, double-diffusive convection due to combined buoyancy forces is present. In addition, both thermocapillary and diffusocapillary flows are induced by surface-tension gradients. Several interesting phenomena were observed:

1. The binary liquid drop underwent a substable type evapporation as characterized by a weak interfacial turbulence.

2. The nature of interfacial turbulence was not affected by internal crystal growth.

3. The drop continued to spread during the course of crystallization and/or evaporation. No distinct flow domain was formed. This is in sharp contrast with the pure DMSO or cyclohexane drop in which the flowing and stagnant liquid regions appeared.

4. In the intermediate stage, a concentric (bright) ring appeared in the shadowgraph of the uncooled drop, Fig. 5-B-b. This ring divided the liquid into two domains. Since evaporation is more rigorous at the central part of the free surface, the less volatile component, namely DMSO, would congregate at the periphery region outside the ring. The domain inside the ring would be rich in cyclohexane. This view is supported by the fact that cyclohexane has a lower refractive index than DMSO, as shown in Table 1, resulting in a brighter image. The

ring vanished in the final stage, Fig. 5-B-c when all cyclohexane has evaporated. Only the DMSO liquid remained for very slow evaporation process.

5. With the cooling case, crystals formed the shape of a sunburst at the intermediate stage, Fig. 5-A-b. Since DMSO has a higher melting point than cyclohexane, see Table 1, crystals were of DMSO. Cyclohexane still remained in a liquid phase. The latter solidified later in the final stage, Fig. 5-A-c. Table 1 provides the pertinent physical properties of DMSO and cyclohexane.

Conclusions

Interfacial instability and natural convection inside an evaporating sessile drop with and without crystal growth are investigated by means of laser shadowgraphy. Both pure liquids and their mixtures are used. Two methods of crystal growth are developed. One is by disrupting a supercooled drop in a metastable state, while the other is by the use of a point heat sink. It is concluded that

1. While cyclohexane drops have a perfectly quiescent interface during evaporation, dimethyl sulfoxide and its mixtures with cyclohexane have weak interfacial turbulence on the drop surface.

2. Internal crystal growth does not change the characteristics of interfacial instability of the drops.

3. The bulk-supercooling method yields suspending crystals in the bulk phase and dendritic growth on the plate around the drop periphery. No distinct flow region is formed.

4. The point-supercooling method produces three distinct regions are produced during the crystallization of pure liquid drops: An inner region representing crystals in growth, an intermediate region corresponding to flow induced by the advancing solid-liquid interface, and an outer region consisting of stagnant liquid. The crystals display a sunburst form in the final stage.

5. No distinct region is observed during the crystal growth of binary liquid drops. The crystals form a sunburst shape in the intermediate stage.

6. Two flow regions are formed in the uncooled but evaporating drop of binary liquid mixtures during the intermediate stage. The inner region consists of the liquid rich in the lower boiling-point component, while the liquid in the outer region is rich in the higher boiling-point component.

7. More detail experimental studies on natural convection are desirable.

References

1. S. Ostrach, Convection in Crystal Growth, Convective Transport and Instability Phenomena (edited by J. Zierep and H. Oertel, Jr.), G. Braun, Karlsruhe, pp. 427-439 (1982).

2. G. Muller, Convection in Melts and Crystal Growth, ibid, pp. 441-467 (1982).

3. F. Rosenberger, Convection in Vapor Crystal Growth Ampoules, ibid, pp. 469-489 (1982).

4. H. J. Scheel and E. O. Schultz-Dubois, The Role of Hydrodynamics in Crystal Growth from High-Temperature Solutions, ibid, pp. 491-513 (1982).

5. M. E. Glicksman and S. C. Huang, Convective Heat Transfer during Dendritic Growth, ibid, pp. 557-574 (1982).

6. C. F. Chen and J. S. Turner, Crystallization in a double-diffusive System, J. Geophs. Res., Vol. 85, pp. 2573-2593 (1980).

7. S. Ostrach, Fluid Mechanics in Crystal Growth-the 1982 Freeman Scholar Lecture, J. Fluids Engineering, Vol. 105, pp. 5-20 (1983).

