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STABLE GROWTH RATES AND TEMPERATURE PROGRAMMING IN FLUX GROWTH

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Theoretical and experimental evidence is presented to demonstrate that the maximum stable growth rate of crystals growing from slowly cooled solutions must decrease as the crystal size increases and the solute concentration decreases. Temperature programs derived for a constant linear growth rate are therefore unlikely to result in the growth of high-quality crystals. A cooling program based on the theoretical maximum stable growth rate is calculated, and it is shown that a constant cooling rate should give stable growth except in the early stage following spontaneous nucleation. Practical procedures are suggested for the growth of large crystals of good quality by slow cooling of high-temperature solutions.

1. Introduction

In most experiments for the growth of single crystals by slow cooling of high-temperature solutions, a linear rate of temperature decrease, of the order of 1 °C/hr, is used. The reason for the choice of a constant cooling rate is mainly one of experimental experience and convenience.

The use of a constant linear growth rate and accordingly non-linear temperature programs has been advocated by a number of authors for aqueous solution growth of TGS[1-3]) and for flux growth[4-6]), since the area of the crystal increases as growth proceeds. If the linear growth rate v is to be maintained constant, this increase in surface area must be compensated by an increase in the cooling rate. The adoption of a constant linear growth rate leads to a so-called "t^3 law", in which the temperature change from the value at which crystallization commences is varied as the cube of the time. For a crystal of cubic shape, this temperature variation is given from the expression for the mass m of the crystal

$$m = K(T-T_0) = 8\rho_c v^3 t^3, \qquad (1)$$

where ρ_c is the density of the crystal, $T-T_0$ the fall in temperature in time t, and K the slope of the solubility curve. A similar relation follows for other crystal shapes but the numerical factor then differs from 8. The deviation of the solubility curve from linearity may be readily included; its effect on the cooling program is relatively small (less than 7% of the total interval of temperature or time at any point for the example considered in section 3). Such a program has been used in aqueous solution growth, for example in the growth of large high-quality TGS crystals from seeds[2,3]).

On the other hand there is experimental evidence from aqueous solution growth[7-11]) that the stable linear growth rate has to decrease with increasing crystal size. The crucial question for the experimental crystal grower is whether or not one should apply a constant linear growth rate, whatever the total time required for the experiment.

In this paper we reason that a constant linear growth rate and the t^3 law are not suitable for crystal growth by slow cooling of high-temperature solutions. This conclusion is based on a number of factors which are analyzed. The lower solute concentration and the slower transport of solute at lower temperatures especially require a decreasing growth rate. Thus if the optimum growth rate is chosen as the most rapid for stable growth at high temperatures, the chosen value will be too great for stable growth at lower temperatures.

A calculation of a temperature program taking into account the most important of the factors affecting growth stability is presented, and this indicates clearly that a constant linear growth rate towards the end of the cooling program results in instability. This conclusion has been confirmed by experiment.

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In addition the temperature region where nucleation occurs is examined qualitatively, and the t^3 law is shown to be inappropriate here also. An alternative cooling procedure is suggested.

2. Constant or decreasing stable growth rate?

The answer to this important question can be found when the factors which determine the maximum stable growth rate are analyzed.

Crystal growth from solution involves transport of solute, driven by the supersaturation, from the bulk of the liquid to a kink or step on the surface of the crystal. The successive stages in the transport process are natural convection or forced flow of the solution, volume diffusion of solute through the stagnant boundary layer, and surface diffusion along the crystal–liquid interface. According to their respective activation energies, all these transport processes will become less effective as the temperature is lowered.

During cooling the size of the crystal increases, causing an increasing boundary-layer thickness which again slows down the transport (volume diffusion) and decreases the interface stability. One significant factor for stable growth by the slow-cooling technique is the decreasing solute concentration, since growth becomes more difficult at lower concentrations. The conclusion to be drawn from the above qualitative reasoning is that the maximum stable growth rate has to decrease appreciably as the crystal grows.

