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Influence of Stirring on Incorporation of Particles during Solidification

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Abstract

The critical freezing rate V_c was measured for glass beads suspended in naphthalene by using the tilt rotating zone melting technique. In horizontal operation with a large gas bubble sweeping along the interface during rotation, V_c increased dramatically with *increasing* tube rotation rate and decreasing mass of beads. Tilting the tube prevented the bubble from contacting the freezing interface and very stongly increased V_c. Siliconized glass beads were pushed as well as nontreated beads, both in horizontal operation with tube rotation and in vertical operation without stirring. Teflon particles were pushed to very high freezing rates in the horizontal rotating configuration. These results differ from those of Omenyi and Neumann, who predicted and observed that both Teflon and siliconized glass beads are not pushed by freezing naphthalene at any freezing rate.

INTRODUCTION

When second-phase foreign particles are incorporated in a growing crystal they not only consitute an impurity and a light-scattering center, but they can also cause generation of dislocations, new grains, and twins. Numerous theoretical and experimental studies have demonstrated that most particles are pushed by a solidifying interface provided that the freezing rate is below a critical value V_c which is on the order of 1 to 5 mm/hr in the absence of stirring (*1–10*). Because V_c depends on the nature of the particles, it has been proposed that particles can be separated into

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bands by using accelerated solidification, i.e., particle chromatography (*11–13*).

In the absence of convection, the critical freezing rate or trapping velocity V_c decreases as particle size increases. The value of V_c increases substantially when stirring is induced by tube rotation during directional solidification (*13–15*). V_c increases as the rotation rate increases, at least at small rotation rates. With the freezing interface below the liquid, V_c increases rapidly as the tilt angle decreases (approaches horizontal) unless and until a gas bubble contacts the freezing interface. The gas bubble dramatically decreases V_c.

The purpose of the study described here was to determine the effect of operating conditions, especially particle size and quantity, on V_c.

EXPERIMENTAL METHODS

The experiments are described in detail elsewhere (*16*). Eastman scintillation grade naphthalene was used as a host material. The particles were glass beads of five size ranges from the Cataphote Division of the Ferro Corp., Cleveland, Ohio. To reduce the gas bubble and impurity content of the naphthalene, it was given two upward zone passes at 2 cm/hr with a 6-cm long molten zone in a 50-cm long charge in a sealed 10 mm i.d. Pyrex tube. After zoning, 4 to 6 cm of the impure naphthalene at the top was discarded and the glass beads added.

The particle pushing experiments were performed using the tilt rotating zone melting technique with a concave freezing interface. Most runs were done horizontally with a gas bubble occupying about $^1/_4$ of the zone and contacting the interface. The zone travel rate was increased manually in increments of 1 mm/hr at hourly intervals. Particle trapping was observed with an optical microscope either during the run or in the solid afterwards. Thus for each run, V_c was up to 1 mm/hr less than the freezing rate at which trapping occurred. The results were perfectly reproducible.

After one run the tube was carefully sectioned, the naphthalene sublimed off, and the mass of trapped beads in each section determined. As shown in Fig. 1, a few beads had actually been trapped below the measured V_c, and many beads had been pushed even at freezing rates above V_c. Thus the values of V_c reported here may be more properly regarded as freezing rates at which the trapping probability increased rapidly without ever reaching unity. A more detailed study of trapping probability vs operating conditions has been made (*15*) and will be reported elsewhere.

Omenyi and Neumann (*9*) reported that Teflon and silicone oil treated glass beads are not pushed ($V_c = 0$) by naphthalene. To check this in our apparatus, both irregular Teflon particles and siliconized glass beads were

