Journal of Crystal Growth 130 (1993) 495–506 North-Holland

# Solidification of $NH_4Cl$ and $NH_4Br$ from aqueous solutions contaminated by $CuSO_4$ : the extinction of chimneys

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Received 20 October 1992; manuscript received in final form 4 February 1993

Results are presented of a series of experiments in which hyper-eutectic aqueous solutions of  $NH_4Cl$  and  $NH_4Br$  contaminated by small amounts of  $CuSO_4$  are cooled from below. The experiments with  $NH_4Cl$  indicate that beyond a contamination of 0.3 wt%, the well-known chimney structure that is associated with solidification from a pure aqueous solution of  $NH_4Cl$  disappears. Subsidiary experiments indicate that at approximately the same level of contamination, the branched dendritic morphology that is usually associated with crystalline  $NH_4Cl$  is suppressed. It is suggested that the macroscopic chimney-driven compositional convection that results from cooling hyper-eutectic aqueous solutions of  $NH_4Cl$  is rather sensitive to the microscopic details of the crystal growth. Solidification experiments with pure hyper-eutectic aqueous solutions of  $NH_4Br$  display a similar chimney-driven convective pattern; however, this is effectively unchanged even in the presence of contaminations of up to 1 wt% of  $CuSO_4$ .

#### 1. Introduction

There has been a great deal of recent interest in the cooling from below and resulting crystallization of aqueous solutions of pure ammonium chloride with compositions beyond the eutectic value of 20 wt% (see, for example, refs. [1–7]). Under these conditions less dense fluid is released upon solidification and, despite the stable thermal profile, strong compositional convection can be driven in the binary liquid above the solid NH<sub>4</sub>Cl. The interest in this situation is driven partly by the somewhat unusual form of the solid crystals and the resulting convective pattern.

When a hyper-eutectic aqueous solution of pure  $NH_4Cl$  is cooled from below, solid  $NH_4Cl$  crystallizes as a closely-spaced array of predominantly vertical, needle-like primary dendrites, with

mutually perpendicular, horizontal secondary and tertiary sidebranches, photographs of which appear in refs. [4,5,7,8] and elsewhere. As reported first by Copley et al. [1], after an initial phase, a mushy layer of such dendrites bathed in interstitial aqueous NH<sub>4</sub>Cl grows up from the base. The overlying, undersaturated aqueous solution is slowly drawn down into the mushy layer where it encounters a temperature field which decreases with decreasing height above the base of the container. The solution thus becomes saturated and promotes further growth of the dendrites. The interstitial fluid, depleted of some of its NH<sub>4</sub>Cl, is less dense and initially rises from the entire surface of the mushy layer, but with time and increased thickness of the mush a lateral component to the migration of buoyant fluid through the mushy layer is induced and the return flow eventually emanates exclusively from isolated, vertical chimneys running through the crystal mush, as sketched in fig. 1. The number of chimneys reaches a maximum and then, along with the overall intensity of the convective motion, generally decreases with time as the thickness of the mushy layer uniformly increases.

Why this form of solidification occurs in aqueous NH<sub>4</sub>Cl is currently a controversial matter. As reported elsewhere [8], while it has been said by some that chimneys can develop under suitable conditions for all solutions, in a variety of crystallization experiments with aqueous solutions of numerous salts we have never consistently observed chimneys other than those grown from aqueous  $NH_4Cl$ , or the closely related aqueous NH<sub>4</sub>Br. Among the suggested explanations of why aqueous NH<sub>4</sub>Cl solidifies as it does are: the crystal mush is of low solid fraction; the energy of formation is high; the crystal has no water of hydration (though this is true of other crystals); the liquidus curve is particularly steep; the concentration of NH<sub>4</sub>Cl at the solidus is so much larger than that in the original solution; there are predominantly horizontal, secondary branches of the mainly vertical dendrites; and that the morphology of NH<sub>4</sub>Cl crystals lies closer to the

roughening transition than all other salts. Not all of these suggestions are completely independent. The aim of the current paper is to present further information on this topic.