8. M. Epstein and F. B. Cheung, Complex Freezing-Melting Interfaces in Fluid Flow, Annual Review of Fluid Mechanics, Vol. 15, pp. 293-319 (1983).

9. M. E. Glicksman, S. R. Coriell and G. B. McFadden, Interaction of Flows with the Crystal-Melt Interface, Annual Review of Fluid Mechanics, Vol. 18, pp. 307-335 (1986).

10. M. G. Velarde and J. L. Castillo, Transport and Reactive Phenomena Leading to Interfacial Instability, in Convective Transport and Instability Phenomena (eds. J. Zierep and H. Oertel, Jr.), G. Braun, Karlsruhe, pp. 235-263 (1982).

11. J. L. Castillo and M. G. Velarde, Buoyancy-thermocapillary Instability: The Role of Interfacial Deformation in One- and two-component Fluid Layers Heated from Below or Above, J. Fluid Mech., Vol. 125, pp. 463-474 (1982).

12. J. L. Castillo and M. G. Velarde, Microgravity and Thermoconvective Stability of a Binary Liquid Layer Open to the Ambient Air, J. Non-Equilib., Thermodyn., Vol. 5, pp. 111-124 (1980).

13. N. Zhang and Wen-Jei Yang, Evaporative Convection in Minute Drops on a Plate with Temperature Gradient, International Journal of Heat and Mass Transfer, Vol. 26, 1479-1488 (1983).

14. Wen-Jei Yang and J. C. Duh, Thermocapillary Flow with Phase Change, Proceedings of the Korea-USA Heat Transfer Seminar in Thermal Engineering and High Technology Systems, October 16-22, 1986, Seoul, Korea.

15. C. Y. Shieh and Wen-jei Yang, Transient Thermocapillary Flow in Rectangular Tanks with Phase Change, to appear in International Heat and Mass Transfer, Vol. 29 (1986).

16. T. Uemura and Wen-Jei Yang, Transient Thermocapillary Convection in Evaporating Minute Liquid Cavities, to be presented at the 4th International Symposium on Multi-Phase Transport and Particulate Phenomena, December 15-17, 1986, Miami Beach.

17. N. Zhang and Wen-Jei Yang, Natural Convection in Evaporating Minute Drops, Journal of Heat Transfer, Vol. 104, pp. 656-662 (1982).

18. N. Zhang and Wen-Jei Yang, Evaporation and Explosion of Liquid Drops on a Heated Surface, Experiments in Fluids, Vol. 1, pp. 101-111 (1983).

19. Wen-Jei Yang, T. Uemura and C. L. Chao, Flow and Instability inside Evaporating Sessile Drops of Binary Liquid Mixtures, Proceedings of International Symposium on Heat Transfer held on October 15-18, 1985 in Beijing, Vol. 1, Paper No. 85-ISHT-I-24.

20. N. Zhang, Y. Xu and Wen-Jei Yang, Thermal Stability in Binary Droplet Evaporation on a Flat Plate by Real-Time Holographic Interferometry, Heat Transfer 1986-San Francisco, Vol. 2, Hemisphere, Washington, D. C., pp. 525-530 (1986).

21. R. C. Weast (Editor-in-Chief), handbook of Chemistry and Physics, 66th edition, CRC Press, Boca Raton, Florida (1985-86).

