

Review: Mechanisms of Crystal Growth from Fluxed Melts

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This review is mainly concerned with the basic mechanisms of crystal growth from the flux and with the origin of defects in these crystals. An outline is given of the theory of growth from solution and this is compared with experiments on aqueous solutions, which are the main source of data against which the validity of this theory may be tested. The analogy between aqueous solution and flux growth is discussed and estimates given for the rate at which crystals grown from the flux in the diffusion-controlled and particle integration-controlled limits. Studies of the surfaces of flux crystals favour a screw dislocation mode of growth, with propagation by a lateral spreading of layers rather than by spirals. The incidence of flux inclusions is discussed and related where possible to the conditions of growth.

1. Developments in Flux Growth

In flux growth the constituents of the desired crystal are dissolved in a molten salt (the "flux") and growth occurs at temperatures well below the normal melting point of the crystal. This method of crystal growth was first used in the mid-nineteenth century, mainly in attempts to crystallise ruby and emerald crystals of gem quality. This application was discontinued after the development of the Verneuil furnace and the flux technique was little used until the early 1950s when it was reintroduced to grow crystals of commercially important materials which could not be prepared from the pure melt.

Perhaps the most important advances were the growth of BaTiO₃ crystals by Remeika [1] and of yttrium iron garnet by Nielsen and Dearborn [2]. Crystals of a large number of materials have now been grown from various fluxes and some of these are listed in reviews by Laudise [3], White [4], Schroeder and Linares [5] and Roy and White [6] who also describe the experimental techniques employed.

In the majority of cases, the materials crystallised from a high temperature solution are still those which cannot easily be grown from the melt, for example those which melt incongruently or become highly non-stoichiometric at the melting point. The limitations on the use of flux growth are that the crystals are often rather small and/or highly imperfect. The recent applications

of crystals in such fields as lasers, bubble domain devices and non-linear optical systems require crystals of good quality and there is an increasing tendency in published work to discuss the perfection of crystals in addition to the synthesis. In this article an attempt is made to correlate the various observations discussed in the literature which relate to an understanding of the mechanism of flux growth and of the origin of the imperfections. Some of the aspects considered here have been discussed in a report by Cobb and Wallis [7], who attempted to specify the optimum conditions for the growth of ruby crystals from lanthanum fluoride flux. While the application to practical systems is clearly of great importance, our emphasis will be on examination of the evidence for the assumptions normally made by crystals growers in explaining observed phenomena.

2. Stages in Crystal Growth from Solution

Since flux growth is an example of growth from solution, the process must be similar to that which takes place in aqueous or organic solvents at much lower temperatures. The process of crystal growth from solution may be considered to occur in four stages:

- (a) Transport of solute to the neighbourhood of the crystal interface;
- (b) Desolvation and diffusion through a bound-

ary layer, often called the "unstirred layer" [8, 9]

(c) Surface diffusion over the crystal interface, and

(d) Integration of solute particles into the crystal.

The method by which solute is transported through the solution will depend upon the design of the experiment and will involve diffusion, convection or forced flow of the solution. If crystal growth is to occur, the process used must produce a supersaturated solution in the neighbourhood of the crystal.

As the crystal grows, it will lower the solute concentration at the interface and thus create, over a finite distance, a concentration gradient normal to the interface. Diffusion of solute towards the crystal will thus occur and Nernst [9] considered the rate of flow of solute through the boundary layer to be the factor which governs the rate of crystal growth.

Surface diffusion may be expected to occur whenever the solute concentration in a direction parallel to the interface is not constant. The direct evidence for a surface diffusion stage is not strong, in contrast to the situation for gas molecules on solids. It is well known that solids adsorb gas molecules and that the rate of migration within the adsorption layer is very rapid. Adsorption is, in fact, used as a standard method for the determination of the specific surface area of solids, and the layer is assumed to be monomolecular. The situation in liquids is not so clearly established and it is convenient to treat surface diffusion as part of the process whereby the solute particles are integrated into the growing crystal. The rate-controlling process is then taken to be either the solute transport stage or the interface kinetic stage.

The earliest theories of the integration process [10] were based on the principle that the equilibrium faces of the crystal will be those having the lowest free energy. Such faces are normally those of low Miller indices and with a high density of atomic packing. These faces were assumed to be atomically flat and the rate determining step is, in this case, the formation of a two-dimensional nucleus, consisting of a group of atoms, which must exceed a critical size if it is to grow rather than decay. Once the nucleus forms, growth may proceed rapidly by the attachment of molecules at steps around the edge of the nucleus.

One of the central predictions of this two-

dimensional nucleation theory is the existence of a critical supersaturation, below which no crystal growth will occur. The predicted growth rates at lower supersaturation were found to differ very markedly from experimental values in a number of cases and this discrepancy was resolved by Frank [11], who first drew attention to the importance in the growth process of screw dislocations. The screw dislocation model is incorporated in the theory of Burton, Cabrera, and Frank [12]. In this BCF theory, the molecules arriving at the crystal interface are assumed either to evaporate or to enter the crystal at a growing spiral which has as its origin a screw dislocation. The velocity v at which the crystal face grows in the simplest case of non-interacting spirals is given by

$$v = \frac{C\sigma^2}{\sigma_1} \tanh\left(\frac{\sigma_1}{\sigma}\right) \quad (1)$$

where σ is the relative supersaturation and the parameters C and σ_1 depend upon such factors as the surface free energy, the surface diffusion coefficient of the molecules and the temperature at the interface. At supersaturations below the critical value σ_1 , equation 1 may be approximated by a square law:

$$v \simeq \frac{C\sigma^2}{\sigma_1} \quad (2a)$$

while for $\sigma \gg \sigma_1$, equation 1 may be approximated by a linear law

$$v \simeq C\sigma \quad (2b)$$

If the growth spirals interact with each other to an appreciable extent, equation 1 must be modified by the inclusion of a factor ϵ and becomes

$$v = \frac{\epsilon C\sigma^2}{\sigma_1} \tanh\left(\frac{\sigma_1}{\epsilon\sigma}\right) \quad (3)$$

The magnitude of ϵ depends on the number of interacting spirals and the form of the interaction but will not normally differ from unity by a large factor.

Equations 1 to 3 were, in fact, derived for crystal growth from the vapour phase, in which case the motion of the molecules to the interface is much more rapid than diffusion over the crystal surface. In solution growth, BCF assumed that diffusion of solute through the boundary layer would be so slow as to provide the rate determining factor. In their treatment, growth is assumed to occur at kinks in a step

which forms part of a spiral, but without any diffusion in a direction parallel to the interface. Their treatment has been extended by Chernov [13], who pointed out that a spiral may degenerate into layers which spread radially outwards from the spiral source. Chernov also assumes that surface diffusion is unnecessary and considers that the diffusional flow of particles through the boundary layer has the form shown in fig. 1. The points a, b, c . . . represent steps at

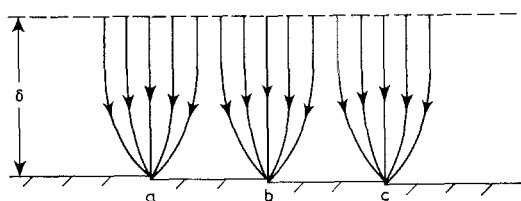


Figure 1 Solute diffusion field near stepped surface of growing crystal, after Chernov [13].

the boundaries between successive layers of which a cross-section is shown. The expression for the growth rate given by this treatment is

$$v = A\sigma^2 / \left(1 + B \frac{\delta\sigma_c}{a\sigma} \sinh \frac{\sigma}{\sigma_c} \right) \quad (4)$$

where A and B are temperature-dependent parameters, δ the thickness of the boundary layer, a the inter-atomic separation and σ_c a critical supersaturation. As in the BCF theory, equation 4 reduces to a square law at low values of σ and a linear law for high σ , but it may be represented over a wide range of σ by the approximation

$$v \propto \sigma^m \quad (5)$$

where the power m varies with σ_c and δ but has a value of about 1.65.

The application of the BCF theory to solution growth has been considered in detail by Bennema [14]. He arrived at a law of the form of equation 3 and stressed the importance of surface diffusion both in his theoretical treatment and in accounting for his experimental observations.

In a recent paper, Gilmer *et al* [15] gave a more general treatment of growth from solution, including simultaneous volume and surface diffusion. Their expression for the growth rate includes contributions from volume diffusion, adsorption, surface diffusion and entry into a growth step. Like Bennema, they conclude that a

better fit to experimental data is obtained if surface diffusion is included.

Brice [16] has given a generalised treatment of crystal growth from solution including mechanisms which do not rely on screw dislocations. The additional cases which he considers are an atomically rough surface on which growth may occur randomly, rather than at specific sites on the edge of a step, and the original postulate of two-dimensional nucleation. The growth rate is given by the general expression

$$v = F \sigma^m T^p \exp(-G/T) \exp(nH/\sigma T) \quad (6)$$

where F , G and H are constants and the values of m , n and p are listed in table I for the various modes of growth. (The parameter N in table I represents the number of molecules in a typical nucleus.)

TABLE I Parameters in equation 6.