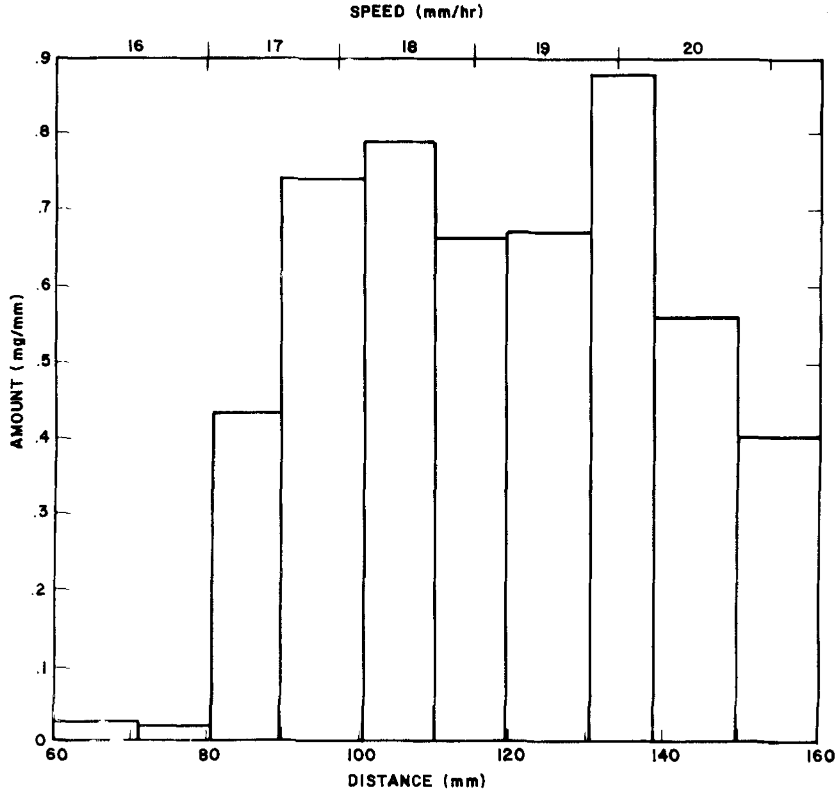

FIG. 1. Particle trapping distribution for a horizontal run containing 0.077 g of 28 to 38 μm beads with 20 rpm tube rotation. V_c observed to be 17 mm/hr. Travel speed changed by 1 mm/hr increments.

used. Glass beads were siliconized by heating in Dow Corning 200 dimethylpolysiloxane for $2^1/_2$ hr at 160°C with occasional stirring. The oil was then poured off and the beads were rinsed five times with isopentane. Wetting by water was significantly reduced by this treatment. Neumann and Omenyi also kindly supplied beads siliconized at the University of Toronto.

RESULTS

Bead Size

Figure 2 shows the influence of bead size on V_c for horizontal zoning with rotation at 20 rpm and 0.31 g of beads present. Unlike previous unstirred studies, V_c *increased* rapidly with increasing bead size. The large 106 to 125 μm beads were not trapped even at the maximum zone travel rate of 25 mm/hr. These results were correlated best ($r^2 = 0.9995$) by

$$V_c = 7.62 \exp(0.0193d) \text{ mm/hr} \qquad (1)$$

where d is bead diameter in μm (taken as 1 μm greater than the lower limit of each particle size range). V_c was taken as 0.5 mm/hr lower than the zone travel rate at which trapping was first observed.