We present the results of a series of experiments which solidify from below aqueous solutions of both NH<sub>4</sub>Cl and NH<sub>4</sub>Br contaminated by small amounts (< 1% by wt) of CuSO<sub>4</sub>. Raz, Lipson and Ben-Jacob [9] investigated experimentally the effects of such contamination on the solidification of a thin layer of supersaturated aqueous NH<sub>4</sub>Cl in which no fluid motion could result. They found that the presence of the CuSO<sub>4</sub> impurity suppressed the creation of sidebranches in the NH<sub>4</sub>Cl crystals and long dendrites of pure NH<sub>4</sub>Cl grew, with either cusped or quasi-parabolic tips. In our case, we show that beyond a contamination of approximately 0.3 wt%, the typical chimney pattern is extinguished, and the mean solid fraction in the mushy layer is generally enhanced as the degree of contamination increases. Our experiments show further that NH<sub>4</sub>Br, which crystallizes with an almost identical branched, dendritic morphology to that of pure NH<sub>4</sub>Cl, exhibits chimneys in mushy layers grown from hyper-eutectic aqueous solutions contaminated by up to 1.0 wt% CuSO<sub>4</sub>.



Fig. 1. A sketch of the plan form and section through a chimney of a typical array of NH<sub>4</sub>Cl crystals grown from an aqueous solution.

In appendix B, Lipson presents the results of two sets of experiments which investigate effects due to the presence of small amounts of CuSO<sub>4</sub> on the microscopic morphology of the resulting crystals. He finds that for NH<sub>4</sub>Cl there is a change from one form of crystal habit to another at approximately the same value of the contamination for which the chimneys are suppressed. The modification of the crystal symmetry is due to the incorporation of contaminant ions within the crystal lattice. By contrast, no such transition in crystal habit is observed for similar contamination of NH<sub>4</sub>Br solutions. We conclude that the macroscopic pattern of convective motions can be strongly influenced by the microscopic form of the crystallization.

### 2. The experiments with contaminated NH<sub>4</sub>Cl

All the experiments were conducted in a thermally insulated Perspex tank  $12.7 \times 12.7 \times 38$  cm high with a thin stainless-steel base, mounted on a brass heat exchanger through which we could pump an appropriate coolant. A sketch of the experimental setup is presented in [8]. Solutions were prepared by dissolving the necessary amounts of technical grade solid NH<sub>4</sub>Cl and  $CuSO_4 \cdot 5H_2O$  in separate volumes of distilled water at 20°C and then mixing the two solutions together, to give a concentration of NH<sub>4</sub>Cl of 27.0 wt%. The contaminant concentration of  $CuSO_4$  was either 0 (2 experiments), 0.10 (3 experiments), 0.20 (1 experiment), 0.30 (3 experiments), 0.50 (1 experiment), or 1.0 wt% (1 experiment). Every final, contaminated solution displayed a greenish-yellow colour, due to the dilute presence of one or more of the various aqueous species of copper(II)chloro complexes. Before each experiment the temperature of the base of the tank was brought down (in about 2 h) to - 16.0°C and maintained at this value throughout the experiment.

Each experiment commenced by rapidly pouring the prepared solution at room temperature ( $\approx 20^{\circ}$ C) into the tank to an initial depth of 36.0 cm. An array of readings was taken throughout each experiment, which we generally continued for about 24 h. The readings and their method of determination were: temperature in the solution at three or frequently more different heights from the base of the tank, either by thermistors or by thermometers; concentration of  $NH_4Cl$  in the solution at the same heights, by withdrawal of approximately 5 cm<sup>3</sup> samples which were then accurately diluted and their refractive indices measured by a hand-held refractometer; depth of the mushy layer, by eye; the number of chimney structures, by eye; and the number of active vents, by observing the resultant plume motion using the shadowgraph technique.