Type of interface	m	n	p
Rough	1	1	0
Flat with (a) large nuclei $v \rightarrow 0$	2/3	2/3	1
(b) large nuclei $v \rightarrow \infty$	0	0	0
(c) small nuclei $v \rightarrow 0$	$1 + N/3$	0	0
(d) small nuclei $v \rightarrow \infty$	$1 + N$	1	0
Flat with screw dislocations			
(a) $\sigma < \sigma_1$	2	2	0
(b) $\sigma > \sigma_1$	1	1	0

A comprehensive review of the theory of crystal growth from solution has been given by Parker [17], who discusses in greater detail many of the points outlined above.

3. Experiments on Aqueous Solutions

Experimental data, which may be used to check the validity of the theories of solution growth outlined above, are available mainly from measurements on aqueous solutions at temperatures in the range from about 20 to 80°C. The most important measurements are those of the growth rate as a function of the relative motion between the crystal and the solution and as a function of the supersaturation.

3.1. Growth Rate Determinations

If the rate of growth of crystals is determined to any extent by volume diffusion through the boundary layer, it will vary if the crystal is rotated or if the solution is made to flow across the crystal. This relative motion between the crystal and the solution decreases the thickness δ

of the unstirred layer and so will increase the rate of crystal growth.

A typical result for the variation of growth rate with solution velocity for a stationary crystal is shown in fig. 2a, which is taken from the data of Cartier *et al* [18]. The growth rate is seen to increase rapidly as the solution flow rate is increased from zero, after which it approaches a steady value at high values of the flow rate. It is normally assumed that the thickness of the boundary layer becomes negligible when the flow rate exceeds some critical value and the rate of growth is then determined by the mechanism of particle integration. Carlson [19], by analogy with the equivalent heat flow problem, concluded that the boundary layer thickness δ is proportional to $u^{-\frac{1}{2}}$, where u is the solution flow velocity. This result is in reasonable agreement with the data of Hixson and Knox [20], who report $v \propto u^{0.6}$, and of Mullin and Garside [21], whose results give a power of 0.65.

Similar results are obtained when the crystal is rotated in a static solution, as shown in fig. 2b. The data in this case were obtained by Coulson and Richardson [22] on sodium thiosulphate. The thickness of the unstirred layer may be approximated by an expression given by Burton, Prim, and Slichter [23]

$$\delta \simeq 2^{2/3} D^{1/3} \nu^{1/2} \omega^{-1/2} \quad (7)$$

where D is the diffusion coefficient, ν the kinematic viscosity and ω the angular velocity of rotation of the crystal. A linear dependence of the growth rate v and $\omega^{1/2}$ is found for curve (i) of fig. 2b, in agreement with equation 7.

If the rate of crystal growth is determined purely by solute diffusion through the boundary layer, the rate at which a plane interface at $x = 0$ will advance will be given by

$$v = \frac{D}{\rho} \left(\frac{\partial n}{\partial x} \right)_{x=0} \quad (8)$$

where ρ is the density of the crystal, D the effective solute diffusion constant and $(\partial n/\partial x)_{x=0}$ the solute concentration gradient normal to the interface. Assuming that the concentration gradient is uniform over a layer of thickness δ ,

$$v = \frac{D}{\rho} \frac{n_s - n_e}{\delta} = \frac{D n_e \sigma}{\rho \delta} \quad (9)$$

where n_s is the solute concentration in the bulk of the solution and n_e that at the interface, which will be equal to the equilibrium concentration in diffusion-controlled growth. A plot of the growth

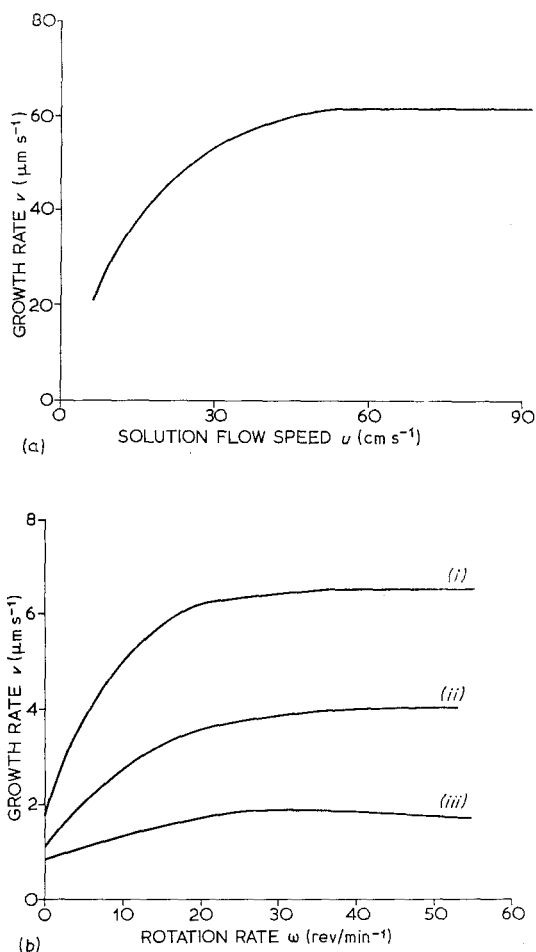


Figure 2 (a) Dependence of growth rate of citric acid on solution flow speed, after Cartier *et al* [18]. (b) Dependence of growth rate of sodium thiosulphate on crystal rotation rate, after Coulson and Richardson [22]. (i) $\Delta n = 1.5$ g/100 g water; (ii) $\Delta n = 1.0$; (iii) $\Delta n = 0.5$.

rate versus the supersaturation $\sigma (= (n_s - n_e)/n_e)$ should therefore be linear if the assumptions made are valid. A linear variation may, therefore, result from either diffusion control or from a mechanism of particle integration such as that described by equation 2b. The two mechanisms which give rise to a linear law may be distinguished experimentally by the dependence on relative motion in the case of diffusion control.

A linear variation is found experimentally for a number of crystals. For example, Rumford and Bain [24] noted a linear dependence of growth rate on supersaturation in the growth of NaCl in the range 52 to 73°C. The activation energy of crystal growth over this range was found to be

similar to that of solute diffusion. Normally, however, discrepancies are observed between growth and dissolution rates at the same temperature, as in the data of Garside and Mullin [25] for potash alum shown in fig. 3.

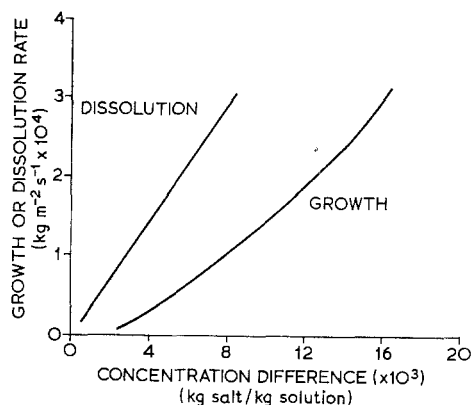


Figure 3 Growth and dissolution rates of potash alum crystals of similar size, after Garside and Mullin [25].

A difference between the growth rate and the dissolution rate under similar conditions indicates the importance of particle integration in solution growth. It is, however, difficult to separate the effects of diffusion and integration in order to ascertain the mechanism of particle integration. Brice [26] has proposed a method which may be applicable when the growth rate is measured as a function of the crystal rotation rate or solution flow speed. If the actual concentration of solute at the interface is n_i , the velocity of growth may be assumed to depend on the m th power of the supersaturation, so that

$$v = K (n_i - n_e)^m \quad (10)$$

where K is a constant. Alternatively, in the steady state, the growth speed may be expressed in terms of the diffusion constant. Comparison with equation 9 gives

$$v = \frac{D}{\rho} \frac{n_s - n_i}{\delta} \quad (11)$$

and elimination of n_i between equation 10 and 11 then yields

$$\left(\frac{v}{K}\right)^{1/m} + \frac{v\rho\delta}{D} = n_s - n_e \quad (12)$$

If the boundary layer thickness varies as $\omega^{-\frac{1}{2}}$ as in equation 7, a plot of $v^{1/m}$ versus $v\omega^{-\frac{1}{2}}$ at constant supersaturation should be linear. Alternatively, if the crystal is stationary while the

solution flows past a chosen face at a velocity u , a plot of $v^{1/m}$ versus $v u^{-\frac{1}{2}}$ should also be linear. Such plots were used successfully by Brice to obtain the order m of the integration process.

The other procedure which is widely used to determine the order, m , of the growth rate versus supersaturation variation relies on the assumption that, when ω or u become very large, the diffusion step becomes negligible and the growth rate is a function only of the particle integration process. The measured velocities of growth are then plotted directly against the supersaturation, the data being taken from those regions, shown in fig. 2, where v is independent of ω or u .

Experimental values of m for representative materials are listed in table II. Equation 12 was used to evaluate m for numbers 1 to 3 and 13 in the table, while the remaining values were obtained from measurements at high crystal rotation or solution flow rates.