Two runs were also made with mixtures of different bead sizes: one

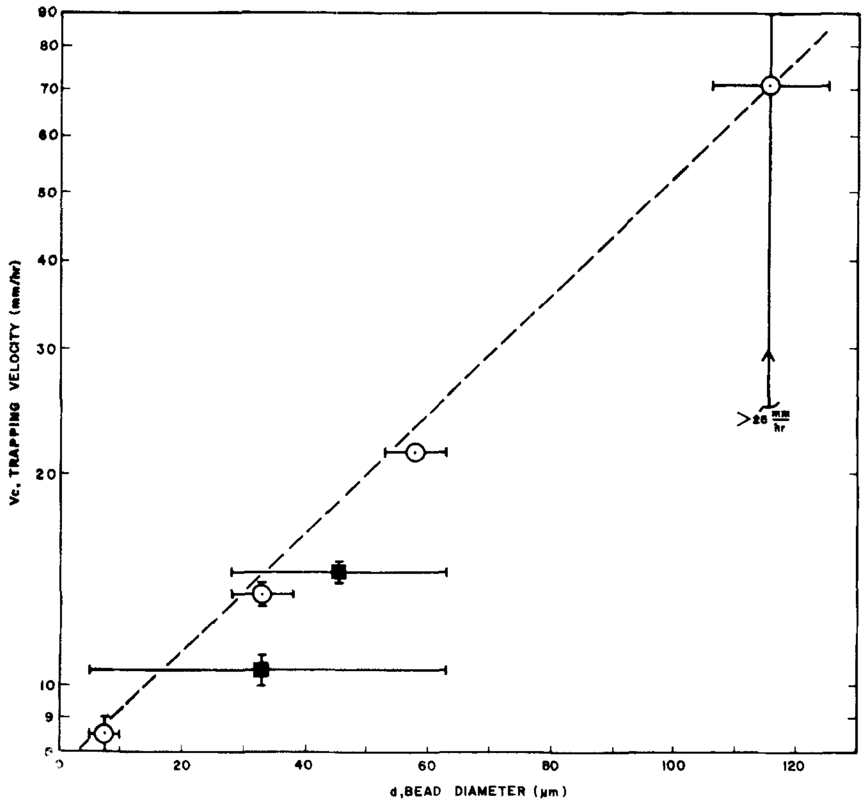

FIG. 2. Trapping velocity V_c as a function of particle size. The largest particles were pushed at the maximum velocity of the apparatus (25 mm/hr). The horizontal runs contained 0.31 g of beads with 20 rpm tube rotation. (○) Beads from one size range only. (■) Beads from two or three ranges mixed. (– –) Equation (1).

with 50% 28 to 38 μm and 50% 53 to 63 μm; and one with $^1/_3$ 5 to 10 μm, $^1/_3$ 28 to 38 μm, and $^1/_3$ 53 to 63 μm. Figure 1 shows that in both cases V_c was about 1 mm/hr higher than V_c for the smallest beads used alone (with the same total mass). Thus the presence of larger beads inhibited the trapping of smaller beads. This caused us to investigate the effect on V_c of the total mass of beads present.

Total Mass of Beads

Figure 3 shows the result of a series of horizontal runs with 28 to 38 μm beads and 20 rpm rotation. The data were best correlated ($r^2 = 0.984$) by

$$V_c = 17.3 \exp(-0.738w) \qquad (2)$$

where w is the mass of particles in grams. Note that when 50% 28 to 38 μm beads were used (as described previously), V_c lay between V_c for the mass ignoring other bead sizes and V_c for the total mass with all beads 28 to 38 μm.

Rotation Rate

Table 1 summarizes horizontal runs at different rotation rates and two different particle sizes, using 0.31 g of beads in each. Within the range investigated, V_c increased nonlinearly with increasing rotation rate [for copper particles it has been found that trapping at the walls increases at higher rotations (*14*)]. At higher rotation rates, V_c increased faster.

Tilt Angle

At 20 rpm tube rotation with the tube tilted 35° to the horizontal, beads from 28 to 125 μm were all pushed at the maximum rate of 25 mm/hr. This increase in V_c was due to removal of the bubble from contact with the interface.

TABLE 1

Trapping Velocity V_c as a Function of Tube Rotation

Particle size (μm)	5 rpm (mm/hr)	20 rpm (mm/hr)	35 rpm (mm/hr)
28 to 38	12	14	>25
53 to 63	19	22	>25