For each experiment, as the solution was poured into the tank a fine layer (less than 1 mm thick) of crystals grew over the base of the tank. Compositional convection, driven by the release of relatively less dense, NH<sub>4</sub>Cl-depleted fluid was observed to be initiated almost immediately over the entire base. This is in agreement with the observations from previous experiments with aqueous NH<sub>4</sub>Cl reported in refs. [5] and [6]. After some time, the value of which varied with the concentration of the contaminant, chimneys were observed to form in the mushy layer, except for those experiments with a concentration of  $CuSO_4$  in excess of 0.3 wt%, for which no chimney structures occurred. The convective plumes emanating from chimneys increased in intensity at the expense of the overall compositional convection until upflow was limited exclusively to the active vents. The experiments with a contamination of 0.3 wt% resulted in just a few chimneys,



Fig. 2. The observed time of initiation of chimneys,  $t_*$ , and the observed height of the mushy layer at that time,  $h_*$ , as a function of the amount of CuSO<sub>4</sub> contamination in an initially 27 wt% aqueous solution of NH<sub>4</sub>Cl.

and we conclude that this value is at approximately the limit of chimney formation. Fig. 2 plots the onset time of chimney formation,  $t_{*}$ , and the concurrent height of the mushy layer,  $h_*$ , as functions of the degree of contamination. Both variables increase as the contamination increases, and reflect the fact that no chimneys form beyond a critical contamination. Fig. 3 plots the number of active vents as functions of time for experiments with 4 different values of the contamination (recall that for contaminations of 0.5 and 1.0 wt% there were no chimneys). In all four cases there is an initially sharp rise in the number of active vents and chimneys. With time, some of the chimneys are no longer sites of active plumes and the number of active vents gradually decreases, consistent with the results reported recently by Tait and Jaupart [6]. The decrease seems to be slightly more rapid as the degree of contamination increases.

Pure NH<sub>4</sub>Cl crystallizes from an aqueous solution of pure NH<sub>4</sub>Cl as fine dendrites with secondary and tertiary sidebranches. Contamination of the solution by CuSO<sub>4</sub>, or by several other transition metal compounds, suppresses the growth of the sidebranches [17]. In the case of contamination by CuSO<sub>4</sub>, Cu<sup>2+</sup> ions are incorporated into the ionic lattice. As the degree of contamination increases, the crystal growth planes change first from  $\langle 100 \rangle$  to  $\langle 111 \rangle$  and then to a star structure, as discussed in greater detail in appendix B by Lipson. He explains there that the transition appears to be a strong function of temperature. This suggests that in our experiments the transition may vary with height within the mushy layer. We conclude, however, from Lipson's experiments, that the transition in morphology on the microscale occurs at approximately the same degree of contamination as the change in the macroscopic convection pattern.

It is interesting to note here, in passing, that just as the contaminants listed above are known to suppress the sidebranching, it is also reported in ref. [10] that contamination of aqueous  $NH_4Cl$ solutions by glycerine, for example, makes the resulting crystal finer and more dendritic. One might therefore wonder what are the relative quantitative contributions to the macroscale convection due to either changes in fluid viscosity [6] or the accompanying diffusion controlled alteration to crystal morphology.

Results from the two experiments with pure  $NH_4Cl$  were virtually identical. In contrast, there was considerable scatter between the three experiments with a contamination of 0.10 wt%, though each particular experiment yielded systematic results, as indicated in fig. 4, which plots the height and  $NH_4Cl$  concentration as functions of time for the three experiments. A similar, though somewhat smaller, scatter was observed in results from



Fig. 3. The observed number of active vents as functions of time for contaminations of 0, 0.10, 0.20 and 0.30 wt% CuSO<sub>4</sub>. The curves have been drawn by eye to fit the data.