The values of m are seen to be normally between 1 and 2, the exceptions (nos. 6 and 7) listed which have $m = 2/3$ are quoted by Brice as examples of growth with large nuclei growing laterally on a singular interface. The BCF theory, which predicts a transition from $m = 2$ to $m = 1$ at a critical supersaturation σ_1 , can thus account for the majority of the experimental data if one assumes a wide variation in σ_1 for different materials. Of the work quoted in table II, perhaps the most detailed investigations are those of Bennema (nos. 9 and 10) and Mullin and co-workers (nos. 12, 15 and 16). Bennema concentrated particularly on measurements at low supersaturation (down to $\sigma \sim 10^{-4}$) and his data on sodium chlorate are in good agreement with the form predicted by equation 1. The quantitative fit to this equation, together with the absence of a dependence of the growth rate on the degree of stirring in the solution, led Bennema to propose that the BCF surface diffusion model, rather than the volume diffusion model, is applicable to solution growth. The results of Mullin *et al* do not confirm the exact form of equation 1, and the data on $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ [21] is, in fact, in better agreement with Chernov's value of $m \simeq 1.65$ [13].

Similarly, recent data of Garabedian and Strickland-Constable [29] on sodium chlorate at higher supersaturation values than those studied by Bennema, indicate a $\sigma^{1.73}$ dependence. These results were also obtained on well stirred solutions and are difficult to account for on the basis of existing theories.

TABLE II Particle integration data for aqueous solution growth.

Material	Author(s)	m (in $v \propto \sigma^m$)	Reference
1. Sucrose	van Hook	2	} [26]
2. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Hixson and Knox	$\begin{cases} 2T < 71^\circ\text{C} \\ 1T > 71^\circ\text{C} \end{cases}$	
3. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	McCabe and Stevens	2 (28°C)	
4. Cyclonite	Bransom, Dunning, and Millard	1	} [16]
5. Alums	Belyustin and Dvoryakin	1	
6. Sucrose	Kucharenko	2/3	
7. $\text{K}_2\text{Cr}_2\text{O}_7$	Todes and Litunovskii	2/3	
8. E.D.T.	Kunisaki	1.66	
9. NaClO_3	Bennema	$\begin{cases} 2(\sigma < 10^{-3}) \\ 1(\sigma > 10^{-3}) \end{cases}$	[14]
10. Potassium aluminium alum	Bennema	1	[14]
11. Itaconic acid	Cartier, Pindola and Bruins	$1 \sigma > 10^{-8}$	[18]
12. Potassium aluminium alum	Mullin and Garside	1.62	[21]
13. Sodium thiosulphate	Coulson and Richardson	2	[22]
14. NaCl	Rumford and Bain	2 (26 to 45°C)	[24]
15. ADP and KDP	Mullin and Amatavivadhana	2	[27]
16. K_2SO_4	Mullin and Gaska	2	[28]
17. NaClO_3	Garabedian and Strickland-Constable	1.73	[29]

While the model of boundary layer diffusion followed by particle integration appears to be generally well confirmed by the aqueous solution data, its detailed application to a particular material is still rather uncertain. For example, although the data of Mullin and Gaska [28] at high flow rates indicate a law for particle integration of the form $v \propto \sigma^2$, a plot of vu^{-2} against $v^{\frac{1}{2}}$ is strongly non-linear, which indicates that one of the assumptions made in the derivation of equation 12 is not valid. (The quantity vu^{-2} in fact increases with v , which is clearly inconsistent with the form of equation 12). A similar discrepancy with this equation is also observed using the data of Cartier *et al* [18] on citric acid.

The problem of detailed interpretation of data on solution growth rates has been stressed by Garside and Mullin [25]. They used dissolution data to calculate the diffusion coefficient which was then used to give the growth rate when the same solution became supersaturated. This procedure did not yield values in agreement with experiment, which indicates that a surface diffusion or desolvation step should be included in the growth process. The thermal activation energy of diffusion of K_2SO_4 in solution was determined by Mullin and Gaska [28] as 4.8 kcal/mole, which clearly differs from a value of 3.4 kcal/mole for the same parameter obtained from dissolution data. The corresponding energy for crystal growth was found to be 4.3 kcal/mole.

The complex behaviour indicated by these latter measurements has not yet been fully explained and has not been taken into account in the model discussed above.

3.2. Observations of Crystal Surfaces

Additional information regarding the mechanism of particle integration in solution growth may be obtained from studies of the crystal surface features. Spiral growths have been observed on a large number of crystals [30] and have been generally assumed to provide direct evidence for the validity of Frank's screw dislocation theory. The spirals which are normally observed are in fact "macrospirals" of step height substantially greater than the unit cell. These features have been explained by Amelinckx *et al* [31] as being due to a bunching of steps caused by some periodic fluctuation in the source of the "microscopic spiral" as illustrated in fig. 4a. "Microspirals" having a step height of the order of unit cell dimensions can, however, be resolved by interference microscopy.

A growth mechanism by the spreading of successive layers has also been reported in particular by Bunn and Emmett [32] who carried out continuous observations of the faces of growing crystals. Layers were frequently seen to originate from points near the centre of a crystal face and to spread outwards, often overlapping from one face onto an adjacent face. The thickness of the layers was of the order of 10^{-5} cm,

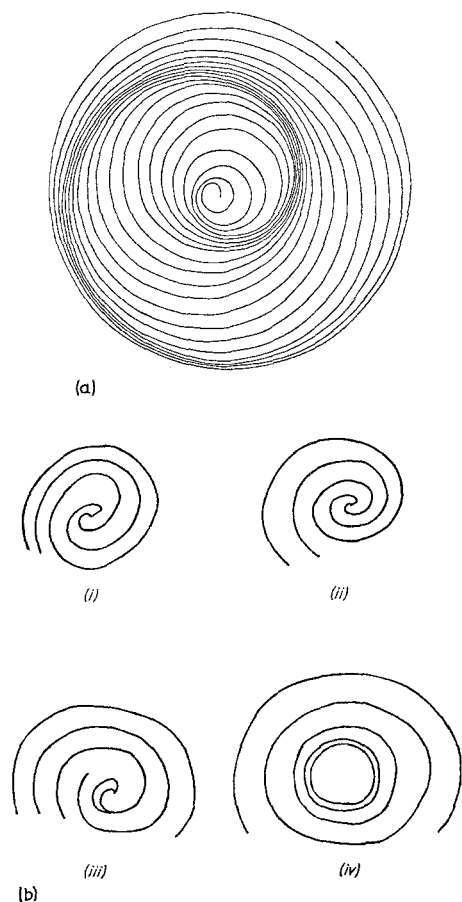


Figure 4 (a) Formation of macrospiral, according to Amelinckx *et al* [31]. (b) Transition from spiral to layer growth, after Chernov [13]. The sequence (i)-(iv) shows successive stages of the observed disintegration of a spiral step.

or several hundred unit cell edges. The authors suggest that the spreading of layers reflects the situation on the atomic scale, but that relatively thick layers tend to form because of the relatively rapid growth of high index faces. However, a layer mechanism does not necessarily contradict the screw dislocation theory since, as pointed out by Chernov [13], a spiral may degenerate into a system of concentric layers over a distance of a few cell edges. This transition from spiral to layer growth is illustrated in fig. 4b.

The experimental data on solution growth may be strongly influenced by quite small concentrations of impurities in the solution. Buckley [33] gives a large number of examples of changes in crystal habit brought about by impurities due to their effect on the relative

growth rates of various faces. The effects of these "poisons" have been considered in detail by Sears [34], who proposes that the modification of the growth process may occur in three ways. Firstly, the rate of motion of steps may be decreased. Secondly, the two-dimensional nucleation rate may increase and, finally, the macrospiral may climb more steeply. The first two effects act in opposition and the dominance of one or the other will depend on the material and on the impurity used. Whatever the detailed mechanism, it is clear that small traces of impurities will have a major effect on the crystal growth rate and morphology only if growth occurs at a few active centres, rather than randomly as on atomically rough surfaces.

3.3. Observation of the Boundary Layer

The concentration distribution of solute ions in the boundary layer around a growing crystal has been measured by Berg [35] and others, using optical interference methods. It is found that the solute concentration is not constant over a chosen face of the crystal, but is highest at the corners and lowest at the centre. This non-uniformity arises from the discontinuity in the flux of solute at the corners, and Boscher [36] has shown that the observed solute distribution can be explained by solving the diffusion equation in the two-dimensional case.

In spite of this non-uniform supersaturation, the crystals are normally observed to grow evenly. However, if the solute is deposited too rapidly from the solution it may be expected that faster growth will occur at the corners or edges of the crystal and this is confirmed experimentally [37].

Goldsztaub, Itti, and Mussard [38] have also measured by an optical method the solute concentration adjacent to a growing crystal and shown that it has the form indicated in fig. 5, where the concentration across the boundary layer is plotted as a function of the distance x measured perpendicular to the interface.

