

Dynamics of surface patterning in salt-crystal dissolution

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We report an experimental study on the pattern dynamics of the salt-crystal (NaCl) surface when dissolved from below by its own aqueous solutions with mass concentrations between 0.0% and 24.0%. The surface pattern roughness grew exponentially for a range of unstable wave numbers with a fastest growing wave number k_c and corresponding maximum growth rate σ_c which both decreased for higher solution concentrations. These results are compared with predictions of linear stability analysis and suggest a model for patterning by turbulent dissolution. [S1063-651X(96)51106-2]

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The interaction of hydrodynamic motion with a moving interface is of fundamental interest in problems such as crystal growth and melting-dissolving systems [1,2]. Recently, solid salt dissolving into aqueous salt solutions was shown to exhibit turbulent solutal convection and patterning of the solid interface [3,4]. This is an interesting system in which to study the interaction of fluid flow and interface morphology not only because it has elements of both turbulence and linear stability, but because it avoids the complications of coupled temperature and concentration fields that arise in directional binary-mixture solidification [5–10] and in convectively driven melting (see [1,2] and references therein), and the patterns form a continuous record of the interactions at the interface. Solutal convection occurs when solid salt is dissolved from below by an aqueous salt solution with mass concentration c . The fluid at the solid interface with salt saturation concentration, $c_{sat} > c$ is heavier than the bulk solution and is unstable to hydrodynamic motion. The mass transport for solutal convection was shown [3,4] to be consistent with a turbulent boundary layer model which gave an effective boundary layer thickness δ of between 0.05 to 0.2 mm as a function of the solutal forcing (proportional to the density difference between the bulk and saturated solutions). The average lateral length scale of the pattern was about ten times δ (it scaled with δ) and was in reasonable agreement with predictions of linear stability analysis of a diffusing solutal front [11,12]. This latter result suggested a strong coupling of the fluid flow in the vicinity of the boundary layer with the process of dissolution. The mechanism for the coupling, however, was not understood nor was the evolution of the pattern studied.

We present an experimental study on the pattern dynamics of NaCl single-crystal surfaces dissolved from below by aqueous salt solutions. Spectral analysis of the surface patterns at different times showed that initially the surface pattern roughness grew exponentially in time with a wave-number-dependent growth rate peaked about the most unstable wave number k_c . Both the maximum growth rate σ_c and k_c decreased with increasing solutal concentration. This result agrees with the previous observation that the dominant surface structures become larger in lateral size at higher concentration [3,4], and is in agreement with the prediction from Foster's linear theory for the convective insta-

bility of a diffusion front [11,12]. Our results also yield a determination of the linear growth rate for the patterning and suggest a possible mechanism for the patterning process in turbulent dissolution.

The experiment is described briefly. The crystals we used were NaCl single-crystal spectrophotometer window blanks with dimensions of 19 mm×38 mm×6 mm [13]. The crystal was sealed by transparent epoxy on all sides except one 19 mm×38 mm side which was the only surface exposed to the solution during the experiment. The solution had a large volume of about 7000 cc to ensure a small concentration change (less than 0.13% during the experiment) in the bulk solution and was temperature regulated at about 20 °C with variations of less than 0.1 °C. The pattern information presented in this report was obtained using a surface profilometer which included a translation stage [14], and a tip coupled to a fixed linear-voltage-displacement transducer [15] for measurement of vertical displacement. The experimental resolution for vertical displacements was better than 0.2 μm . The main experimental uncertainty came from the finite tip size (radius about 0.13 mm) and a small amount of lateral freedom in the profilometer mounting. We estimate that the lateral positional reproducibility was about 20 μm which did not affect significantly the measurements of the low wave number portion of the surface profile. Only the central portion of the pattern with an area 20 mm×10 mm was scanned with a resolution of 512×256 to minimize edge effects [16]. Each profile measurement took about 12 h.

We measured time series of the surface height $h(x,y,t)$ for solutions with mass concentrations of $c=0.0\%$, 15.0%, 20.0%, and 24.0%. The crystals were immersed in the solution for a dissolution time interval Δt between two consecutive profile measurements. We used the following values of Δt in our measurements: 1 and 2 min for $c=0.0\%$, 4 and 6 min for $c=15.0\%$, 8 min for $c=20.0\%$, and 28 min for $c=24.0\%$. We used different values of Δt for $c=0.0\%$ and 15.0% to study the effect of the measurement interruption on the formation of the surface patterns.

