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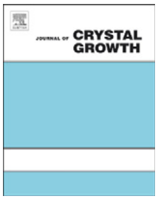

Rim formation on crystal faces growing in confinement

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ABSTRACT

A crystal face growing from solution while exerting a normal force on a confining surface is often observed to develop a growth rim surrounding a hollow core. The interpretation has been that this is a manifestation of steady state growth due to the balance between the concentration gradient and stress gradient along the confined crystal surface. In this paper, we present experimental results which show that the growth rim is instead formed as a consequence of faceted growth on the confined surface. Steady state growth is not ensured by a gradient in normal stress, but rather a gradient in step density along the crystal face. The loaded crystal surfaces display a high degree of roughness, and the stress is not uniformly distributed across the surface, but transmitted at discrete asperities. We discuss the implications of these findings for the interpretation of previous experimental results, and for the thermodynamics of crystal growth subject to normal stress.

1. Introduction

The so-called force of crystallization, or crystallization pressure, has been an intriguing topic in geology and geophysics for at least 150 years. This refers to the situation where a crystal growing from a supersaturated solution performs mechanical work by displacing a neighboring wall. The resulting stresses may lead to fracturing and damage in porous materials. The force of crystallization is important in engineering, because of the deteriorating effects of salt weathering [1,2] and delayed ettringite formation in cement [3]; and in geophysics, where it is the mechanism behind pseudomorphic replacement [4,5] and can drive vein formation [6,5].

The first experimental rapport on the force of crystallization was made by Lavalle [7] who noticed that crystals were able to push themselves upwards through growth on their lower surface. Becker and Day [8] showed that centimeter sized alum crystals growing from a supersaturated solution could “raise a weight of a kilogram through a distance of several tens of a millimeter”. Later Taber [9] and Correns [10,11] followed up with experiments demonstrating the same phenomenon using several different salts. Most recently Sekine et al. [12] studied the pressure exerted by a single crystal growing in a microfluidic channel using photoelastic stress measurements.

In the experiments of Becker and Day [8] and Taber [9], quantitative measurements of the mean surface normal stress were not feasible due to the appearance of growth rims on the loaded crystal faces, which made it impossible to define the area over which the applied load was distributed. Becker and Day reported that “a terraced cup forms below the crystal so that the bearing surface remains a mere edge throughout its growth”. Such growth rims are also commonly observed on the bottom face of crystals grown from solution in a glass dish. Taber [9] used a colored crystal seed to show that the growth rims were formed by growth on the confined face of the crystal as opposed to dissolution of the interior. He concluded that “no material is deposited on the under side of the crystal except along the advancing outer edge, and that the cavities $(\cdots)$ are due to the downward growth of the outer edge”. In both of these studies the width of the rim was assumed to increase with increasing normal stress on the crystal face. The width of the rim was not measured, however, due to experimental limitations.

As will be explained in Section 3 of this paper, there are at least two plausible hypotheses for the formation of such growth rims. In the first hypothesis, which has been worked out theoretically in the classical paper of Weyl [13], the rim is produced as a consequence of the normal stress distribution on the loaded surface. We will refer to this as the stress distribution model. The second hypothesis has not been previously proposed in the context of crystallization under load, and will be thoroughly explained in this paper. In this model, the rim is formed as a result of stepwise growth of a faceted crystal in a concentration gradient, analogous to the formation of hopper crystal morphologies [14]. This will be referred to as the surface kinetics model.

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2. Motivation for this study

To measure the force generated by a growing crystal in a well controlled experiment is notoriously difficult, as illustrated by the fact that only one proper quantitative measurement, that of Correns [10,11] has been reported to date (for a discussion of the validity of these results, see [15]). Among the issues which need to be studied experimentally are the properties of the thin liquid film which feeds the confined growth region (see Section 3.1). The original motivation for this study was to measure the width of growth rims as a function of applied load, and use this as an indirect means of studying the stress dependence and transport properties of the thin liquid film (Section 3.2).

As the study progressed we found, however, no apparent agreement between our experimental results and the stress distribution hypothesis. Upon further theoretical analysis we found the surface kinetics hypothesis to be a more viable alternative. The implications for our understanding of the force of crystallization will be discussed in Section 7.

3. Theory

3.1. Transport of growth units in a thin liquid film

A schematic illustration of rim development on a crystal growing in confinement is shown in Fig. 1(a). A crystal is placed in a supersaturated solution and confined between two inert surfaces. A load may be applied to the upper surface. During crystal growth, the upper surface is displaced.

The vertical faces of the crystal experience free face growth (f). In order for the confining surfaces to be displaced, there must be growth on the confined faces of the crystal (c). The formation of a growth rim requires that the growth in the central part of the crystal is negligible (n).