The equation of solute flow in one-dimension is normally written as

$$D \frac{\partial^2 n}{\partial x^2} + v \frac{\partial n}{\partial x} = \frac{\partial n}{\partial t} \quad (13)$$

and the second term may be omitted in the case of pure diffusion. The solution of this equation is of the form

$$n(x, t) = n_i + (n_s - n_i) \operatorname{erf} \frac{x}{2(Dt)^{\frac{1}{2}}}$$

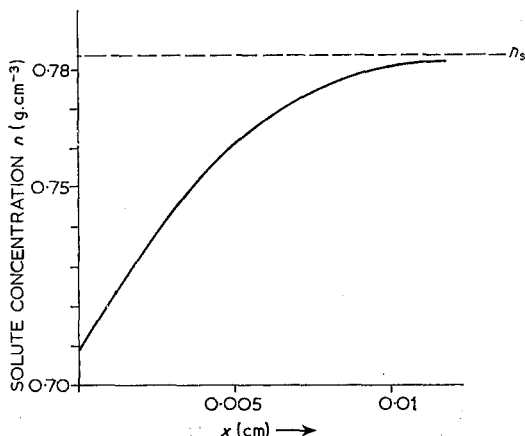


Figure 5 Solute concentration as a function of distance from the crystal interface, after Goldsztaub *et al* [38].

where the symbols have been defined above, and this solution indicates that a characteristic length, such as the boundary layer δ , will tend to vary as $t^{\frac{1}{2}}$ in the time-dependent case. Goldsztaub *et al* draw attention to the fact that the factor $(\partial n/\partial x)_{x=0}$, which determines the rate of crystal growth, will in general vary with time and that integration over some finite interval of time will normally be necessary if a measured growth rate is to be compared with theory. Agreement with theory in their experiments is not obtained using diffusion alone [38] and the discrepancy is attributed to convection in the solution. This conclusion implies that the second term in equation 13 should not be neglected, although its quantitative inclusion may be difficult in practical examples.

3.4. Nucleation

A discussion of the important factors in solution growth would be incomplete without some mention of the initial stage where nucleation of the crystal occurs. When a supersaturated condition is produced in a solution, the solution may remain in a metastable state or, depending on the supersaturation, nucleation may occur homogeneously or at specific sites. The initial particles, or embryos, formed on nucleation will grow provided that this growth decreases the free energy of the system.

According to the theory of Becker and Döring [39], the free energy will contain contributions from the difference in volume between the crystal and the solution, the interfacial surface energy and the strain associated with replacing part of a liquid matrix with a solid

phase. The change in Gibbs free energy on formation of a cubic crystal of edge a may thus be written as

$$\Delta G = -a^3 \Delta G_v + 6a^2 \gamma + \Delta G_E$$

where ΔG_v is the difference in the bulk Gibbs free energy per unit volume between the solid and liquid phases, γ the interfacial free energy per unit area and ΔG_E represents the strain energy. It may be readily shown that, assuming ΔG_E to be negligible, the energy will increase up to a critical size a^* and then decrease, where $a^* = 4\gamma/\Delta G_v$.

Kingery [40] discusses the case of precipitation under steady state conditions. By taking the rate at which nuclei of critical size are formed and the rate at which atoms join each nucleus, he arrives at an expression for the nucleation rate of

$$I = \left(\frac{N^*RT}{h} \right) N \exp - \left(\frac{\Delta G^* + \Delta F_D}{kT} \right) \quad (14)$$

where N^* is the number of atoms adjacent to the surface of a nucleus, ΔG^* is the value of the Gibbs free energy associated with a^* , N the molar concentration of solute and ΔF_D the activation energy for diffusion of solute atoms. This expression is given by Cobb and Wallis [7], in terms of the supercooling, as

$$I = \frac{C_1}{(\Delta T)^2} \exp - \left(\frac{C_2}{\Delta T^2} \right) \quad (15)$$

where C_1 and C_2 are parameters which depend on the system considered.

In crystal growth experiments, the important parameters are the supersaturation required to produce the initial nucleation, and the difference between this quantity and that required for subsequent crystal growth. Few examples have been given of comparative data for the nucleation rate and the crystal growth rate versus supersaturation, but data for K_2SO_4 have been given by Mullin and Gaska [28] and are shown in fig. 6. The nucleation curve may be fitted approximately to equation 15, although the authors point out that a better fit is obtained for the part of the curve where appreciable nucleation occurs by an equation of the form

$$I = \text{const } \sigma^9$$

The results indicate that nucleation is negligible below a supersaturation of 0.1, beyond which it increases very rapidly. Crystal growth occurs at supersaturations well below this value and

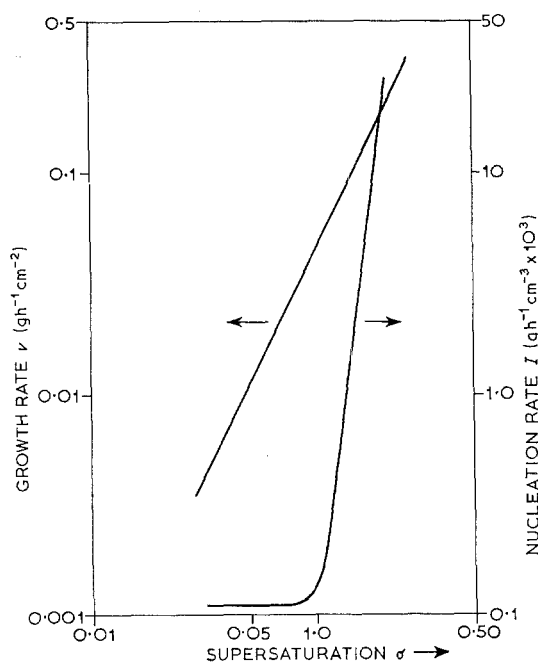


Figure 6 Growth and nucleation rates of potassium sulphate, after Mullin and Gaska [28].

nucleation could be neglected if growth were to take place at a supersaturation of, say, 0.02.

4. Experiments on Flux Growth

4.1. The Nature of Fluxed Melts

The techniques of flux growth are similar to those used in crystal growth from aqueous solutions, but severe limitations are imposed by the relatively high temperatures and by the extreme reactivity of most of the fused salts used as fluxes.

It is in general difficult to specify *a priori* the ideal solvent for crystal growth of a given material. Desirable physical properties of fluxes include a low volatility and low melting point, but the chemical specifications are normally limited to high solubility for the crystal constituents, low solubility for platinum or some alternative crucible material and the possession of a common ion with the crystal in order to minimise the number of constituents in the melt. Clearly, also, the flux should not contain ions which readily enter the crystal lattice as impurities.

In practice the flux is normally chosen by a trial and error procedure, taking into account previous experience. White [41] has proposed that the most widely used fluxes may be classified into four groups:

(a) *Simple ionic salts*, such as NaCl or LiF. These are the best understood of all fused salts, as extensive investigations have been made of their properties. They are, in fact, not used very frequently in crystal growth, probably because of their low solvent power for many materials of interest. The outstanding exception is the use of potassium fluoride in the growth of barium titanate [1].

(b) *Polar compounds*, such as Bi_2O_3 and lead compounds. PbO [42], PbO/PbF₂ mixtures [2] and PbF₂ alone [43] have probably been used more widely than any other fluxes in spite of their high volatility and relatively high toxicity. They exhibit a large increase in electrical conductivity on melting and PbO has a conductivity of about 1 ohm cm at its melting point [40]. They are thus highly ionic, although complex ions appear to be formed. White and Brightwell [43] have found evidence for the existence of ions such as PbF^+ , PbF_3^- , AlO^+ and AlO_2^- in solutions of Al_2O_3 in PbF₂ while Nielsen [2] has found a phase YOF in solutions of yttrium iron garnet in PbO/PbF₂.

The reasons why these lead compounds are such effective fluxes are not fully understood.

(c) *Network forming liquids*, such as borax and BaO-B₂O₃ compounds [45]. Borate fluxes have also found wide application, mainly on account of their low volatility which makes them particularly suitable for experiments in which a seed crystal is introduced near the surface of the solution [46]. B₂O₃ has a very high viscosity, some 10⁵ poise at its melting point of 450°C [44], and is not suitable by itself as a flux because of the low degree of convective mixing in very viscous liquids. The addition of metal oxides, such as those of the alkali metals and alkaline earths, greatly lowers this viscosity by breaking up the rigid O-B-O chains, although the borates are not ideally suited to experiments which rely on spontaneous nucleation.

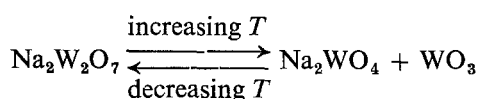
A detailed study of solutions of NiO in various alkali borate liquids has been made by Berkes and White [47] and this forms one of the most valuable contributions to our understanding of the chemistry of flux growth. Accurate liquidus curves were determined by a quenching method and the results compared with that of an ideal solution in which the solubility n obeys the relation

$$n = n_{\infty} \exp(-\phi/RT) \quad (16)$$

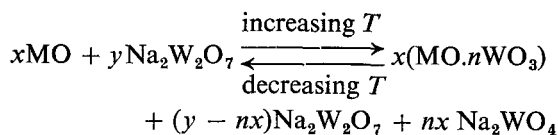
where n_{∞} and ϕ , the heat of solution, are

independent of temperature. The observed departures from ideality were attributed to clustering of the boron and oxygen atoms. At low temperatures, 8.5 B_2O_3 units were calculated to be bonded together, the size of the cluster decreasing with increasing temperature and falling to 2 B_2O_3 units in sodium borate at 1120°C and 3 B_2O_3 in potassium borate at 1168°C. These clusters exclude the Ni^{2+} ions, which are therefore weakly bonded in large interstitial sites in the boron-oxygen network. The energy required to free the Ni^{2+} ions from the solution during crystal growth is therefore small, so that growth can occur at low supersaturation. This weak bonding between the crystal constituents and the liquid appears to be a desirable property since growth can proceed at low supersaturation, with little nucleation.