A relation between the maximum rate of stable growth and the size of a crystal was observed experimentally as long ago as 1939 by Yamamoto[7]). He observed the growth of alkali-halide crystals from aqueous solution and measured the critical growth rate for the incidence of inclusions in crystals of various sizes. His results led him to propose that the linear growth rate should decrease in proportion to the increase in area of the growing face. The incidence of inclusions at higher growth rates was related to the spreading of layers across the crystal face. Under unstable conditions leading to inclusion formation, successive layers formed before the previous layer had covered the face of the crystal. Only one advancing layer could be seen on a given face at any time in the stable growth regime.

The relation between crystal size, growth rate and interface instability has not received great attention, although it was stressed by Egli and Zerfoss[8]) and later by Egli[9]), Carlson[10,11]) and by Cobb and Wallis[6]). Some qualitative confirmation is, however, also available from the theoretical treatment by Mullins and Sekerka[12]) and by Coriell and Parker[13]) for spherical crystals growing in solution. They showed that the sphere is stable only up to a certain radius, beyond which it becomes unstable due to a transition from kinetic-controlled to diffusion-controlled growth. Their treatment is not directly applicable to crystals which exhibit large facets (as do most flux-grown crystals) but confirm a need for the investigation of size-dependent stability effects.

It is difficult to give a reliable, quantitative treatment of maximum stable growth rates because a satisfactory stability theory for growth from solutions taking into account all the relevant parameters and real crystal faces does not exist. In general, however, excessively rapid deposition of solute at a growing crystal interface will cause instability. This instability can be expressed in terms of local inhomogeneities in the solute concentration at the interface leading to growth-rate variations. Inclusions will be trapped in the "valleys" of the resulting irregular surface.

This problem of stable crystal growth from solution was considered by Carlson[10,11]) with reference to the formation of veils of solvent in ADP crystals. He specifically stressed the necessity of high flow rates at the growing crystal faces and demonstrated a decrease of solute concentration with the distance from the leading edge of a face. In order to prevent "starvation" of solute the distance from the leading edge, i.e., the length of a crystal face, should not exceed a critical value y which is given by

$$y = 0.214\, Du/P_{\mathrm{D}}^{\frac{1}{3}}\, [v\rho_{\mathrm{c}}/(n_{\mathrm{s}}-n_{\mathrm{e}})]^2. \qquad (2)$$

Here D is the solute diffusion coefficient, P_D the Schmidt number $\eta/\rho_s D$, with ρ_s the density of the solution, η the viscosity of the solution, n_e the equilibrium solute concentration and n_s the concentration in the bulk of the solution.

Cahn[14]) also examined the condition for stable growth of a flat interface but assumed solute transport only by diffusion. He solved the Laplace equation for the solute distribution and concluded that stable growth is possible if the length of the facet is below a value y_1 given approximately by

$$y_1 = D(n_s - n_e)/\rho_c v. \tag{3}$$

This condition is clearly analogous to that of Carlson [eq. (2)] except that the critical size is found to depend on $(n_s - n_e)/v$ rather than on the square of this quantity. The values of the stable growth rate predicted by eq. (3) for macroscopic crystals are smaller by one or two orders of magnitude than typical experimental values. A temperature program on the basis of this equation would thus require an unrealistically long growth period. The discrepancy between Cahn's theory and that of Carlson as well as normal practice is presumably due to the fact that natural convection and stirring are not taken into account. Therefore our further analysis is based on Carlson's theory.

The condition for stable growth is expressed by putting $y = a = 2vt$ as the maximum size of the crystal at any time t. Eq. (2) then becomes

$$2vt = 0.214\, Du\sigma^2 n_e^2 / P_D^{\frac{1}{3}} v^2 \rho_c^2, \tag{4}$$

where the concentration difference has been written in terms of the relative supersaturation $\sigma = (n_s - n_e)/n_e$. If the substitution is made for the product $v^3 t$ from eq. (4) into the equation for the rate of mass deposition obtained by differentiation of eq. (1), the expression for the maximum stable rate of mass deposition becomes

$$\mathrm{d}m/\mathrm{d}t = 2.57\, Du\sigma^2 n_e^2 t / P_D^{\frac{1}{3}} \rho_c. \tag{5}$$

Rearrangement of eq. (2) gives the maximum stable linear growth rate for a crystal of length a as

$$v_{\max} = (0.214\, Du\sigma^2 n_e^2 / P_D^{\frac{1}{3}} \rho_c^2 a)^{\frac{1}{2}}. \tag{6}$$

Eq. (6) is based on bulk transport of solute and therefore only realistic for macroscopic crystal lengths.