A sequence of selected profiles of NaCl in the 15.0% solution with a Δt of 4 min is shown in Fig. 1. The plotted surface area is 10 mm×10 mm with a resolution of 256×256. The surface was very flat before dissolution (Δh less than 10 μm over the measured area), and gradually became

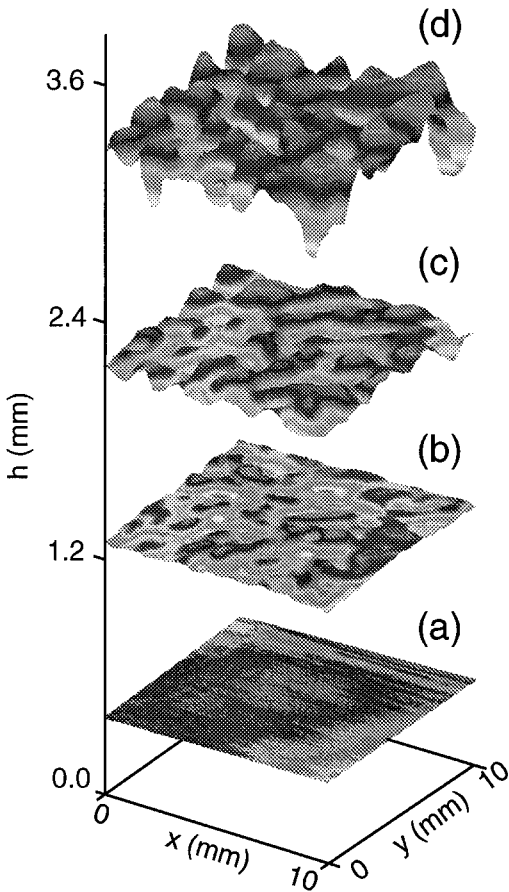


FIG. 1. Gray-scale-coded profile plots for NaCl in the 15.0% solution after accumulated dissolution time of (a) 0, (b) 16, (c) 32, and (d) 48 min. The plots are offset but the vertical scale in mm applies to all four plots.

more corrugated as dissolution proceeded. The fact that the initial surface was flat and featureless ruled out the possibility that the ensuing surface patterns resulted from preexisting surface structures. Even after an accumulated dissolution time of 48 min in which almost all of the crystal had dissolved, the growth of the surface roughness did not saturate. Whereas the surface roughness changed visibly from one measurement to the next, the horizontal positions of the main structures remained almost unchanged.

Quantitative information about the surface profile was obtained from Fourier transform (FFT) analysis. Because the surface pattern was nearly isotropic azimuthally, the power spectrum of the two-dimensional Fourier transform at time t was averaged azimuthally to obtain the power per unit k , $P(k,t)$ where $k = \sqrt{k_x^2 + k_y^2}$. Additionally, our 512×256 height data were split into two 256×256 segments, and the power spectra were then averaged over these two segments. The power spectra gave not only a measure of the surface roughness, but also the relative contribution from each wave number k . In Fig. 2, we show a log-log plot of a sequence of power spectra for selected surface profiles for the 15.0% solution with $\Delta t = 4$ min (only every other sequence is plotted). The spectral power increased monotonically with the accumulated dissolution time, indicating a continually growing surface roughness. There was a falloff at high wave number

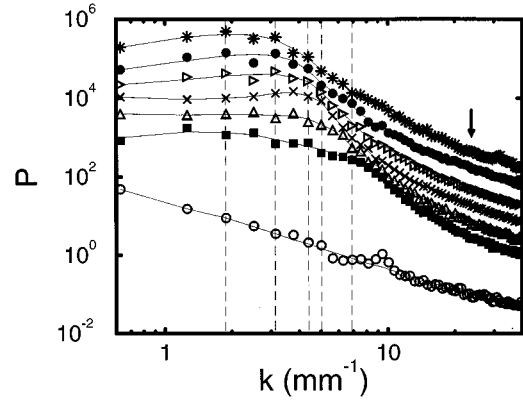


FIG. 2. Power spectra for NaCl surface patterns in the 15.0% solution after accumulated dissolution time of 0 (○), 8 (■), 16 (△), 24 (×), 32 (▷), 40 (●), 48 (*) min, from bottom to top. The arrow indicates an upper cutoff wave number set by the diameter of the profilometer tip (about 0.25 mm). Solid lines are guides to the eye. Vertical dashed lines indicate values of k used for Fig. 3.

in each power spectrum, so that spectral components far beyond the falloff wave number had essentially no contribution to the overall surface roughness; only those with substantial power at lower wave numbers contributed significantly to the visible surface structure. The falloff wave number corresponded to the apparent characteristic inverse length scale of the dominant surface structure. The power of the initial flat surface was very small compared with those at a later time, and resembled that of an inclined plane which has power proportional to $1/k^2$ [4].