(d) *Complex forming* liquids such as the tungstate and molybdate fluxes. While the application of these fluxes is not widespread, their use does appear to contradict the specification of weak bonding between flux and crystal constituents proposed by Berkes and White. Kunnmann *et al* [48] described their use of polytungstate fluxes in terms of Lewis acid-base theory. The basic oxides which form the desired crystal are dissolved by the Lewis acid WO_3 (an electron pair acceptor) and then precipitated by the Lewis base Na_2WO_4 (an electron pair donor). The crystal growth process utilises the dissociation with temperature of sodium pyrotungstate,



The dissolution and growth of an oxide MO takes place by a reaction of the form



These principles appear to have been verified by the extension of this model to grow a range of vanadium spinels such as $Co_{1+\delta}V_{2-\delta}O_4$ by electrolysis of the fluxed melt [49]. The application of this flux system to many materials suggests, however, that the $MO.nWO_3$ complex may not be bonded together strongly, otherwise crys-

als of good size and quality would not be expected for such a wide range. WO_3 and MoO_3 are effective solvents in their own right.

4.2. Comparison between Aqueous Solution and Flux Growth

In view of the differences between the various fluxes used successfully for crystal growth, generalisations about their properties are difficult. Most fluxes are mainly ionic in character, so their general behaviour may be expected to conform to that described by Bloom and Bockris [50]. Such properties as surface tension are similar to those of water, while density values are, on average, somewhat higher and the viscosity of a flux is typically about 10 centipoise [7]. The diffusion coefficients of solute ions in simple ionic liquids are normally found to be of the order of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is comparable with the values measured for ions in aqueous solutions.

The conceptual similarities between flux and aqueous solution growth suggest that the description outlined in section 3 should be applicable to flux growth. The evidence for this assumption is extremely small as very few experiments of real significance have been performed with a view to establishing the mechanism of crystal growth from a flux.

So far as the authors are aware, the variation of growth rate with supersaturation has not yet been reported for any system, probably because of the experimental difficulties of measuring the growth rate and the temperature distribution in the melt. Since it is not possible to observe the growing crystal interface directly, the growth rate may only be monitored continuously by a thermogravimetric method. Thermocouples may be inserted in a seed crystal or into the melt itself, but these tend to disturb the temperature distribution, and the thermocouples themselves may become contaminated.

Only one determination of the variation of growth rate with rotation rate has been reported [3], for yttrium iron garnet, and the result is similar to those shown in fig. 2 for aqueous solutions. The growth rate v is independent of crystal rotation rate if this is greater than about 50 rev./min while v varies approximately as $\omega^{\frac{1}{2}}$ for low values of the rotation rate ω , although there are too few points on the graph to permit a quantitative interpretation. The experimental technique used in this experiment is not ideal, since the growth rate was determined over a

range of temperature during cooling rather than under isothermal conditions.

One difference between flux and aqueous solution growth, pointed out by Cobb and Wallis [7], is that the supercooling will normally be much higher in the former case. If the Helmholtz free energy for crystal growth at temperature T is written as

$$\Delta F = \frac{\phi}{T} \Delta T$$

where ϕ is the heat of solution and ΔT the supercooling, then an increase in T from say 300 to 1500 K will require ΔT to be increased by a factor 5 to maintain the same free energy, provided that ϕ remains constant.

The supercooling required to maintain the same supersaturation must be increased by an even larger factor. For an ideal solution (equation 16), the supersaturation will be

$$\sigma = \frac{\Delta n}{n} = \frac{\phi \Delta T}{R T^2} \quad (17)$$

In practice the temperature difference across a crucible during a flux growth experiment is typically 1 to 20°C, an order of magnitude higher than the values used in aqueous solutions. The values of ΔT used are, however, probably lower than those indicated by equation 17 since ϕ is often higher for refractory oxides and similar materials grown from the flux than for materials grown from aqueous solutions.

4.3. Surface Studies

Since evidence from growth rate determination is almost totally lacking, the main body of data concerning particle integration in flux growth is obtained from observations by optical microscopy of the surfaces of as-grown crystals. This evidence is rather indirect since it relies on the validity of some postulate regarding the origins of the observed features, and dynamic observation of a growing crystal face is not possible since the melts are opaque. However, such studies have proved valuable not only as an indication of the growth mechanism, but also because of the information they provide regarding the source of imperfections in the crystals, as will be discussed in section 5.

One of the most detailed studies of the surface features of flux grown crystals is that of Lefever and Chase [51] on garnets grown from PbO-PbF₂ fluxes. The initial stage of growth in the case of spontaneously nucleated crystals was found

to be highly dendritic as might be expected if, as in the example shown in fig. 6, a high supersaturation is required for nucleation compared with that for subsequent growth. The dendrites grow in the fast-growth directions and this stage must be followed by a period during which the region between the dendrite arms is filled in. The rate at which the filling in takes place will normally be most rapid at the ends of the arms where the supersaturation is high. If the filling rate is low, the faces of the growing crystal will be terraced until the filling is complete and the equilibrium face of the crystal is established. If growth is terminated in the terraced stage, hopper crystals are formed as reported by Lefever and Giess [52]. Hopper crystals will be more likely if the initial dendrites are of large dimensions and so incorporate a large fraction of the available solute.

If the crystals attain their equilibrium faces, the features observed will depend on the temperature of growth as well as on the composition of the crystal. On garnet crystals grown at higher temperatures, Lefever and Chase [51] noted layers spreading across a crystal face from points at an edge or corner of the face. The layers resulting from this corner and edge nucleation are normally curved in a direction concave from the point of origin, as indicated in fig. 7. This curvature arises because the growth rate increases with distance from the centre of the face since the supersaturation increases towards the edges.

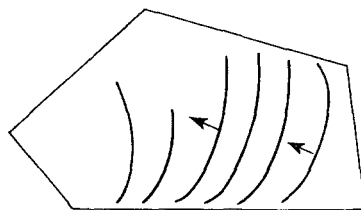


Figure 7 Growth steps on a (211) face of yttrium iron garnet, following Lefever and Chase [51].

When crystals were grown at lower temperatures (below about 1000°C), the characteristic features observed were numerous growth hillocks. In crystals grown below 900°C the hillocks became fewer in number and frequently a single growth feature was seen to dominate a whole face. The change in appearance of the surfaces may have been due to a

decrease in supersaturation with fall in temperature at a constant cooling rate. The growth process appeared to be by a spreading of layers outwards from the growth hillocks, the step heights varying from less than 5 nm near the centre of the hillocks to several hundred nm towards the edges of a crystal face. On the (211) faces, Lefever and Chase saw a more irregular pattern of steps, also originating from a point on the crystal face.

For the present discussion, the most important question concerns the nature of the growth centres. Etching of the crystal surfaces was found to result in an oriented etch pit at the centre of each hillock, indicating the presence of a dislocated region. On some crystals which were grown very slowly, growth spirals were observed and so the evidence appears strongly to favour a growth mechanism based on screw dislocations.

Similar surface features to those of the garnets were observed by Chase [53] on In_2O_3 crystals grown from a $\text{PbO-B}_2\text{O}_3$ flux. The crystals which were removed from the furnace at 1100°C exhibited growth steps resulting from corner and edge nucleation, these steps showing a similar curvature to those on the garnets. Crystals grown at a lower temperature exhibited growth hillocks with small steps parallel to the $\langle 110 \rangle$ directions in the (100) equilibrium surface. The initial stage of growth was again highly dendritic.

Quon and Sadler [54] also investigated the surface features of yttrium iron garnet crystals, grown in this case from $\text{BaO-B}_2\text{O}_3$ fluxes. The majority of features could be classified into the categories described by Lefever and Chase. The layers were again mainly nucleated at corners or edges of the crystals and concave from the point of origin, but exhibited a greater tendency to break up into a multi-layered structure. Hillocks were observed on both (110) and (211) faces, being either in the form of stacked layers of rhombic units or multiple thin circular growths. The authors saw only one growth spiral.

A wide variety of flux grown crystals was examined by Sunagawa [55] using a phase contrast microscope with a height resolution of 0.2 nm. His results generally confirm the observations reported above, although Sunagawa refers to different "types of spirals". Spirals of monomolecular step were seen on magnetoplumbite $\text{PbO} \cdot 6\text{Fe}_2\text{O}_3$, on Fe_2O_3 , Al_2O_3 and yttrium iron garnet. The features observed

on spinel were pyramidal in shape, but could be seen under high magnification to be formed from layers spreading from a central point. Growth hillocks were observed on Al_2O_3 crystals, together with pyramidal growths. Curved layers, similar to those observed on the garnets, could be shown in some cases to be formed from a large number of thin layers.

Our own investigations of a number of ferrite spinel and garnet crystals by optical and scanning electron microscopy have also revealed growth hillocks and, particularly, layer structures. Fig. 8 shows a pair of hillocks on the equilibrium (111) face of a nickel ferrite crystal grown by gradient transport in a $\text{BaO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ flux at 1230°C . The form of these hillocks is similar to those seen by Quon and Sadler (their fig. 7) and by Sunagawa (his fig. 5). The large depth of focus of the scanning electron microscope clearly reveals that the hillocks are built up of thin circular layers which interact to form sharp lines at 120° to each other.