In (6) a higher stable growth rate is predicted for higher supersaturation. However, even with very high flow rates, there must be a limit of the stable growth rate, and hence of the supersaturation, due to the surface kinetic processes (which for various systems can be nucleation and attachment kinetics, desolvation, and surface diffusion) as was mentioned by Scheel[15,16]). The solute concentration ($n_e \approx n_s$) is also a decisive factor, as high growth rates, of the order of 1000 Å s^{-1}, are reported for the top-seeded solution growth technique of Belruss et al.[17]), where solute concentrations of 70–90 wt % are used. In more typical cases of flux growth, the maximum stable growth rate is 200–500 Å s^{-1} (refs. 15, 18). The effect of the other parameters of eq. (6) on the maximum stable growth rate is mainly through their individual temperature dependences, and is comparatively small.

No theory exists at present which would predict maximum stable growth rates at very high flow rates and supersaturations. It is a complex problem since any of the surface kinetic processes mentioned above can dominate in various solute–solvent systems.

Only one aspect of the relation between surface kinetics and the stable growth rate will be discussed here, namely, the improvement in crystal quality as growth proceeds at a constant, slow cooling rate. Spontaneous nucleation (and the resulting dendritic growth) as well as the initial growth on a seed crystal inevitably result in a high concentration of defects such as dislocations and low-angle and twin boundaries. The concentration of these defects tends to decrease as stable growth proceeds[19]). This has been frequently observed with crystals grown from aqueous and especially from high-temperature solutions: crystals spontaneously nucleated at the beginning of the cooling program show many growth hillocks on their surfaces when they are small, whereas on crystals grown to large size (above 1 cm^3) often one or a few growth centers control one complete face. In accordance with Burton, Cabrera and Frank[20]) this fact can be explained by rearrangement of the dislocations. The most active growth centers[20]) become dominant, and a small growth rate is observed. This effect would have to be taken into account in a theory which would predict quantitatively the maximum stable growth rate limited by surface kinetics. An interesting question is still whether crystals growing continuously with the maximum stable growth rate would also show the decrease of growth hillocks, since this decrease has been observed on crystals almost certainly grown at lower than the critical rate.

So far the effect of the temperature gradient on stable growth has not been discussed, since quite often the growing crystals are immersed in the solutions and therefore are exposed to small temperature gradients. However by cooling the crystal either through the crucible wall or by pulling it out of the solution, the interface stability is increased due to the constitutional supercooling criterion[16,21–23]). If crystal cooling is combined with high solution flow rates, relatively fast stable growth rates can be achieved[15-18,23]).

3. Temperature program for stable growth

The temperature program is obtained by integration of eq. (5) with the appropriate temperature dependence of the various terms included. The diffusion coefficient will vary exponentially with temperature with an activation energy of about 20 kJ/mole, and so its effect will be relatively small since it is much less than that due to non-linearity of the solubility curve. P_D will have a similar temperature dependence and its effect will be even smaller since it appears as the $\frac{1}{3}$ power. ρ_c will change only by a few percent over the range considered, and for simplicity we ignore any temperature dependence of u. It is further assumed that stable growth occurs at constant supersaturation, which implies that some interface stability condition exists which breaks down if σ exceeds some critical value, as mentioned above. With these assumptions, integration gives

$$\frac{1.28\, Du\sigma^2}{P_{\mathrm{D}}^{\frac{1}{3}}\rho_{\mathrm{c}}}\, t^2 = \int_{t=0}^{t} \frac{\mathrm{d}m}{n_{\mathrm{e}}^2} = V\left(\frac{1}{n(T)} - \frac{1}{n_0}\right), \tag{7}$$

since $n = m/V$. Here $n(T)$ is the solubility at temperature T, n_0 the solubility at the commencement of the program, and V the volume of the solution.