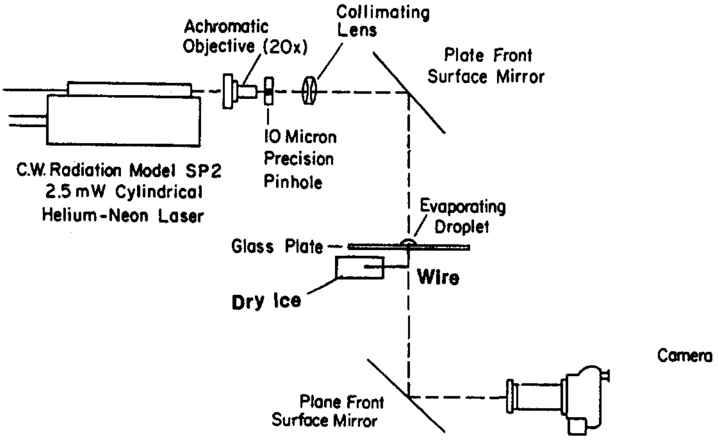

Fig. 1 A schematic diagram of shadowgraphic setup

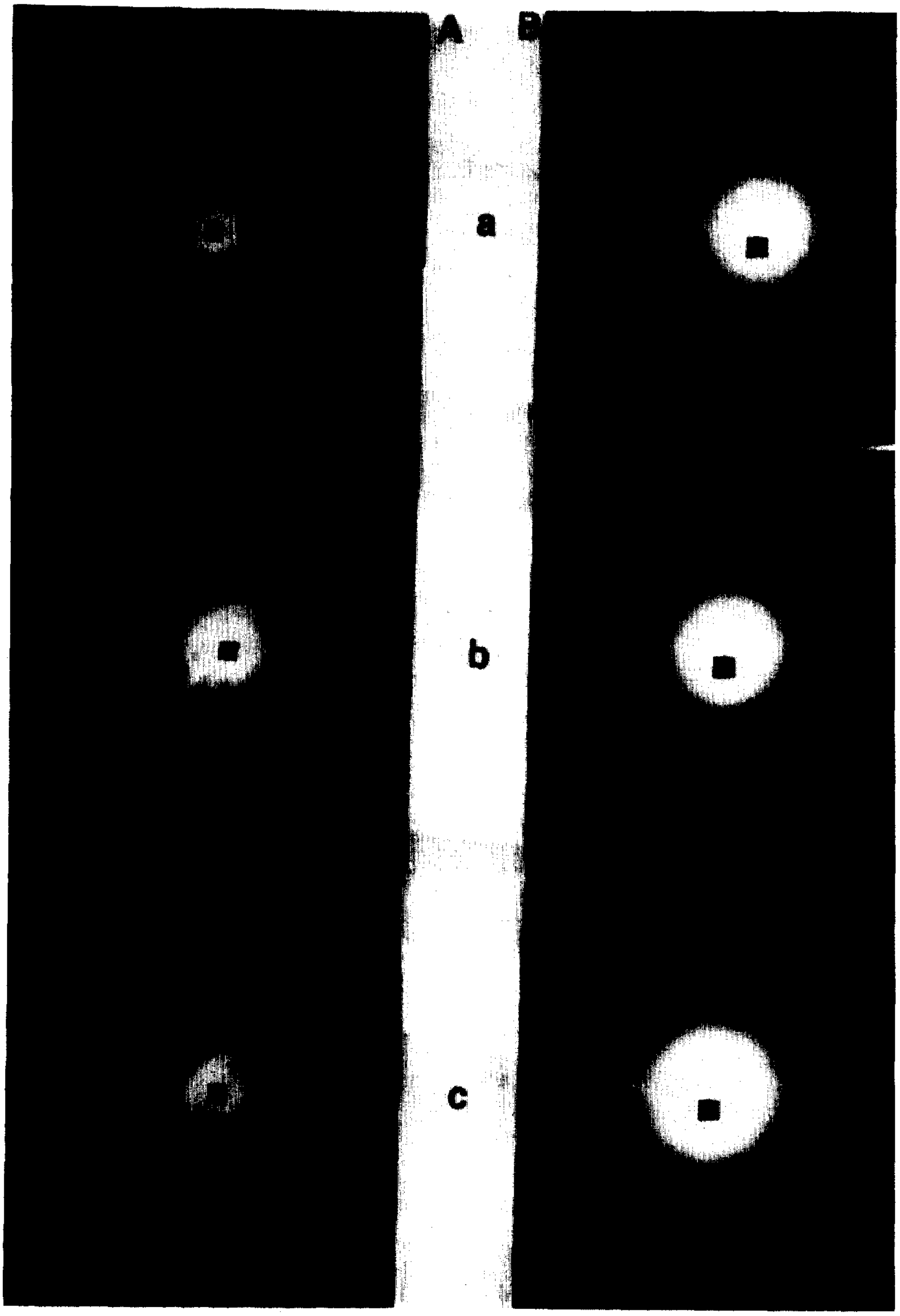

Fig. 2 Shadowgraphs of dimethyl sulfoxide drop, (A) with and (B) without crystal growth induced by bulk-supercooling method