The features which were observed most frequently were layers, with steps of the order of 10^{-5} cm in height. Fig. 9 shows the corner of a single step on the surface of a magnetoplumbite crystal, with a smaller step ending at the corner. On all our crystals the steps normally had straight edges and appeared to coincide with a low index face. The appearance of these layers suggested the mode of growth observed by Bunn and Emmett [32], with layers originating at some point on the surface of the crystals and spreading

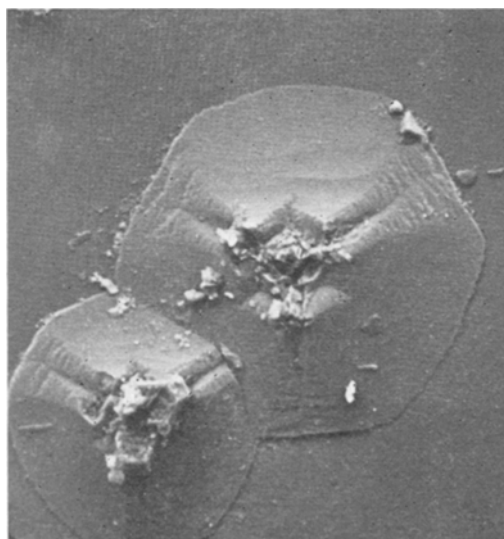


Figure 8 Growth hillocks on (111) face of nickel ferrite.



Figure 9 Growth step on magnetoplumbite crystal.

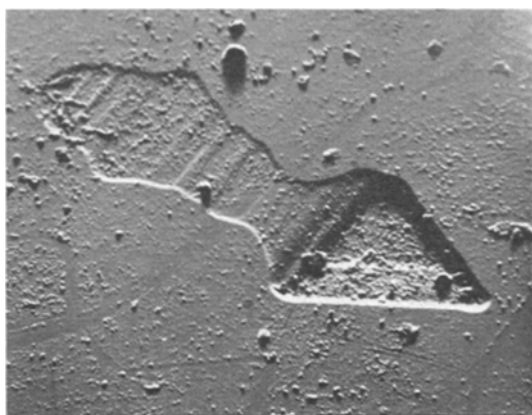


Figure 11 Depression at centre of (111) face of nickel ferrite.



Figure 10 Triangular growth layers on (111) face of lithium ferrite.

outwards. The clearest example of this mode of growth is seen in fig. 10 in which a (111) surface of lithium ferrite is shown. This crystal was grown by slow cooling from a $\text{PbO-PbF}_2\text{-B}_2\text{O}_3$ flux [56]. The layers exhibit a triangular shape with edges parallel to those of the crystal face. Successive layers appear to spread from a central point on the feature, although some inhibition must apply to growth in one direction. The height of the larger steps is about 10^{-5} cm and this is presumably due to bunching of smaller steps.

No evidence was found for nucleation of layers at the corners or edges of a crystal face although the depression at the centre of a (111) face of nickel ferrite (fig. 11) may indicate preferential growth of layers nearer to the edges of the face.

On the garnet crystals which were examined the only clear features were the single "window frame" patterns due to a single growth centre [51]. The vicinal faces of these features are inclined at a very small angle to a plane interface and their detailed structure could not be discerned by scanning electron microscopy.

It may be concluded from the various studies of flux grown crystal surfaces that most faces are atomically flat, with growth occurring preferentially at specific sites. Atomically rough surfaces have been reported [41] but they occur extremely rarely. The actual mechanism of crystal growth is probably based on screw dislocations, although pure spirals are seldom seen. The most likely mode of stable growth under conditions of low supersaturation is by a spreading of layers from a few points on the crystal face, probably originating by the mechanism illustrated in fig. 4b.

4.4. The Velocity of Growth

According to the considerations outlined in the foregoing discussion, the factors which are most likely to determine the rate of advance of a growing crystal face are boundary layer diffusion and particle integration, the latter being based on a screw dislocation mechanism. It should therefore be possible to predict approximate

values for the growth rate in the limiting cases where only one stage is effective.

Boundary layer diffusion control of the growth rate is most likely in a static solution, in which case the growth rate will be given by equation 9, namely $v = D\sigma n_e/\rho\delta$. Taking $D \simeq 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ as in aqueous solutions and in simple ionic melts, $\rho \simeq 5 \text{ g cm}^{-3}$, $n_e \simeq 1 \text{ g cm}^{-3}$ (representing, say, a 25% solubility in a solution of density 4 g cm^{-3}), $\delta \simeq 10^{-2} \text{ cm}$ and $\sigma \simeq 5 \times 10^{-3}$ (a typical value for slow growth from aqueous solutions), we obtain a value $v \simeq 10^{-6} \text{ cm s}^{-1}$. This value indicates that a 1 cm thickness of crystal will take about ten days to grow, which is in agreement to the order of magnitude with the period used experimentally for flux growth in unstirred crucibles.

When a seed crystal is rotated rapidly, it may be expected that a stage will ultimately be reached where the growth rate is determined by the particle integration process. If it is assumed that the growth rate is then given by the BCF surface diffusion theory (equation 1), the value of v will clearly depend on the choice of the parameters C and σ_1 . Since experimental data which will allow evaluation of these parameters is not available for any flux system, it is again necessary to use values for aqueous solutions. The mean values used by Bennema [14] are $C = 10^{-4} \text{ cm s}^{-1}$ and $\sigma_1 = 10^{-3}$. Comparison is then possible with experiments such as those of Smith and Elwell [57] in which the growth of nickel ferrite by gradient transport was effected using a supersaturation of $\sigma \simeq 0.04$. Substitution gives $v \simeq 4 \times 10^{-6} \text{ cm s}^{-1}$, which is in good agreement with the observed value of 0.2 mm/h or $6 \times 10^{-6} \text{ cm s}^{-1}$. (The growth rate quoted by Laudise [3] at high crystal rotation rates is 0.06 mm/h or $2 \times 10^{-6} \text{ cm s}^{-1}$.)

The estimated growth rates both for diffusion-controlled and particle integration-controlled growth are clearly valid only for order-of-magnitude estimates and so a comparison of the values predicted in the two limits is of little value. The values quoted do appear, however, to be typical of those used experimentally.

In these estimates and throughout the above discussion, the liberation of the heat of crystallisation has been neglected. That this heat is unlikely to be of great importance in determining the rate of growth may be shown by consideration of an example. The heat of solution of nickel ferrite in barium borate is found to be 73 kJ/mole [58]. With the growth rate of $6 \times 10^{-6} \text{ cm s}^{-1}$

given above, the rate of liberation of heat is of the order of $10^{-2} \text{ J cm}^{-2} \text{ s}^{-1}$. If the crystal has a thermal conductivity of the order of $10^{-1} \text{ J cm}^{-1} \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}$, a typical value for refractory oxides at 1200°C , the heat generated will be immediately conducted away through the crystal if the temperature gradient is only $10^{-1} \text{ }^\circ\text{C cm}^{-1}$. Since the actual temperature gradient is likely to be much larger than this value, and heat may also be removed by the solution, there appears to be ample justification for the assumption that growth is directly controlled by the solute concentration.

5. Crystal Imperfections

The imperfections which occur most commonly in flux grown crystals are flux inclusions, striations, dislocations and substitutional impurities. The incorporation of substitutional ions depends directly on the choice of flux and the purity of the chemicals used, and may normally be reduced to a tolerable level by the use of a suitable flux. It is also important that the flux should not attack platinum appreciably, since inclusions of platinum metal may be found in flux grown crystals [59], and rhodium or chromium from the crucibles may also be present as impurities.

Since flux growth occurs at temperatures well below those of the corresponding pure melts, the concentration of vacancies and interstitials will be lower than in melt grown crystals. Moreover, since the temperature gradients are normally lower, the flux grown crystals may have lower dislocation densities than those produced from the melt, apart from the outstanding exceptions such as pulled silicon.

The defects which are likely to be the most troublesome are flux inclusions and striations. It is probable that these defects may be reduced considerably by careful attention to the experimental conditions and the remainder of this section will be devoted to considerations of the incidence of these defects.

5.1. Flux Inclusions

The incidence of flux inclusions may often be directly related to the mode of growth, as revealed by observations of the crystal surfaces. The initial dendritic stage of growth by spontaneous nucleation occurs, as discussed in section 4.3, under condition of high supersaturation and it is probable that the rapidly growing dendrite arms will join up to trap particles of the flux. Examples of crystals which exhibit a dendritic

initial stage with a high concentration of trapped flux have been found by Lefever, Chase, and Torpy [60] and White [4]. If the supersaturation for nucleation is not high compared with that for subsequent growth, many nuclei will tend to form on cooling and the dendrites will reach only small dimensions. It is frequently observed that, when a slow cooling experiment results in many small crystals, the concentration of inclusions is not so high as at the nucleation centre of larger crystals. Such a decrease in flux inclusion concentration with increase of nucleation was found by Chase and Tippins [61] on adding MgO to a fluxed melt used to grow In_2O_3 crystals. Conversely, if nucleation is restricted to a single site as in the experiments of Scheel and Schulz-Dubois [62], the initial stage is likely to be highly dendritic. However, this dendritic region then occupies only a small fraction of the crystal and many specimens can be cut from the remainder.