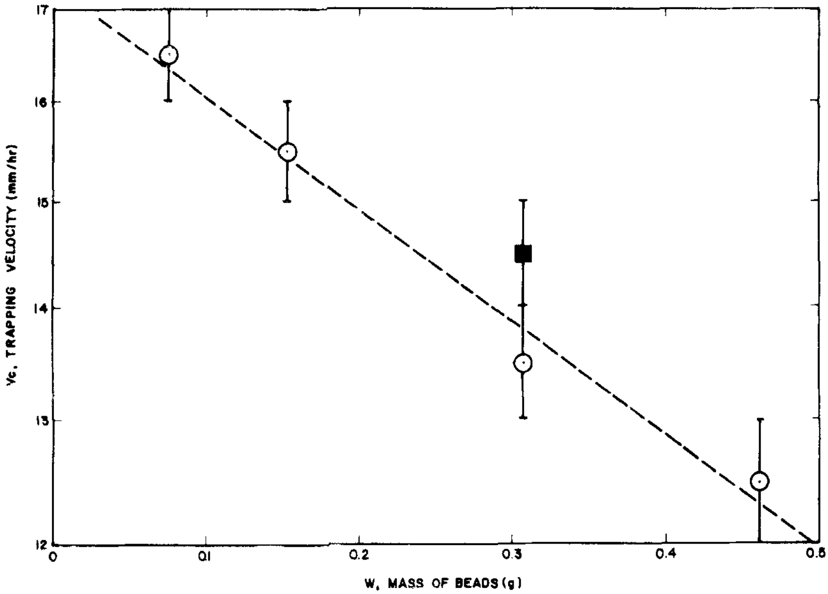

Fig. 3. Trapping velocity V_c as a function of mass w of particles initially present. Horizontal runs with 28 to 38 μm beads, 20 rpm tube rotation. (○) Beads all 28 to 38 μm. (■) Beads half 28 to 38 μm and half 53 to 63 μm. (- -) Eq. (2).

Teflon Particles and Siliconized Glass Beads

In horizontal runs with 20 rpm tube rotation, Teflon particles, 212 to 250 μm glass beads siliconized here, and glass beads siliconized by Omenyi were *all* pushed at the 25 mm/hr maximum rate.

Runs were also performed using a vertical tube with no rotation. The particles rested on the conave interface with no apparent motion. With a charge of 0.31 g of 212 to 250 μm beads, both siliconized and non-siliconized beads were pushed at 1.3 mm/hr and trapped at 2 mm/hr. Pushing distances were on the order of 14 cm, with no trapping observed. Siliconized beads from the University of Toronto were similarly pushed at 1.25 mm/hr and trapped at 2 mm/hr.

DISCUSSION

With stirring, the bead pushing-trapping phenomenon is apparently much more complex than in the absence of stirring. In order to be trapped, a particle must sit at the interface long enough for the interface to grow around the bead. If the contact time is the same for beads of all sizes, then one might expect V_c to be proportional to particle size d. We found that V_c increases much faster than linearly with d. Thus hydrodynamics are clearly important. The larger bead sizes would experience a greater shear stress by the fluid and a greater gravitational torque, tending to remove them from the interface and lowering the residence time. An increased amount of particles may increase the residence time, although heavier particles are more effective on trapping of small particles. Increased rotation and tilt, and the absence of a bubble, all apparently lower the residence time.

The disagreement with Omenyi's results on Teflon and siliconized glass is intriguing. Since Omenyi performed his experiments with a horizontal thin film contained between microscope slides, we suspected that the silicone treatment merely increased the drag of the glass beads on the slides. Perhaps their Teflon particles also adhered to the glass slide. However, Omenyi, at our suggestion, showed that siliconized beads roll down an inclined glass plate immersed in molten naphthalene at a very small angle (*9*). We now suspect that some difference in impurity contents of our naphthalene caused significant differences in the surface properties between glass beads, melt, and solid interface. Indeed, Gupta has found that small impurity additions stongly increase both V_c and the force that freezing naphthalene exerts on a fixed glass bead (*15*).

These results have strong implications for crystal growth. To avoid particle incorporation, stirring should be used, a gas bubble should not contact the growing interface, and the interface should not be under the melt. In the absence of convection, large particles are much more likely to be trapped than small particles. Stirring reduces the chance of particle engulfment, particulary for large particles. Thus, among typical melt growth techniques, particle trapping problems should increase dramatically as one goes from Czochralski growth, to tilt rotating zone melting at an angle, to horizontal Bridgman and zone melting growth without rotating, to horizontal zone melting with rotation, to vertical zone melting with the zone moving upward, to the vertical Bridgman-Stockbarger technique.

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