Fig. 4. The height of the mushy layer and the concentration in the fluid above the mushy layer as functions of time for three experimental realizations with a contamination of the initial aqueous  $NH_4Cl$  of 0.10 wt%.

the three experiments with a contamination of 0.30 wt%.

We interpret this scatter as an indication of the large effect of relatively small amounts of contaminant. The variation of contaminant between experiments with nominally identical initial values arises in two ways. First, our making up of the initial solution differed slightly from one realisation to another, although we tried to minimize this difference. Second, accidental small variations in the concentration of the contaminant within the mushy layer as it evolves, maybe even reflecting the way the solution was poured into the tank and was initially solidified, could lead to the observed variations.

We hence decided to describe the results of experiments with a contamination of 0.1 wt% by the data of the "middle" experiment, depicted by squares in fig. 4. We made a similar decision for the experiments with a contamination of 0.3 wt%. (Note that the results from these "middle" experiments have been used in drawing up fig. 3.) Fig. 5 then plots the heights of the mushy layer and concentrations as functions of time for experiments with the six different values of the contamination. We see that at any fixed time the height of the mushy layer decreases by quite a large amount as the degree of contamination is increased. Again there is a fairly large variation from experiment to experiment, but the variation does not appear to be systematic.

By conservation of NH<sub>4</sub>Cl, mean values of the volume fraction of solid within the mushy layer,  $\overline{\phi}$ , can be evaluated. Denoting the initial concentration of NH<sub>4</sub>Cl as  $C_0$  in a layer of depth *H* and density  $\rho_0$ , which after time *t* results in a fluid layer of concentration *C* and a mushy layer of depth *h* made up partially of solid crystals of density  $\rho_x = 1.53$  g cm<sup>-3</sup>, we obtain, as indicated in appendix A, that

$$\overline{\phi} = \frac{H}{h} \frac{\rho_0}{\rho_x} \frac{C_0 - C}{1 - C} \,. \tag{1}$$

Note that during the early stages of an experiment, when  $h \approx 0$  and  $C \approx C_0$ , small measure-



Fig. 5. (a) Heights of the mushy layer as functions of time for aqueous  $NH_4Cl$  solutions initially contaminated with 0, 0.10, 0.20, 0.30, 0.50 and 1.0 wt% CuSO<sub>4</sub>. (b) Concentration of  $NH_4Cl$  in the fluid above the mushy layer as functions of time for aqueous  $NH_4Cl$  solutions initially contaminated with 0, 0.10, 0.20, 0.30, 0.50 and 1.0 wt% CuSO<sub>4</sub>. The same symbols have been used as in



Fig. 6. The mean volume fraction of  $NH_4Cl$  in the mushy layer,  $\overline{\phi}$ , as functions of time for aqueous  $NH_4Cl$  solutions initially contaminated with 0, 0.10, 0.20, 0.30, 0.50 and 1.0 wt% CuSO<sub>4</sub>. The same symbols have been used as in fig. 5a.

ment errors in either h or C will lead to large errors in the evaluation of  $\overline{\phi}$ .

Fig. 6 plots  $\overline{\phi}$  for the six different values of the contamination, from which we see that solidification from pure NH<sub>4</sub>Cl leads to values of  $\overline{\phi}$  which increase monotonically with time. Fig. 6 also indicates that at any particular time  $\overline{\phi}$  increases monotonically with the degree of contamination (over the range considered), but that for the contaminations of 0.5 and 1 wt%, for which no chimneys were observed,  $\overline{\phi}$  generally seems to *decrease* with time. Thus the extinction of chimneys by the contamination of the original solution is clearly reflected in the mean volume fraction of the resultant mushy layer.

The total mass of NH<sub>4</sub>Cl solidified is given by  $M_x = \rho_x Ah\overline{\phi}$ , where A is the cross-sectional area of the tank. Values of  $M_x$  are plotted as functions of time in fig. 7. At the end of some of the experiments, we drained off the liquid and weighed the residual solid. To within a fair degree of accuracy the mass so determined was equal to  $M_x$ , the mass determined from our evaluation of the mean volume fraction  $\overline{\phi}$ .