The dendritic stage may be eliminated by seeding provided that the supersaturation is not too high when the seed is introduced. The seed should preferably have equilibrium faces otherwise the initial growth stage may again contain a high concentration of inclusions. White and Brightwell [43] found, in the growth of Al_2O_3 crystals, that seeds cut parallel to the c -axis became serrated by the formation of the (012) and (104) habit faces, with layers of flux being incorporated in the valleys between the serrations until the crystals attained their equilibrium habit. Layered inclusions are also likely to occur in crystals which exhibit hopper faces.

Inclusions in equilibrium faces will depend upon the mode of growth and may be absent if the growth is slow and uniform. If growth occurs by a layer mechanism with corner and edge nucleation, inclusions may be formed in the centre of the face between the advancing layers if these spread too rapidly. Such inclusions due to incomplete layer formation near the centre of the crystals have been observed in both garnet [60] and In_2O_3 crystals [61].

The types of inclusions listed above are relatively easy to recognise and thus to eliminate. However, even when crystals are grown under "good" conditions and exhibit regular equilibrium faces, flux inclusions are frequently present. These may not be detectable by optical microscopy but are revealed by X-ray topography as shown by Belt [63] for the (111) faces of lithium ferrite. It is therefore important to know the conditions under which an equilibrium face of

a crystal will grow without the development of instabilities, which will normally result in flux inclusions. Attempts to obtain a limiting condition for stable growth will be discussed in the next section.

5.2. Condition for Stable Growth

The condition for stable growth of a plane interface in the case of crystallisation from a melt containing impurities has been known for some time and is well confirmed by experiment. Rejection of impurities by the growing crystal interface results in a depression of the liquidus temperature in the region immediately in contact with this interface; any protuberances on an otherwise smooth interface will thus encounter a region of higher supercooling and will tend to grow more rapidly than the surrounding interface. This constitutional supercooling may be avoided if a steep temperature gradient is imposed on the melt at the interface, and the condition for stable growth may be written [64]

$$\frac{dT}{dx} > \frac{mn_i(1-K)v}{KD} \quad (18)$$

where m is the fractional change in liquidus temperature per unit concentration, n_i the impurity concentration, K the partition coefficient, v the growth rate and D the impurity diffusion coefficient. Mullins and Sekerka [65] included the effect of thermal conduction through the crystal and obtained a more general stability condition

$$\frac{\kappa_S}{\kappa_S + \kappa_L} \left(\frac{dT}{dx} \right)_S + \frac{\kappa_L}{\kappa_S + \kappa_L} \left(\frac{dT}{dx} \right)_L > \frac{mn_i(1-K)v}{KD} \quad (19)$$

where κ is the thermal conductivity and the suffixes S and L refer to the solid and liquid phase respectively. If the temperature gradient in the solid is expressed in terms of that of the liquid, it is found possible to have constitutional supercooling without instability if the growth rate is sufficiently slow.

White [4] has pointed out the similarity between the case of a doped melt and flux growth, since the latter case solvent must be rejected at the melt interface, and Tiller [66] has applied equation 18 directly to flux growth. However, as has been argued above, the growth rate in this case will depend on solute rather than on thermal transport and it is therefore instructive to consider directly the condition for the absence of

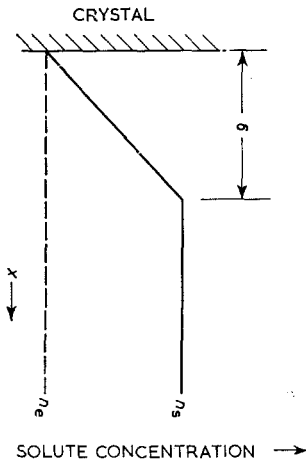


Figure 12 Variation of solute concentration with distance from crystal interface, in simplest case.

constitutional supersaturation, i.e. that the supersaturation does not increase with distance from the interface.

Since crystals growing with a stable morphology from fluxed melts are bounded by habit faces, we consider the case of a planar crystal face. The more complex problems of growth anisotropy and habit modification cannot be treated quantitatively until a better understanding of the plane interface has been obtained. The growth rate is assumed to be slow compared with the diffusion rate so that the interface can be considered static. In the simplest case where growth is determined by volume diffusion through the boundary layer, the distribution of solute in the absence of convection will have the form shown in fig. 12, with the concentration at the interface equal to the equilibrium value at the interface temperature T . With this approximation, the solute gradient will be

$$\frac{dn}{dx} = \frac{n_s - n_e}{\delta} \quad (20)$$

If the solution is ideal, the equilibrium concentration will vary with temperature as $n_e \propto \exp(-\phi/RT)$ so the variation of the equilibrium concentration ahead of the interface will be

$$\frac{dn_e}{dx} = \frac{n_e \phi}{RT^2} \frac{dT}{dx} \quad (21)$$

where dT/dx is the variation with distance from the interface of the temperature of the solution.

The condition for the absence of constitutional supersaturation is thus that, at the interface,

$$\frac{dn}{dx} < \frac{dn_e}{dx} \quad (22)$$

or, on substitution from equations 20 and 21,

$$\frac{dT}{dx} > \frac{\sigma RT^2}{\phi \delta} \quad (23)$$

in which the supersaturation σ has been written for $(n_s - n_e)/n_e$. As in melt growth, therefore, this approach leads to the conclusion that the temperature gradient ahead of the interface should exceed a critical value.

An alternative form is obtained by substituting for σ from equation 9, which gives the critical temperature gradient in terms of the speed of growth as

$$\frac{dT}{dx} > \frac{RT^2 \rho v}{\phi n_e D} \quad (24)$$

If the values of these quantities from section 4.4 are substituted into equation 24, with $T = 1200^\circ\text{C}$, the critical gradient is found to be of the order of 100 deg/cm. This value is unrealistically high, since good quality crystals may be grown in crucibles in which the temperature gradients are very low. Moreover, if δ is decreased by rotating the crystal, an even higher gradient would be required by equation 23 for stable growth and Hurlé [67] has pointed out that convection will also tend to increase the value of dn/dx when crystals are grown by thermal gradient transport. In practice, convection and seed rotation normally lead to improvements in crystal quality without any change in the imposed temperature gradient.

In the other limit where the volume diffusion step tends to zero, the solute gradient dn/dx may be neglected and the equilibrium condition then becomes

$$\frac{dT}{dx} > 0 \quad (25)$$

This condition and that of equation 24 indicate that the heat of solution should be removed through the crystal itself rather than through the solution. This situation is likely to apply when a cooled seed is used or when crystals grow by spontaneous nucleation on the walls of a crucible or on the surface of the melt. Examples are known, however, [68] where crystals of good quality have been grown in the centre of a solution and this is particularly the case for aqueous solutions to which the same theory should apply. Equation 25 is unsatisfactory in

that it does not predict a critical growth rate or supersaturation for stable growth.

The failure of a constitutional supersaturation approach to predict a realistic condition for stable growth is presumably due to neglect of the stabilisation due to the surface energy of the crystal, since any perturbation represents a departure from an equilibrium face. Thus, as pointed out by Tiller and Kang [69], a protuberance may not grow even if the local variation in supersaturation favours the development of this perturbation.

An alternative approach to the problem of growth stability has been proposed by Brice [70]. Rather than a negative supercooling or supersaturation gradient ahead of a growing interface, he proposes that stable growth will occur if the gradient of the growth rate is negative, that is if

$$\frac{dv}{dx} < 0 \quad (26)$$

Under this condition, a projection on an otherwise plane interface will grow less rapidly as it advances and so will tend to decay. The advantage of this approach is that particle integration may be included through the relation between growth rate and supersaturation. The resulting condition for stable growth from solution is rather complex and data for comparison with experiment is unfortunately not available for any example of flux growth. However, equation 26 does produce the constitutional supercooling equation if the supersaturation is small and is thus open to the same criticisms made to equation 24. Moreover, if the assumption is made that v is described by the BCF surface diffusion expression (equation 1), the only conclusion which may be reached is that $d\sigma/dx$ must be negative, which corresponds to equation 22.

The main criticism that can be made of Brice's method is that it is one-dimensional and therefore cannot describe the behaviour of a real protuberance. Shewmon [71] has given a treatment of the stability of a planar interface in solution based on the method of Mullins and Sekerka [72]. The stability condition is discussed in terms of sinusoidal perturbations of different wavelengths, since any perturbation can be described by a superposition of sine waves. If the y -axis lies in the interface, a perturbation is taken to have the form

$$x = \epsilon(t) \sin \omega y$$

The perturbation causes local changes in the supersaturation at the interface which tend to increase the instability, but the resulting concentration gradients along the y -axis tend to smooth out the sine wave. In the case of diffusion control, the rate of change of the amplitude ϵ is given by

$$\frac{\dot{\epsilon}}{v_0} = \omega \epsilon (1 - n_e \Gamma \omega^2 / G) \quad (27)$$

Here v_0 is the rate of growth of the interface at $\epsilon = 0$, G the solute gradient dn/dx at the interface and $\Gamma = \Omega \gamma / RT$, where Ω is the molar volume of the crystal and γ the surface tension. The condition for stable growth is that $\dot{\epsilon} < 0$, or

$$\omega > (G/n_e \Gamma)^{\frac{1}{2}} \quad (28)$$

The critical frequency is decreased, and the stability thus enhanced, by surface diffusion which will clearly tend to smooth out the perturbation.