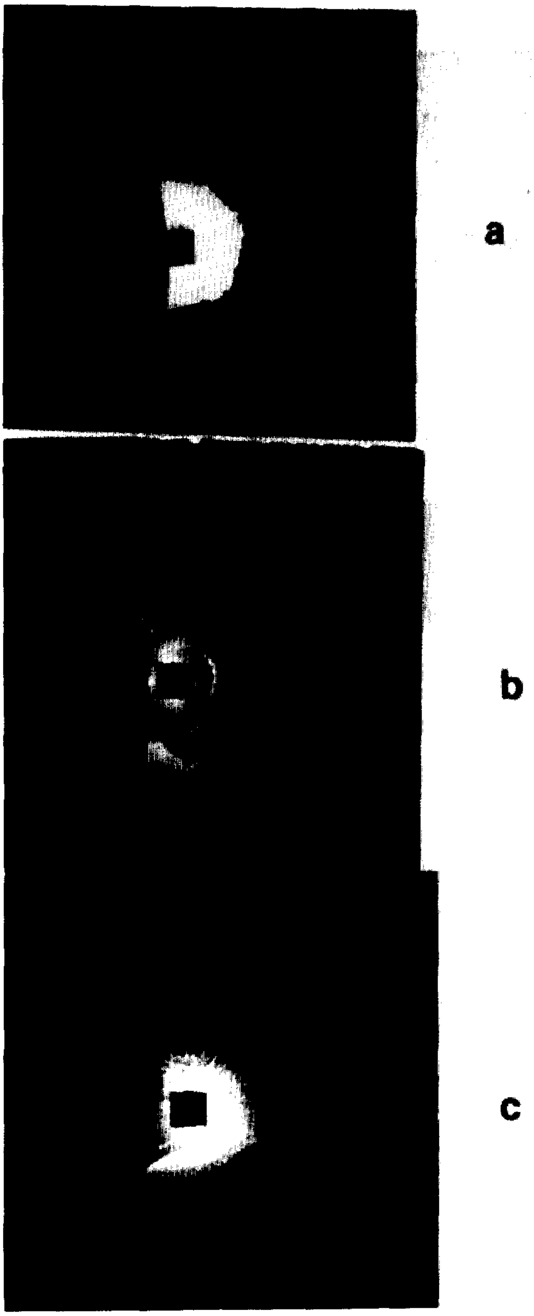

Fig. 3 Dimethyl sulfoxide drops with crystal growth induced by point-supercooling method