To quantify the time evolution of the power of each individual wave number, we plot, in Fig. 3, $kP(k,t)$ on a logarithmic scale for 5 wave numbers versus dissolution time. For small and large wave numbers the growth was almost exponential over the whole time interval we studied, i.e., $kP(k,t) \propto e^{\sigma(k)t}$. For intermediate wave numbers the growth was initially exponential, but then showed signs of saturation. The slope of the straight-line fit gave the initial, linear growth rate which is presented in Fig. 4. The data showed that the spectral components with intermediate wave num-

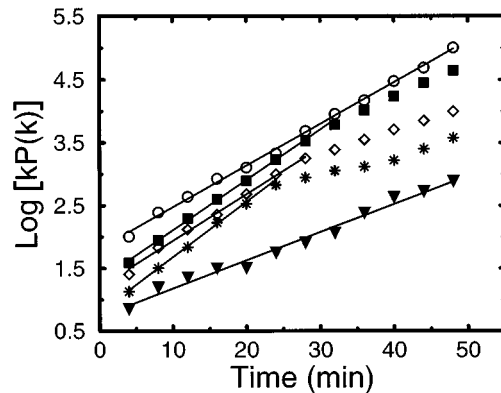


FIG. 3. $\text{Log}_{10}(kP)$ vs dissolution time for spectral components with $k=1.88$ (○), 3.14 (■), 4.40 (◇), 5.02 (*), and 6.91 (▼). The solid lines are linear least-square fits to the initial data. Note that the multiplication of P by k spreads the curves for better presentation but does not affect the slope of the lines (i.e., the growth rate).

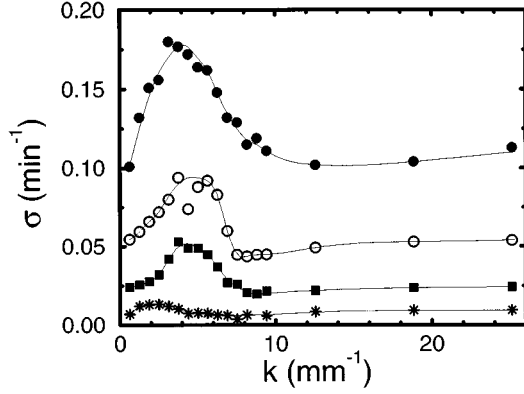


FIG. 4. Growth rate σ vs wave number k for the surface pattern of NaCl dissolved in solution with concentration c and dissolution time interval Δt : 0.0%, 1 min (●); 15.0%, 4 min (○); 20.0%, 8 min (■); and 24.0%, 28 min (*). The lines are guides to the eye.

bers grew faster (steeper slopes), and consequently, they approached saturation earlier than lower or higher wave number components with smaller growth rates. The small thickness of each crystal (about 6 mm) prevented us from dissolving it further to see the saturation of all the spectral components; even the fastest growing modes did not saturate completely as shown in Figs. 2 and 3.

Because we could not measure the surface profile continuously, the possibility that removing the sample affected the surface growth rate was investigated. At the highest dissolution rate with $c=0\%$, the measurement with a shorter Δt (1 min) yielded a 50% lower growth rate than the one with a longer Δt (2 min). On the other hand, measurements with two dissolution time intervals (4 and 6 min) for $c=15.0\%$ gave the same growth rates to within experimental uncertainty. This is consistent with a disruption of the flow owing to removal and reinsertion of the crystal; the shorter the dissolution time interval (Δt), the larger the fraction of dissolution time was taken for the fluid to establish a constructive pattern-etching process. We estimate that the initial random flow time after each immersion was about 30 sec which is roughly consistent with relevant time scales for the diffusive growth of the boundary layer and the development of convective circulation [17].

In Fig. 4, we compare the growth rates for different concentrations. In the figure, we present only the data with shorter dissolution time intervals ($\Delta t=1$ min for $c=0\%$ and $\Delta t=4$ min for $c=15\%$), because with the same amount of crystal to dissolve, those measurements had more time-sequence data points, thus less uncertainty in determining wave-number-dependence of the growth rate. The growth rate varied with both wave number and solution concentration. Both k_c and σ_c moved to smaller values as the concentration increased. There was an approximately linear relationship between σ_c and the mass dissolution rate j , indicating that the faster the salt crystal dissolved, the faster the pattern roughness grew in magnitude.