Growth units must be supplied to the confined crystal faces by transport through a thin liquid film, as depicted in Fig. 1(b). In this thin film transport is presumably dominated by diffusion. Assuming that the film is sufficiently thin to neglect concentration gradients in the vertical direction, the diffusional flux in the two-dimensional case is given by Fick's law through the relation

$$J_D = -D\frac{dc}{dx}, \tag{1}$$

where J_D is the diffusional flux, D is the diffusion constant and $c(x)$ is the local ion concentration. This implies that in order for ions to be transported to the growth region, the concentration of ions must be continuously decreasing from the edge of the crystal towards the center.

At steady state, the diffusional flux must balance the flux of ions incorporated into the growing crystal surface, denoted J_k. If growth only takes place on the rim, this requires that

$$J_D^0 h - \int_0^\delta J_k \, dx = 0, \tag{2}$$

where J_D^0 and h are the diffusional flux and film thickness at $x=0$, and δ is the width of the rim.

Steady state growth also requires that J_k is independent of x. Since we have established the requirement of a gradient in c along the crystal surface, this implies that the local surface growth rate cannot be a function of local concentration only. In the following subsections we will demonstrate how the concentration gradient can be balanced by either a surface normal stress gradient or a gradient in step density to ensure steady state growth, and how both of these may lead to the formation of a growth rim.

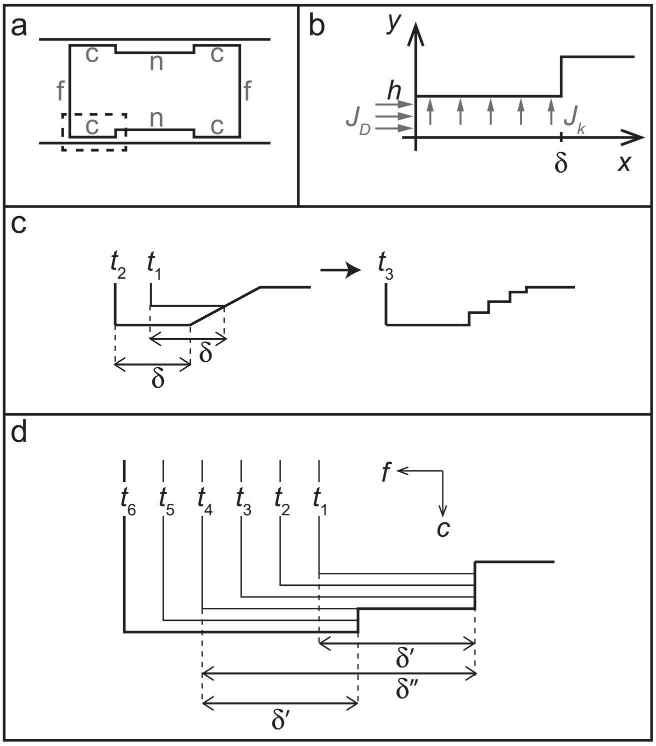

Fig. 1. (a) Crystal with growth rim, growing from solution between two inert surfaces. The various faces of the crystal display free face growth (f), confined growth (c) and little or no growth (n). (b) Schematic diagram of region shown in dashed lines in (a). The crystal is located above the solid line starting at $y=h$, and the inert surface is located at $y=0$. Ions are supplied from the bulk liquid located at $x<0$. The diffusional flux of ions into the growth region is denoted by J_D and shown as gray horizontal arrows at the entrance of the confined liquid film. The flux of ions which are incorporated into the crystal surface during growth is denoted J_k and shown as vertical gray arrows. During rim formation there is presumably no growth for $x>\delta$. (c) and (d) Two hypotheses for staircase formation. In (c) the distance δ from the free surface to the edge of the rim is constant during growth, and the staircase develops due to surface energy minimization by reorganization in the cavity. (d) shows how new steps form when the rim becomes wider than a critical value δ''. Arrows show the direction of free face (f) and confined (c) growth.

3.2. Stress distribution model

When two solid surfaces are brought close to contact in an aqueous environment, a very large force may be needed to expel the film of liquid between them. This is a consequence of the difference in surface energies for a wet and dry contact. If the sum of the crystal–liquid (cl) and wall–liquid (wl) surface energies is smaller than the crystal–wall (cw) surface energy

$$\gamma_{cl} + \gamma_{wl} - \gamma_{cw} < 0 \tag{3}$$

then it may be energetically favorable to maintain a liquid film between the solid surfaces even when subject to large confining forces [11,16].

At separations larger than a few molecular diameters, the interfacial forces which arise when the solid surfaces are brought into contact are due to the combination of electrostatic and van der Waals forces, and is described by the so-called DLVO theory [17]. When the surfaces are very close, the interaction energy is dominated by effects related to the discrete molecular nature of the surfaces, solvent and ions [18,19]. Interfacial forces corresponding to disjoining pressures of more than 100 MPa have been measured for mica surfaces in concentrated salt solutions [19]. Due to electrostatic screening, interfacial forces do not become significant until the separation is less than about 10 nm in concentrated solutions [20,21].