#### 3. An experiment with pure $NH_4Br$

We conducted an additional experiment with an aqueous solution of ammonium bromide. Single crystals of  $NH_4Br$  have been grown previously



Fig. 7. The total mass of solidified  $NH_4Cl$ ,  $M_x$ , as functions of time for aqueous  $NH_4Cl$  solutions initially contaminated with 0, 0.10, 0.20, 0.30, 0.50 and 1.0 wt% CuSO<sub>4</sub>. The same symbols have been used as in fig. 5a.

from supersaturated melts in a sufficiently small space that convection played no role [11,12]. The resulting dendritic crystals displayed the typical side branching observed for  $NH_4Cl$ . Our interest here centred on the form of convective motion, the shape of crystals, the rate of growth of the crystal pile and the interdendrite spacing when a large array of crystals is grown from an aqueous solution.

Part of the phase diagram of aqueous  $NH_4Br$ is graphed in fig. 8. The eutectic point is at a composition of 32.1 wt% and a temperature of  $-17.0^{\circ}C$ . From this point the liquidus rises to  $20^{\circ}C$  (nominally room temperature) at 43.0 wt%.



Fig. 8. Part of the phase diagram for the  $H_2O-NH_4Br$  binary system. The solid circle marks the initial condition of the experiment, while the open circles indicate the conditions in the fluid above the mushy layer as the experiment progressed.

The number beside each circle is the time in hours.

Accordingly, we prepared a 42.25 wt% solution, which is slightly undersaturated at room temperature, and poured it into the tank to a depth of 32.0 cm. The base of the tank had been precooled to -15.8°C (slightly above the eutectic temperature) and was maintained at that value throughout the experiment. Accurate temperature measurements were recorded automatically every 5 min from 9 vertically stacked thermistors. In addition, the composition of the solution was again measured every hour, as before.

As the warm aqueous solution was poured into the tank, a fine layer of  $NH_4Br$  crystals formed immediately over the entire base of the tank. Strong compositional convection was initiated almost at once and by 15 min the upward motion was almost entirely confined to plumes coming from one of approximately 400 vents. With time the vigour of the compositional convection slowly diminished and the number of active vents decreased, as seen in fig. 9.

The thickness of the dendritic layer as a function of time is plotted in fig. 10 along with the corresponding values for pure  $NH_4Cl$ . We see that the two curves are similar in form, but that the thickness of the  $NH_4Cl$  layer significantly exceeds that of the  $NH_4Br$  layer. However, in making this comparison one should bear in mind that the phase diagrams of the two aqueous salts are quantitatively different as were the initial concentrations of the two solutions. If the data presented in fig. 10 are replotted on logarithmic scales they still show considerable curvature,



Fig. 10. The thickness of the mushy layer as a function of time for the solidification from below of an uncontaminated aqueous solution of  $NH_4Br$ . The result for an uncontaminated aqueous solution of  $NH_4Cl$ , already presented in fig. 5a, is also shown.

which makes it clear that it is not possible to draw a simple power law through the data.

The three composition readings taken at different heights at any one time agreed to within the experimental error (+0.5 wt%) and we conclude that the composition was spatially uniform throughout the solution. Fig. 11 presents the data of this mean composition as a function of time. Combining these data with those of fig. 10 and using (1) with  $\rho_x = 2.43$  g cm<sup>-3</sup>, we can evaluate the mean volume fraction  $\overline{\phi}$  and the total solid mass deposited  $M_x$ , as presented in fig. 12. The functional form of the solid fraction for NH<sub>4</sub>Br is similar to that for  $NH_4Cl$ , but is considerably greater, indicating that the NH<sub>4</sub>Br is more closely packed. The total mass deposited in the NH<sub>4</sub>Br systems exceeds quite considerably that deposited in the NH<sub>4</sub>Cl system.