As an example of the application of eq. (7), consider a crucible of 100 cm^3 capacity which is 80% full of solution. If the densities of the crystal and the solution are both 5 g cm^{-3} and the solubility is 15% at 1600 K and 5% at 1300 K, the result of an idealized cooling experiment for a crystal of cubic shape will be a single crystal of mass 40 g and side 2 cm. Curve III of fig. 1 shows the calculated cooling program for an ideal solution and with $D = 10^{-5}$ cm^2 s^{-1}, $\sigma = 10^{-2}$, $P_D = 420$ ($\eta = 2.1$ cpoise) and $u = 10$ cm s^{-1}.

The deviation of the calculated program from a linear plot (II of fig. 1) with a constant cooling rate of 1.3 °C hr^{-1} is quite small. According to the calculation, the cooling rate should be increased to 1.75 °C hr^{-1} in the middle of the range but slower cooling rates should be used at the beginning and at the end of the program. This result conflicts strongly with the t^3 program which is shown on fig. 1 as curve I for a constant growth rate of 275 Å s^{-1}. The final cooling rate in the latter case is 16.6 °C hr^{-1} which differs from our value by a factor of 13. It should be remembered that the temperature dependence of the diffusion coefficient, viscosity, interface kinetics, etc. have been neglected. An even greater discrepancy would result if these factors were included.

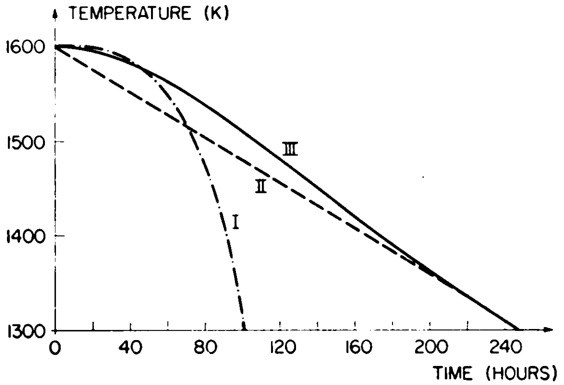

Fig. 1. Temperature programs for flux growth by slow cooling. (I) For constant linear growth rate; (II) constant cooling rate; (III) for maximum stable growth rate according to eq. (7).

The change in linear growth rate corresponding to the use of the calculated program is plotted in fig. 2 as curve III. It is seen that the required decrease in the growth rate over the whole range is by a factor of four in our example. This factor depends on various parameters and will be discussed in the last section. The reduction of the growth rate is significant compared to the constant linear growth rate proposed by several authors[1-5]) and shown as line I in fig. 2. Curve II gives the linear growth rate for the case of a constant cooling rate of 1.3 °C hr^{-1} and shows very high values at the beginning of the experiment corresponding to rapid, dendritic growth. Fig. 2 illustrates clearly the importance of a very slow cooling rate during the first few hours following nucleation.

A similar form for the temperature program may be calculated for volume diffusion limited growth using the formula for the thickness of the solute diffusion boundary layer given by Carlson[11]) and by Bennema[24]),

$$\delta = \left[\frac{2}{3}\left(\frac{\eta}{\rho_s D}\right)^{\frac{1}{3}}\left(\frac{\rho_s u}{\eta X}\right)^{\frac{1}{2}}\right]^{-1}. \tag{8}$$

The numerical factor in this equation is different from 0.463 used by Carlson[11]) to derive eq. (2) and which was chosen in our former calculation. Apart from this difference (8) gave the same result as (7), as expected.