We now compare k_c with the previous steady state results [3,4] and with the boundary layer stability theory. The linear stability results [11,12] yield a characteristic lateral wave number for the boundary layer:

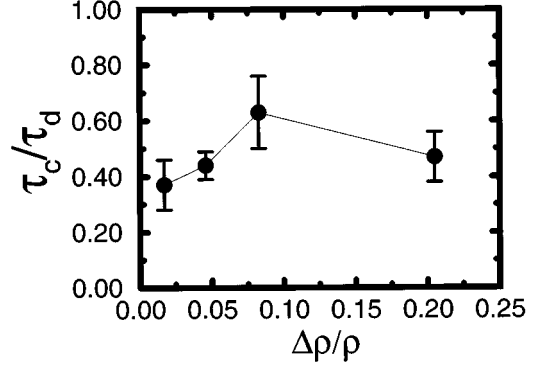


FIG. 5. Ratio of the growth time scale τ_c and dissolution time scale τ_d . The line is a guide to the eye.

$$k_0 = (g/D\nu)^{1/3}(\Delta\rho/\rho_0)^{1/3} \quad (1)$$

where $\Delta\rho \equiv \rho_{sat} - \rho$, ρ_{sat} and ρ are the solution densities at concentrations c_{sat} and c respectively, g is the acceleration of gravity, D is the mass diffusion coefficient, ν is the kinematic viscosity, and $\rho_0 = (\rho + \rho_{sat})/2$. Since $\Delta\rho \propto c_{sat} - c$, k_0 decreases as c increases. The comparison of k_0 with an experimentally measured wave number assumed that the linear growth in the fluid boundary layer imprinted a pattern on the solid interface. It also ignores possible nonlinear effects of boundary layer stability [12]. There is no prediction that we are aware of for the coupled problem. In our experiment, there are two possible wave numbers to consider: the fastest-growing wave number k_c (in Fig. 4) and the wave number where the power started to decrease dramatically (in Fig. 2). The latter wave number was time dependent, but reached a constant asymptotic value k_f in approximately the time the growth at k_c began to saturate. It was determined systematically using a method presented elsewhere [4]. Both k_c and k_f decreased as the concentration increased (a slight increase for $c=0.0\%$ is within experimental error), agreeing qualitatively with the scaling implied by Eq. (1). Further, the two agree with each other to within experimental uncertainty. This, along with a more detailed test of the scaling behavior of k_f in [4], indicates that Foster's linear theory for the diffusion front gives a reasonable description of the lateral length scale for the surface patterns. But what sets the time scale for the pattern growth and how is the lateral length scale of the boundary layer imposed on the surface?

Since surface patterning and dissolution are intertwined, we compare their relative speeds. Surface patterning exhibits exponential growth with a shortest time scale $\tau_c = 1/\sigma_c$ (we correct τ_c for the initial random interruption effect). The mean displacement of the surface owing to dissolution is linear in time, i.e., the interface moves with a constant velocity $v = j/\rho_{salt}$ where ρ_{salt} density of the solid salt. In order to define a time scale for dissolution we need to choose some characteristic length. The only length scale in the problem is the boundary layer thickness δ since the lateral length scale $\lambda_c = 2\pi/k_c$ is linearly related to δ . We choose λ_c because this yields scaled growth times of order one. The dissolution time scale τ_d is then defined by $\tau_d = \lambda_c/v$. In Fig. 5, the scaled growth rate is shown as a function of the solutal forcing, $\Delta\rho/\rho$. There is some variation but the ratio is fairly constant at about 1/2 indicating a reasonable scaling relation

compared to the difference in unscaled values of τ_c of about 20. The success of the scalings of wave number and growth rate gives us an important clue about the hydrodynamic-interfacial interaction.

Based on the above discussions, the following scenario for linear instability leading to surface patterning is proposed (a similar flow profile was conjectured previously for a combined melting-dissolving system [18] but without quantitative support and not in the context of linear stability). The lateral instability of the boundary layer causes spatially structured up and down streams separated by a characteristic wavelength λ_c . The salt-crystal surface dissolves faster at the fresher up-flow and correspondingly slower at the denser return flow since the fluid picks up mass as the salt dissolves. As a depression develops the return flow strengthens because

of buoyant forcing along the increasingly steep surface. Since the strength of the return flow depends on the depth of the depression, this process is linearly unstable and produces uneven dissolution. The saturation of linear growth should occur when the depth of the depression is of order of its lateral dimensions. Detailed modeling and more experiments are needed to fully understand the exponential growth and dynamics of surface patterning occurring in convection-enhanced crystal growth, solidification, dissolution, and melting.

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