Fig. 9. The number of active vents as a function of time for the solidification from below of 42.5 wt% aqueous solution of  $NH_4Br$ .

Fig. 11. The concentration of  $NH_4Br$  in the fluid above the solidifying mushy layer as a function of time.

On completion of the experiment, the tank was drained, the dendritic block removed and photographed. It was clear that the dendritic structure was in general very similar to that produced with the uncontaminated ammonium chloride solution.

## 4. The experiments with contaminated NH<sub>4</sub>Br

We conducted a series of experiments with aqueous solutions of  $NH_4Br$  contaminated with varying amounts of  $CuSO_4$ , specifically 0.1, 0.3, 0.5 and 1.0 wt%. The details of the experimental procedures were the same as has been reported in the previous sections, and so we concentrate here on discussing the observed data.

The major result is that the contamination by CuSO<sub>4</sub> affected but little, and not at all qualitatively, the resultant solidification, compositional convection and chimney formation. In particular, very approximately the same number of chimneys were formed independent of the degree of contamination. We cannot be completely definite about this conclusion because the addition of CuSO<sub>4</sub> caused the aqueous solution to turn a deep, virtually opaque red-brown colour, due to the presence of hydrated copper(II)bromide complexes, and the number of chimneys could only be estimated by extrapolation from the number observed against the sidewalls of the tank. At the end of each experiment the tank was drained and the remaining crystal block carefully examined to

yield very approximately the same number of vent structures.

Curves of h,  $\overline{\phi}$  and  $M_x$  are plotted in fig. 13 from which it is seen that these quantities are only very weak functions of the amount of contamination.

As discussed in appendix B by Lipson, he found that the presence of  $CuSO_4$  up to 1 wt% does not affect the formation of individual crystals of  $NH_4Br$  on the microscale. It appears that  $Cu^{2+}$  ions cannot coordinate in the same way with  $Br^-$  ions in a body-centred cubic  $NH_4Br$ lattice as they do with  $Cl^-$  ions. The resulting lack of modification to the mesoscale convective pattern supports the hypothesis that the two are intimately associated.

# 5. Conclusions

We conclude that a small amount of contamination by  $CuSO_4$  of an aqueous solution of  $NH_4Cl$ can significantly change the resulting macroscopic solidification process. This is accompanied by a change of the crystal morphology on the microscale. Our experiments indicate that a contamination in excess of 0.3 wt% prohibits the formation of chimneys in the crystal mushy layer and the compositional convection accompanying the solidification is then similar to that observed during the solidification of almost all other aqueous solutions. The solidification of aqueous  $NH_4Cl$  is



Fig. 12. (a) The mean volume fractions of  $NH_4Cl$  and  $NH_4Br$  in the mushy layer and (b) the total mass of solidified  $NH_4Cl$  and  $NH_4Br$  as functions of time for the solidification of uncontaminated solutions.



Fig. 13. (a) The height of the mushy layer, (b) the mean volume fraction within the mushy layer and (c) the total mass deposited as functions of time for aqueous  $NH_4Br$  solutions initially contaminated with 0, 0.1, 0.3, 0.5, 1.0 wt% CuSO<sub>4</sub>.

of one particular form and can be easily changed by incorporation of certain impurities.

#### Acknowledgements

We gratefully acknowledge stimulating discussions with E.C. Constable and M.G. Worster. An

earlier version contained many more figures reporting experimental data; a copy of this version can be obtained from the authors. Our research is partially funded by a grant from Venture Research International.