An example of a transition from stable to unstable growth which was produced by increasing the cooling

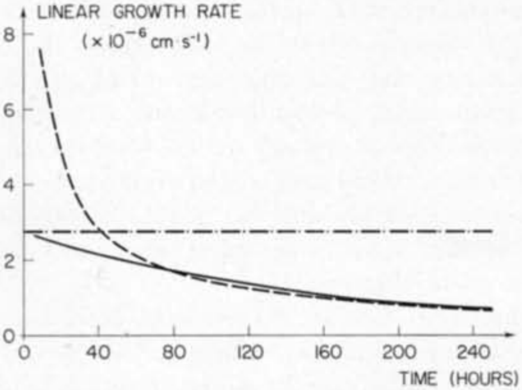

Fig. 2. Linear growth rate for the cooling programs (I)–(III) of fig. 1. Dash-dotted line I, dashed curve II, solid curve III.

rate at a relatively late stage in the development of the crystal is shown in fig. 3. This shows a view through a section of one of two gadolinium aluminate crystals which were grown in a 140 cm^3 crucible by the accelerated crucible rotation technique[15,25,26]. In this experiment a rather high initial cooling rate of 0.6 °C hr^{-1} was used and the inner zone of the crystal, which appears dark with bright inclusions, is characteristic of rapid, dendritic growth. This stage was followed by a period of stable growth at the same cooling rate until, at the stage corresponding to the position indicated by the arrow in fig. 3, the cooling rate was increased to 1.2 °C hr^{-1}. This change resulted in a zone of unstable growth with a high concentration of inclusions, since the slope of the cooling curve in this region was higher than the maximum predicted value for stable growth. The outermost zone of the crystal is again inclusion-free, indicating that the maximum cooling rate for stable growth changed in this particular system to a value above 1.2 °C hr^{-1} just before the termination of growth.

4. Seeding and spontaneous nucleation

The temperature program outlined above has to be matched to the type of experiment and should be modified according to whether seed crystals are used or the crystallization process starts after spontaneous nucleation.

For seeding, the liquidus curve has to be known so that the seed is not dissolved but only etched before crystal growth starts. The cooling program has then to take into account the size of the seed, which has a major effect on the initial cooling rate because of its relatively large surface area. For example, if the seed is 1 cm in length, or 6 cm^2 in area, the initial cooling rate for stable growth is 1.53 °C hr^{-1}. The corresponding linear growth rate is then 254 Å s^{-1}. Thus the application of seed crystals allows the elimination of the initial part of the program in which very low cooling

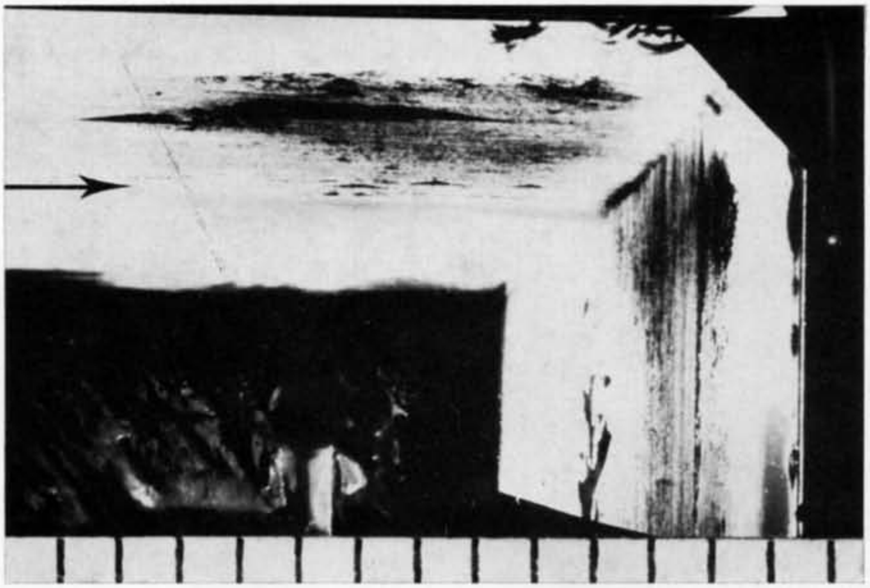

Fig. 3. Corner of a flux-grown gadolinium aluminate crystal grown partially in unstable and stable regimes (scale in mm).

rates are required, and so leads to considerable saving in experimental time.