Shewmon also considered the case of interface kinetic control and concluded that the stability condition is unchanged although $\dot{\epsilon}$ is no longer given by equation 27. The condition represented by equation 28 predicts as expected that the stability will increase with increase in surface tension and with decrease in the solute gradient. Absolute stability (for all frequencies) requires that $G = 0$, which corresponds to our condition for interface kinetic control, represented by equation 25.

All the treatments described fail to provide an expression for a maximum rate of stable growth, which could be compared with experiment. The derivation of such an expression should be the principal aim of future work in this area. Any realistic theory must take into account the stabilising effect of the habit faces and of surface diffusion.

5.3. Striations

Striations are periodic variations in the composition of crystals due to changes in the relative concentration of the components or in the impurity concentration. They have been observed in a wide variety of materials by a number of authors, but their origin is still not clear.

In yttrium iron garnet, Lefever *et al* [60] found that a banded appearance was due to finely divided inclusions about $0.1 \mu\text{m}$ in diameter. They believed that divalent iron was involved in the observed striations since the effect could be reduced by growing the crystals in

an oxygen atmosphere or by reducing the concentration of silica in the melt. FeO is soluble in yttrium iron garnet at high temperatures but the solubility decreases with decreasing temperature and it would therefore precipitate out of the lattice on cooling.

Chase [53] found a variety of striations in indium oxide crystals. Those in the innermost zone were very clear bright and dark bands, decreasing in width with distance from the growth centre. The intermediate zone showed large striations, up to 1 mm across, but having a fine structure. In the outermost zone these fine striations were absent but less well-defined variations in colour were observed. The various striations were associated with different modes of growth, being respectively dendritic layer growth with corner and edge nucleation, and spiral growth resulting in growth hillocks. Chase concluded that the striations could be correlated with fluctuations in the furnace temperature resulting from an imperfect controller and this conclusion was also reached by Chase and Wilcox [73].

Striations corresponding to variations in the Cr^{3+} concentration were observed in the ruby crystals studied by White and Brightwell [43]. These were thought to arise because of preferred adsorption on different faces, giving rise to a series of sharp boundaries in some crystals cut parallel to the c -axis.

If the controller does not give rise to periodic fluctuations in the furnace temperature, striations may still be present due to convection in the melt. Temperature oscillations due to convective motion in fluids are well known but their importance in crystal growth has not been appreciated until comparatively recently. Wilcox and Fullmer [74] showed that the temperature oscillations which occurred during growth of calcium fluoride from the melt could be correlated with regular fluctuations in the dopant concentration, and many examples of the correlation between normal oscillations and growth striations have now been reported [75].

The occurrence of temperature oscillations in a pure melt depends upon the Rayleigh number

$$R = \frac{g \alpha L^3 \Delta T}{K \nu} \quad (29)$$

where α is the volume expansion coefficient, L the depth, K the thermal diffusivity and ν the kinematic viscosity of the fluid and ΔT the temperature differences across it. Oscillations

occur if R exceeds a critical value, and turbulent convection is observed at higher values of R .

In solutions, convection may occur due to a gradient either in the temperature or in the solute concentration. The conditions for the onset of stable or unstable convection can be described in terms of the Rayleigh number R and a solute Rayleigh number R_s defined by

$$R_s = \frac{g \beta L^3 \Delta n}{K_s \nu} \quad (30)$$

Here β is the rate of change of density with concentration, Δn the solute concentration difference across the fluid and K_s the diffusivity of the solute. Since K_s is normally lower than the thermal diffusivity by some orders of magnitude, convection can occur at very low values of solute gradient. The conditions for stable and oscillatory convection in solution are given by Baines and Gill [76] and it is found that convection can occur when either the solute or the thermal gradient is de-stabilising, even if the bulk density in the solution increases with distance from the upper surface.

Itti [77] has observed well-defined striations in sodium chlorate crystals grown from an aqueous solution in which convection was taking place. These striations were not present when the solute was transported purely by diffusion. In the flux pulling experiments of Smith and Elwell [57], the melt depth was normally only about 3 cm, but oscillations of amplitude 0.5°C were measured at a point 4 mm below the surface. The amplitude of the oscillations was reduced somewhat by rotating the crucible as shown in fig. 13 [78].

A fairly detailed study of striations in flux grown orthoferrite crystals was reported by Giess *et al* [79]. The bands in these materials were from 2 to 60 μm in width and parallel to the growth interfaces. The lead concentration was found to vary from 1.10 to 0.72% in the darker and lighter bands respectively, but the silicon was 0.04% in both regions. The authors were unable to distinguish whether the Pb was in the orthoferrite lattice or in submicroscopic inclusions. The location of the striations in the crystal could be explained by a layer growth mechanism.

The explanation of striations such as those observed by Giess *et al* in terms of oscillatory convection in the solution has not been firmly established. Crystals of up to 1 cm in size were grown in about 130 h, an average growth rate of $2 \times 10^{-6} \text{ cm s}^{-1}$. Thus a striation 30 μm in width

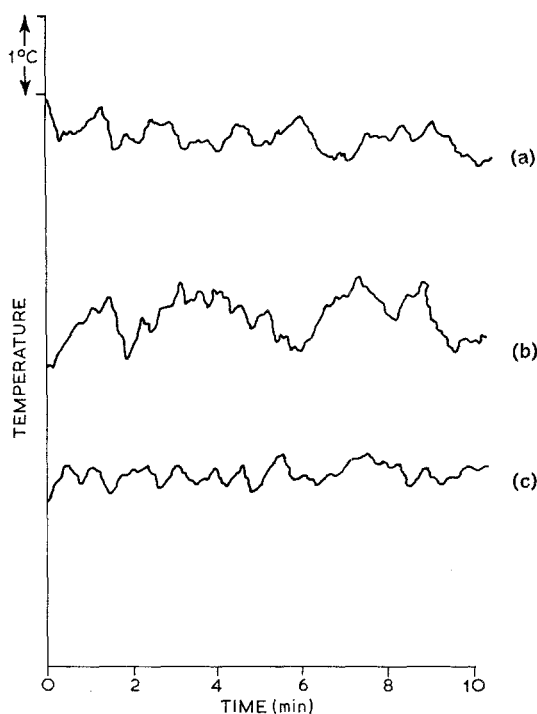


Figure 13 Temperature oscillations in nickel ferrite-barium borate fluxed melt [78]. (a) At surface with crucible stationary. (b) 4 mm below surface with crucible stationary. (c) 4 mm below surface with crucible rotated at 10 rev./min.

would be associated with a period of about 25 min. The period of the oscillations shown in fig. 13 is about 3 min. Unless much slower oscillations occur in some systems, or the period of the oscillations corresponds to some multiple of the thermal oscillations, it appears that there is no direct relationship between striations and oscillatory convection. It is, however, even more unlikely that different furnace controllers in several laboratories would exhibit regular periodic fluctuations and so imperfect temperature control is a rather implausible cause of all the observed striations.

If the concentration of solute $n(x, t)$ is obtained by solution of the diffusion equations, oscillatory behaviour may be found in terms of the distance x from the interface, but not in terms of the time t . Volume diffusion may therefore be excluded as the source of the striations, provided that the growth rate is low. An oscillatory interface kinetic process has not been proposed although Frank's "kinematic wave" theory [80], which describes the motion of a bunch of steps across

the crystal surface, might provide such an effect.

In view of Itti's observations, an explanation of the origin of striations in terms of convection appears most probable, although the detailed process requires clarification. Experimental work which might lead to an understanding of this process is clearly desirable. The observation by Giess *et al* [79] that striations are associated with impurity taken from the flux suggests that they may be eliminated even in the presence of unstable convection provided that experimental conditions otherwise favour stable growth.

6. Conclusions

The general description of the processes by which crystals grow from the flux appears to be similar to that for growth from aqueous solution. Perhaps the most striking impression obtained from a survey of the literature of flux growth is the absence of parameters such as diffusion coefficients and viscosities which are necessary in any detailed confrontation with theory. Surface studies of as-grown crystals lead to the conclusion that the mode of growth on crystal habit faces is by screw dislocation mechanism. Estimates of the rate of growth for boundary layer diffusion and for particle integration control both yield values of the order of 10^{-6} cm s $^{-1}$.

Inclusions which are formed at the initial stage of growth by spontaneous nucleation may be eliminated by the use of a seed and those which form because of non-uniformity of growth over a surface will be avoided if the melt is well stirred. Cobb and Wallis [7] recommend rotation of the crucible as a means of achieving stirring but we would agree with Scheel and Schulz-Dubois [62] that pure rotation is unlikely to be wholly effective and that their technique of accelerated rotation is preferable. Even if a perfectly homogeneous solution is achieved, some flux will be included if a critical speed of growth is exceeded. No satisfactory expression for the critical growth condition is available at present and a constitutional supersaturation approach does not lead to a realistic stability criterion. The stabilising effect of the habit faces is thought to be responsible for the good quality exhibited by some crystals grown from the flux.

Striations probably arise from temperature oscillations within the melt, but a suitably designed experiment is necessary before their origin can be firmly established.

It is hoped that this discussion will stimulate further experimental and theoretical work aimed

towards solving some of the outstanding problems.

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