# Appendix A. The mean volume fraction $\overline{\phi}$

The aim of this appendix is to derive a relationship for the mean volume fraction  $\overline{\phi}$  in terms of the height of the crystal layer h and the NH<sub>4</sub>Cl concentration in the overlying fluid C, as well as the height H, concentration  $C_0$  and density  $\rho_0$  of the initial fluid layer. Denoting the mass of crystalline NH<sub>4</sub>Cl in the mushy layer by  $M_x$ , we seek

$$\overline{\phi} = M_{\rm x} / \rho_{\rm x} Ah, \tag{A.1}$$

where  $\rho_x$  is the density of the crystals and A is the cross-sectional area of the container. If  $M_0$ represents the initial mass of NH<sub>4</sub>Cl in solution and  $M_w$  the accompanying mass of water,

$$C_0 = M_0 / (M_0 + M_w), \qquad (A.2)$$

$$C = (M_0 - M_x) / (M_0 + M_w - M_x), \qquad (A.3)$$

where, in deriving (A.3), we have neglected the changes of concentration in the crystal layer whose height  $h \ll H$ . Substituting

$$M_0 + M_w = \rho_0 A H \tag{A.4}$$

into (A.2) and substituting the result into (A.3), we obtain, on rearranging terms, that

$$\rho_0 C_0 H = \rho_x h \overline{\phi} + \rho_0 C H - \rho_x C h \overline{\phi}. \tag{A.5}$$

The term on the left-hand side of (A.5) is the total mass of NH<sub>4</sub>Cl in the initial solution. The first term on the right-hand side of (A.5) is the mass of crystalline NH<sub>4</sub>Cl in the mushy layer. The sum of the last two terms thus represents the total mass of NH<sub>4</sub>Cl that remains in the solution. Rearranging (A.5), we obtain the expression for  $\overline{\phi}$ 

$$\bar{\phi} = \frac{H}{h} \frac{\rho_0}{\rho_x} \frac{C_0 - C}{1 - C}.$$
 (A.6)

## Appendix B by S.G. Lipson

We suggest here an explanation for the results described in the main part of the paper. It is presented as an appendix because it is based mainly on experiments which were carried out after the main series was completed, and had no direct influence on them.

It has been known for a long time (ref. [10] and references therein) that small amounts of some additives to NH<sub>4</sub>Cl cause significant changes to the morphology of its crystal growth. Pure NH<sub>4</sub>Cl grows very quickly with a fine  $\langle 100 \rangle$  dendritic morphology [13]. The effect of the additives is to promote a much slower-growing  $\langle 111 \rangle$  dendritic morphology, which has high growth resistance (defined as the degree of supersaturation divided by velocity of growth) compared to the pure crystal even at low supersaturations. To investigate whether this effect is related to the extinction of chimneys, we carried out a series of experiments in which drops of 28 wt% NH<sub>4</sub>Cl solution containing various proportions of contaminant were crystallized at 6°C under a microscope. The experiments with  $CuSO_4$  additive showed that the transition to the  $\langle 111 \rangle$  growth occurred at an impurity level of about 0.03 wt%. As the impurity concentration increased, the crystals grew as needles with less and less prominent side-branches, the  $\langle 111 \rangle$  orientation being indicated by 70° angles. At an impurity level of about 0.3% they became essentially faceted, growing very slowly with beautiful star-like shapes. It was clear by observation of the colour density of the solution before and after crystallization that the impurity was preferentially absorbed into the crystals. The increase in the growth resistance indicates a greater degree of local supersaturation at the surface of the growing crystal when the impurity was present. Similar effects were found with  $Cu^+$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$  and  $Fe^{2+}$ anions, whereas  $Cr^{3+}$ ,  $Zn^{2+}$  and  $Ca^{2+}$  had no effect. The cation seemed to be irrelevant; no difference was observed between sulphates and chlorides. However, when the NH<sub>4</sub>Cl was replaced by NH<sub>4</sub>Br, the solution having the same saturation temperature, the growth morphology remained  $\langle 100 \rangle$  up to 3 wt% impurity.