In most flux-growth experiments no seed crystals are used. Spontaneous nucleation occurs by slow cooling through the metastable region below the liquidus. This metastable temperature range is frequently called the Ostwald–Miers region and in high-temperature solutions has a typical width of 1–30 °C. Generally, spontaneous nucleation will yield many crystals, particularly when an effective means of localization is not available. The initial small size of the crystal has been considered in the temperature program described and particularly in the t^3 law which requires a very slow cooling rate at the beginning of the cooling experiment. It has been argued by Laudise[27]) that cooling rates which are not at least comparable with the temperature fluctuations due to inaccurate regulation are pointless. A very slow initial cooling rate is also impractical when the supersolubility curve is not known with sufficient accuracy so that crystallization is not reached in a reasonable time. Since the object of a crystal-growth experiment is to grow a small number of large crystals in a reasonably short time, cooling procedures are proposed which allow a selection of the nuclei even when means of precise localization of nucleation are not available. The principle is shown in fig. 4. After the mixture of solvent and solute has been held for sufficient time (typically 15 hr) at a temperature A, 50 °C above the liquidus T_L, to ensure complete dissolution, the temperature is lowered to $B = T_L$ where cooling at about 1 °C hr^{-1} is commenced. When the point C is reached the temperature is raised to D, approximately 1–5 °C below T_L, so that many of the nuclei formed below the metastable region (T_L to T_M) are dissolved and a small number of nuclei (ideally one) will remain. This selection process may take some time (to E) after which the programmed cooling should start. This type of nucleation control can only be used when the liquidus as well as the critical undercooling are precisely known. The necessary knowledge can be readily obtained by the thermogravimetric method of Smith and Elwell[28]) for nonvolatile solvents.

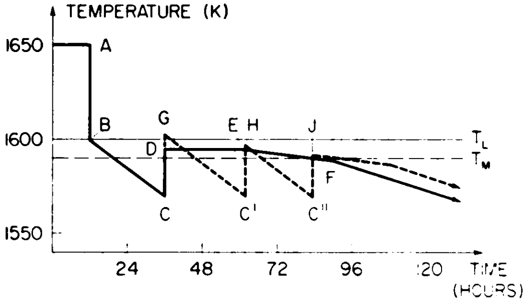

Fig. 4. Temperature programs for minimization of the number of crystallites formed on nucleation: $A \to F$ when liquidus temperature T_L and limit of metastable region T_M are known; $A \to J$ when these are known only approximately.

Often exact data are not available, expecially with volatile solvents, and T_L is then guessed by trial experiments. In this case the procedure according to the dotted line in fig. 4 is proposed. After initial soaking at A and cooling to C, the cycle of heating to G and slow cooling to C', heating to a lower temperature H and cooling to C'', and so forth is continued until the upper point (J) is expected to lie below the liquidus, and then the temperature programming is commenced. In a number of experiments for the growth of $GdAlO_3$, $LaAlO_3$, $Y_3Al_5O_{12}$, $Y_3Fe_5O_{12}$:Ga, and $GdVO_4$ this selection procedure had a beneficial effect. In order to suppress continuous nucleation during the later stages of the slow cooling experiment, a homogeneous solution should be produced by stirring, as discussed by Scheel[15,16]) and by Scheel and Schulz-DuBois[25]). On the other hand stirring has the disadvantage that it narrows the width of the metastable region.

Hintzmann and Müller-Vogt[29]) proposed an oscillatory cooling curve during the entire cooling program with an amplitude of 20 °C, a period of 8 min, and an average temperature slope of 2 °C hr^{-1}. The resulting crystals of rare-earth orthophosphates, arsenates and vanadates were small and of bad quality. This one would expect since the rate of growth during the cooling half-cycles must be excessive for stable growth unless crystallization occurs at extremely low rates over a period of several months. We therefore propose the use of an oscillating temperature only at the start of the cooling program for the purpose of reducing the number of nuclei.