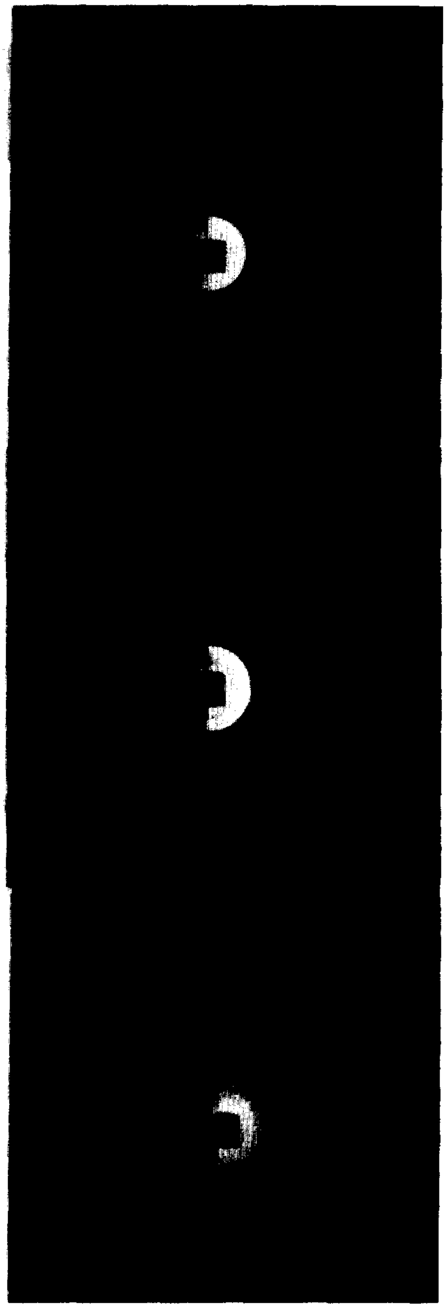

Fig. 4 Cyclohexane drop with crystal growth induced by point supercooling method

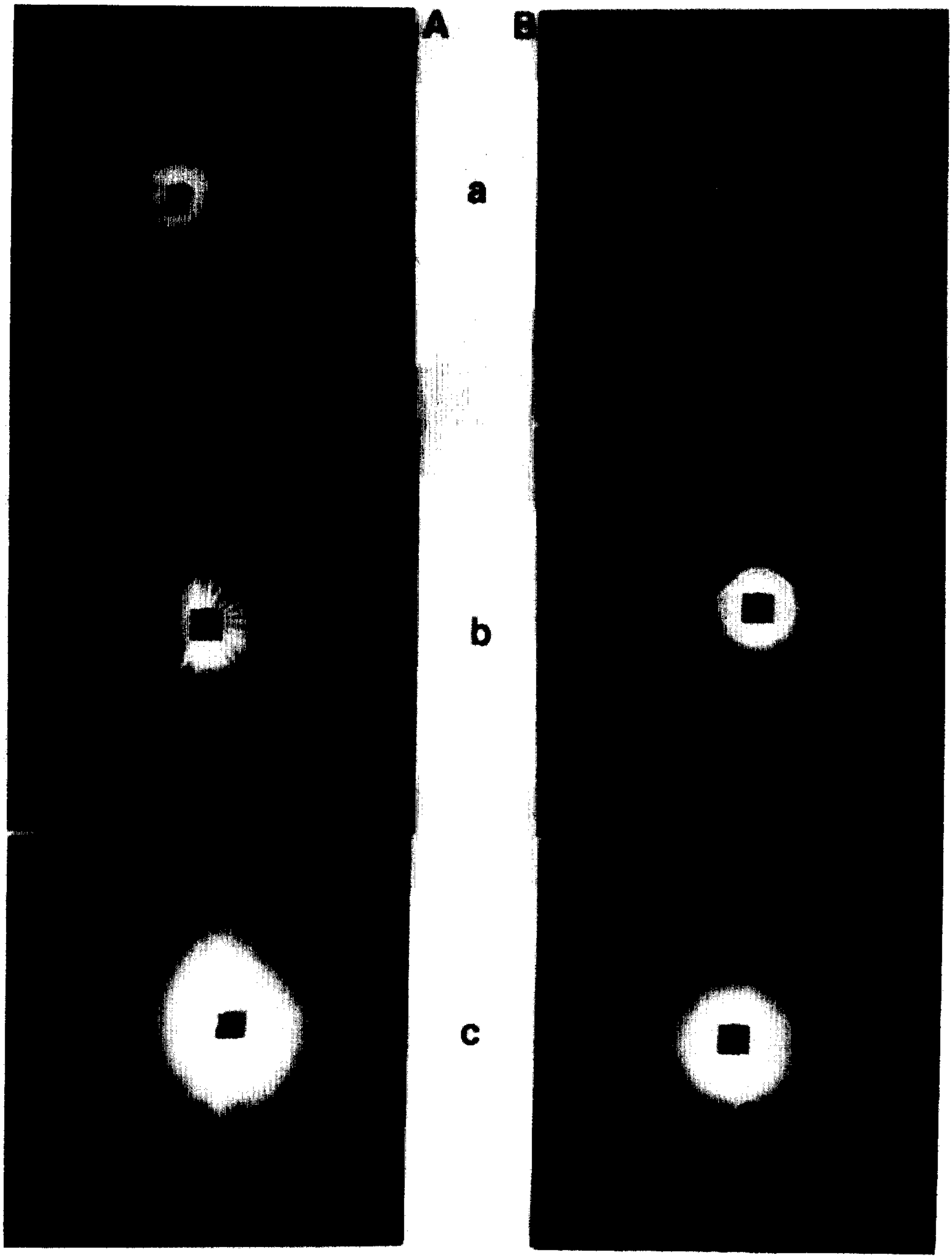

Fig. 5 Shadowgraphs of 25%-dimethyl sulfoxide/75%-cyclohexane drops, (A) with and (B) without crystal growth induced by point-supercooling method