From the microscopic point of view, a reasonable explanation of the observed facts is that the ions form ligands such as  $(CuCl_A)^{2-}$ , whose presence can be deduced from the typical vellowish colour of the solution [14,15] and which preferentially attach to the  $\langle 100 \rangle$  facets of the growing crystal where they inhibit further growth on them. The impurities observed to have the morphological effect are all transition metals which form such ligands. Moreover,  $(CuBr_4)^{2-}$  occurs only weakly, which explains the absence of corresponding effects in NH<sub>4</sub>Br solutions. It is clear that the blocking of growth on the  $\langle 100 \rangle$  facets would increase the growth resistance and we shall assume that the growth resistance is a continuous and increasing function of impurity concentration, which is suggested by the growth curves h(t)shown in fig. 5a.

How does all this affect chimney formation? The accepted explanation of chimneys assumes that at each level of the mush there is temperature and concentration equilibrium between the solid and liquid fractions. The colder and therefore less concentrated solution at lower levels convects upwards. When it reaches a level at which it is undersaturated it dissolves the crystals in its path, thereby opening a passageway which encourages further convection along the same route. We now ask what will happen if there is a large growth resistance so that the solution in contact with the growing mush must be considerably supersaturated. It can still be less saturated, and therefore lighter, than the warmer solution above it, so that there is still a driving force for convection. However, as the solution rises it may remain supersaturated at the temperature of the higher levels and therefore does not dissolve the crystals and form chimneys. It is possible, if the growth resistance is high enough, that solution from the base of the mush could convect right through it and exit from the top surface still supersaturated with respect to the solid; it is also possible that the rising solution could reach the saturation level at some intermediate level in the mush, at which level chimney formation would begin. The height of this occurrence would therefore be an indication of the degree of supersaturation maintained at the bottom.

This hypothesis suggests that the both the reduction of the number of chimneys and the transition to  $\langle 111 \rangle$  growth should occur at about the same concentration of impurity. We therefore carried out experiments in a vertical Hele-Shaw cell, 2 mm thick, with its base cooled to  $-15^{\circ}$ C. The cell had insulating double windows. Since the typical chimney dimension is also about 2 mm (fig. 1) the crystal morphology could be observed together with the dynamics of chimney formation. The function h(t) measured in this cell with pure NH<sub>4</sub>Cl was the same as that in the three-dimensional tank (fig. 5a) although the impure salt grew somewhat faster than did the same concentration in the tank. Fig. 14 shows a chimney in pure NH<sub>4</sub>Cl; the crystals are clearly  $\langle 100 \rangle$  and there is evidence of dissolution in the breaking off of bits of crystal which can be seen as they fall down the channel. Fig. 15 shows the initiation of a chimney



Fig. 14. Chimney observed in the Hele-Shaw cell during growth of pure  $NH_4Cl$  from a base at  $-15^{\circ}C$ . Small bits of detached crystal are falling down the chimney. Same magnification as fig. 15.



Fig. 15. Initiation of a chimney in a solution with 0.014% CuSO<sub>4</sub>. The crystals are growing with mixed orientation, and the chimney started in the  $\langle 100 \rangle$  region.

in a solution containing 0.014 wt% CuSO<sub>4</sub>, which is growing in a mixed morphology; parts are  $\langle 111 \rangle$ and parts are  $\langle 100 \rangle$ , and the chimney is forming in the latter region. It is interesting that the transition to  $\langle 111 \rangle$  growth and the repression of chimneys in the Hele–Shaw cell occurred at about 0.03 wt%, not 0.3 wt% as in the three-dimensional cell.

A remaining point for discussion is the way in which the form of  $\phi(t)$  changes as the impurity concentration increases (fig. 6). When the impurity concentration is high, because of the high growth resistance we have seen that there is essentially no "post factum" change in the solid fraction once the mush has grown, so that the first and coldest-grown region has the highest solid fraction. The pure phase, however, grows initially very fast in the finely branched and relatively open  $\langle 100 \rangle$  mode, and as convection proceeds the lower part continues to grow and thicken because of the low growth resistance. Thus the form of  $\phi(t)$  and the extinction of chimneys both seem to be connected with the same change in growth resistance.

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