5. Experimental variables and the attainment of stable growth

The factors which influence the maximum stable growth rate by limiting the transport of solute are summarized in table 1. Other factors such as the temperature gradient at the interface and also the increas-

TABLE 1

Factors influencing the maximum stable growth rate

Transport-limiting experimental parameters	Affected by	Description
Solute concentration	Phase diagram and temperature	Eq. (6) and section 2
Mass deposition rate	Volume of the solution (crucible size) and by the degree of supersaturation through cooling rate (possibly also through evaporation rate or gradient transport rate)	Eq. (5) and sections 1, 2 and 4 and in the following
Crystal surface area (boundary layer thickness)	Spontaneous nucleation or seed crystal, and by total growth and by the habit	Eq. (6) and sections 1, 2 and 4
Solution flow rate	Degree of convection or stirring	Section 2 and in the following
Material parameters (viscosity, diffusion coefficient, densities of solute and solution)	Temperature	section 2 and in the following

ing crystal quality during growth have been discussed in section 2.

The effect of viscosity, solution flow rate and crucible size on the maximum stable growth rate and therefore on the temperature program is illustrated with a few examples in fig. 5. The viscosity values of 2 and 20 cpoise are typical for such fluxes as PbO–PbF_2 and PbO–B_2O_3, respectively[30]. Solution flow rates of 10 and 0.1 cm s^{-1} correspond respectively to the conditions pertaining with a good degree of stirring[15,16] and with natural convection[6,15,16]. A melt volume of 80 cm^3 is an average value for general experiments and 4000 cm^3 is approximately the largest crucible which has been used for flux growth [Van Uitert et al.[31] used eight liter crucibles].

The most important parameter which can be derived from fig. 5 is the total duration of a crystal-growth experiment. A value of 10^3 hr or 6 weeks is fairly typical while twice this value would normally be considered prohibitive. It can be seen from the examples illustrated that experiments of reasonable duration for the stable growth of one crystal are possible only in stirred solutions. The period calculated for an unstirred solution would be less than 2000 hr only for a flux of low viscosity and a solution volume of less than 80 cm^3. The periods calculated for the large solution volume with stirring are clearly shown to be excessively long, and unstable growth as well as multinucleation must result. On the other hand when allowance is made for initial multinucleation and dendritic growth or when large seed crystals of a size appropriate for the crucible size are used, the cooling program may be shortened as was mentioned in section 4.

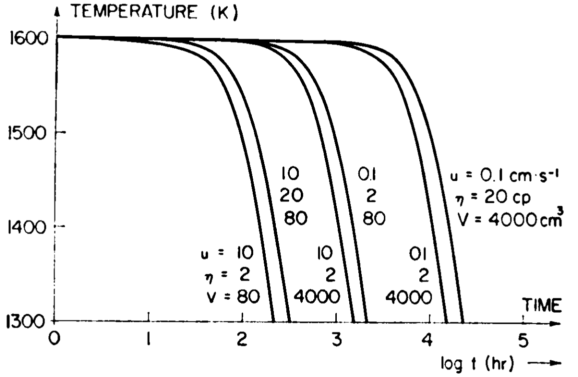

Fig. 5. Temperature programs according to eq. (7) for various values of viscosity η, solution flow rate u and solution volume V.

The effect of the flux viscosity, though appreciable, is shown to be less important than the other parameters considered. However, the rate of solution flow by natural convection is likely to be much less than 0.1 cm s^{-1} in a very viscous flux.

