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MORPHOLOGICAL STABILITY OF A CRYSTAL GROWING IN SOLUTION

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ABSTRACT

A brief outline is given of the problem of the stability of growth of a polyhedral crystal growing in solution in the presence of supersaturation inhomogeneity. An experiment is proposed for a low gravity environment which should provide data for confrontation with the various theoretical approaches to this problem. The validity of this data rests on the assumption that growth occurs in a convection-free environment.

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INTRODUCTION

The importance of satellite experiments in the crystal growth area is primarily that experiments may be performed under conditions where the fluid dynamics is well characterized. In the case of solution growth, the absence of convection is expected to be a handicap in growing large crystals, since the maximum rate of stable growth may be unreasonably low for practical purposes. The most likely method to be used for routine solution growth in low gravity is the isothermal solution reaction technique which seems appropriate for difficult biological and other organic crystals. However, the greatest value of the Space Shuttle for solution growth is more probably for testing models of the growth process and so for improving our understanding of growth mechanisms. Morphological stability is one example of an important area where few detailed and careful experiments have been performed.

THE PROBLEM IN OUTLINE

Crystals grown from solution are normally polyhedral because of the strong tendency to form low-energy facets. If the resulting polyhedron is to grow in a stable regime its shape will not change with time and the theoretical problem of predicting the conditions for the morphological stability has received considerable attention. If the crystal does not grow in a perfectly stirred solution, the supply of solute varies across any face of the crystal between the face center and the edge, and interferometric measurements such as those of Bunn (1949) indicate that this supersaturation inhomogeneity can be as high as 25 percent. As a result of the higher supersaturation at the edges, crystals tend to develop dendritic forms when grown at high rates or to exhibit terraces stepped from the center to the edges (the so-called "hopper" morphology) when grown under less unstable conditions.

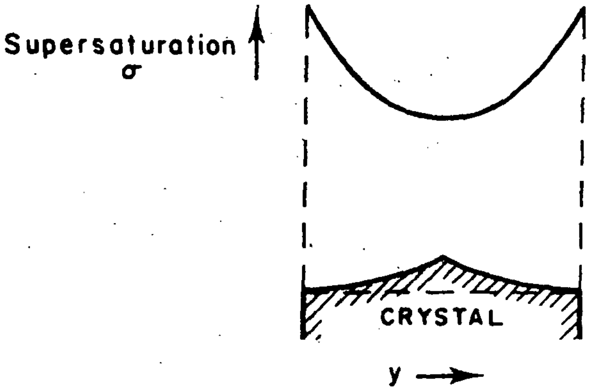

Figure 1: Supersaturation inhomogeneity and compensating change in slope for a crystal face (after Chernov, 1972).

The onset of a terraced growth form limits the rate at which crystals can be grown and so it is important for crystal growers to be able to predict the growth rate at which this instability occurs. Theoretical approaches to solving this problem normally rely on the assumption that solute is transported over the crystal surface only by diffusion in the solution. Cahn (1967) took as his condition for the onset of instability the requirement that the supersaturation should not fall to zero at the face center. He arrived at the following expression for the maximum rate of stable growth:

$$v_{max} = \frac{D(n_s - n_e)}{\ell \rho} \qquad (1)$$

where D is the solute diffusion coefficient, n_s the solute concentration in the bulk solution and n_e the equilibrium value, ρ the density of the crystal and ℓ the length of the face. For a 1cm crystal, $D = 10^{-5} cm^2 s^{-1}$, $n_s - n_e = 5 \times 10^{-2} g\ cm^{-3}$ and $\rho = 5\ g\ cm^{-3}$, this gives $v_{max} \approx 10^{-7} cm\ s^{-1}$ which is lower than experimental values by two orders of magnitude. This discrepancy may be due to convection in the solution or to the stabilizing effect of the interface kinetic mechanism by which the crystal grows.

This latter aspect was considered in more detail by Chernov (1972) who proposed that the supersaturation inhomogeneity may be partially compensated by a variation across the crystal surface in the kinetic coefficient which relates the growth rate to the local value of the supersaturation (see Fig. 1). A higher than average value of the kinetic coefficient is to be expected at the face center because of the tendency of dislocations to propagate from the center of the crystal in a direction normal to the surface.

More recently Wilcox (1977) reviewed the morphological stability of a cube growing in a convection-free solution and gave a careful analysis of the factors governing instability. Numerical calculations were made by Kuroda et al (1977) who presented data in the form of limiting supersaturation for stable growth as a function of crystal size.

EXPERIMENTAL TEST

Spacelab presents an ideal opportunity to test these various treatments of morphological instability since it will permit the measurement of the limiting linear growth rate (or supersaturation) for stable growth under diffusion-limited conditions. For this experiment to be valid, it must first be established that the Fluids Experimental System can give convection-free conditions for long periods in orbit. In principle such experiments could be made under convection-free conditions on earth (see the proposed cell of Tiller, 1968) but confirmed success in growing crystals under conditions of pure diffusion is still lacking.

One practical advantage of morphological stability experiments in Spacelab (rather than experiments aimed at the growth of perfect crystals) is that the growth rate is relatively rapid so that the rather short time normally available for experiments is not a serious limitation.

Sodium chlorate $NaClO_3$ would appear a suitable choice as the material for this investigation since it grows as crystals of cubic shape and there exist a number of good experimental studies of its growth, including concentration profiles in the solution by an interference method (Mussard and Goldsztaub, 1972). In addition, the most detailed study to date of the role of convection in solution growth (Chen et al, 1979) was made on this material.

A particular aspect which could be investigated in this experiment is the profile of the crystal surface using Tolansky interference microscopy. This technique permits the determination of the slope of the crystal surface to the crystallographic habit plane by the use of monochromatic multiple reflection fringes (Tolansky, 1969). In principle it would be desirable to measure the surface profile during growth, but the optical requirements of such a measurement conflict with those for observation of solute concentration profiles within the liquid. A recent study of yttrium aluminum garnet crystals grown from high temperature solution (Roberts and Elwell, 1979) showed inclinations to the habit plane of 21-54' according to whether the hillocks were of polygonal or elliptical shape and also depending on the crystallographic face considered and the direction within the face. In some cases the slope was found to decrease with distance from the hillock center.

At a later stage of studies in low gravity, it would be desirable to study the morphological stability of a crystal in a unidirectional flow of solution. The measurement of a maximum stable growth rate as the solution is swept across one face of the crystal has become particularly important since Janssen and Bennema (1977) drew attention to the importance of hydrodynamic eddies in inclusion formation.

The practical goal of a sound theory of morphological stability in crystal growth is that it becomes possible to devise optimum programs relating the crystal growth rate to its size as growth proceeds. Temperature programming for solution growth was considered by Scheel and Elwell (1972) using an approximate theory for the maximum stable growth rate but a refined treatment could lead to considerable savings in time and energy if used on a wide scale.

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