The program specified by eq. (7) was calculated on the basis that the growth rate should have its maximum stable value at all temperatures. In practice it is clearly desirable to use a growth rate which is less than the maximum value by some appreciable margin, particularly since the temperature regulation possible with the best commercial controllers is not much better than ± 0.1 °C at 1200 °C. In the example considered in section 3, a sudden temperature drop of only 0.1 °C will result in the deposition of about 13 mg of solute. If this drop were to occur in 10 s on a crystal of total area 1 cm^2, the resulting growth rate would be 26000 Å s^{-1} which is enormously greater than the maximum stable rate. In practice, the effect of this drop will not be so drastic since the resulting supersaturation is created throughout the melt rather than at the crystal surface, but on the other hand temperature variations of several times 0.1 °C are common with simple regulation and programming and in unstirred melts due to thermal convection. This example indicates the importance of good temperature regulation and also of a "safety margin" in the temperature program actually used. *The temperature regulation and the cooling rate have to be adjusted in such a way that the slope of the effective cooling curve (including any oscillations or fluctuations) never exceeds the slope of the calculated cooling curve for stable growth at the corresponding temperature.*

Fig. 6 (curve I) shows the cooling rate for the maximum growth rate using the data corresponding to the most rapid cooling program of fig. 5 (u = 10 cm s^{-1}, η = 2 cpoise, V = 80 cm^3). Unless a computer is used for process control, a continuous change in the cooling rate due to curve I is not easily achieved. Therefore a less ideal procedure indicated by the dotted line II is suggested. Apart from the first few hours where extremely slow growth rates are required by the calculated program, this procedure allows a reasonable margin against temperature fluctuations. The actual values of the cooling rate proposed are as follows: 0.2 °C hr^{-1} for 48 hr, 0.5 °C hr^{-1} for 24 hr, and 1.2 °C hr^{-1} for the remainder of the growth period, i.e., about 221 hr. The total time of nearly 300 hr for the proposed cooling program exceeds the minimum required by the theory by about 25%. An extra 60 hr or so will of course be required for the nucleation procedure outlined in section 4.

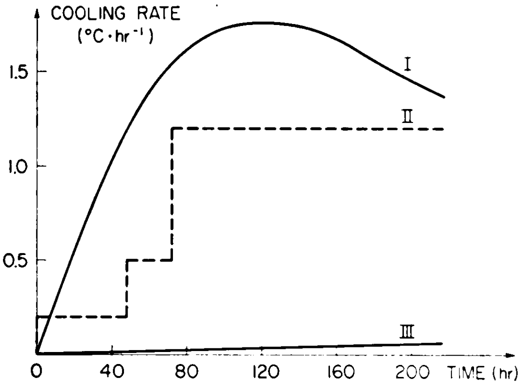

Fig. 6. Cooling rates for stable growth: (I) for a stirred solution, (II) suggested experimental procedure; and (III) for an unstirred solution.

Shown as curve III of fig. 6 is the cooling rate required by the program of eq. (7) for the same conditions but with an unstirred melt, i.e., with an assumed solution flow rate of 0.1 cm s^{-1} with η = 2 cpoise and V = 80 cm^3. The maximum value of the cooling rate is 1/10th that of curve I, i.e., 0.175 °C hr^{-1}, and the total time required by the program is about 2400 hr. Since such a long period would be regarded as unacceptable by most crystal growers, we propose the use of a constant cooling rate of 0.3 °C hr^{-1} or preferably 0.2 °C hr^{-1} (provided that the temperature is regulated to better than ± 0.1 °C) for the whole growth period following the nucleation procedure. Although such a program will produce more than one crystal, a relatively small number of crystals should result and these should contain a substantial portion of inclusion-free regions.

An uncertainty in the above calculations exists since no determination of the maximum stable growth rate has yet been made on any crystal growing from a high-temperature solution. Presumably this rate is dependent on the individual solute-solvent system with its many chemical and physical parameters, and on impurities. Therefore it has to be determined experimentally. One single determination at one temperature should be sufficient for the whole program to be calculated. In the absence of exact measurements, the values of 200–300 Å s^{-1} for stirred solutions and 60 Å s^{-1} for unstirred solutions may be taken on the basis of previous growth experiments[15]).

The analysis of the stable growth rate and the proposed temperature programming have been worked out for high-temperature solutions. However the principles are applicable to growth from solutions generally.

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