

Supporting Information

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Temporal Sequence of Reacted Crystal Surfaces

After each reaction step, the surface topography was analyzed using VSI. This method is capable of analyzing sample-surface height changes within a range of 1 nm using a Mirau interferometry system, thus making the method suitable to track minute changes in material flux from reacting surfaces. We applied a ZeMapper interferometer system (Zemetrics) equipped with five interferometry objectives. Measurements were performed using white-light mode. Before and after the dissolution experiment, the sample-surface topography was measured by VSI including both a masked and a reacted surface portion. Fig. S1A illustrates the pitted topography of a ZnO (000-1) surface after a reaction time of 8 h. Subsequent analysis of the crystal surface shown in Fig. S1B after each reaction step resulted in the sequence of rate maps shown in Fig. 2. Fig. S2 illustrates the sequence of topographies that were used for subsequent calculations. This sequence visualizes the evolution of surfaces during superimposition of step-waves emanated from neighbored screw dislocations. The large pit (*Left*) superimposes a flat-bottomed pit during ongoing reaction. The two pits of Fig. S2 (*Right*) are separated from each other by a narrow wall that is persistent during the observed reaction periods.

Calculation of Maps of the Rate and Rate Derivatives

Using the inert surface section as a height reference, multiple height-difference maps were calculated (Fig. S3). The height difference (dz) per reaction time (dt) of each (x,y) map point contains information about the height retreat velocity (dz/dt). The material flux map was used to calculate the rate map by dividing each (dz/dt) value by the molar volume. The second and third temporal derivatives, that is, the subsequent difference map calculations, result in acceleration and jerk maps.

Calculation of Zeros of the Derivatives of Velocity (Rate), Eq. 1

We set Eq. 4 = 0 and get

$$0 = \frac{v_{step} \left(\frac{\sigma\bar{V}}{r^2kT} - \frac{2C\bar{V}r}{(r_h^2 + r^2)^2kT} \right) e^{[C\bar{V}/(kT(r^2+r_h^2))] - [\sigma\bar{V}/(rkT)]}}{1 - e^{\Delta G/(kT)}}. \quad [\text{S1}]$$

Zeros of this function occur for two possibilities, either $v_{step} = 0$ (the trivial solution) or

$$\left(\frac{\sigma\bar{V}}{r^2kT} - \frac{2C\bar{V}r}{(r_h^2 + r^2)^2kT} \right) = 0. \quad [\text{S2}]$$

After some transformations and the consideration that the summand

$$\sigma\bar{V}r_h^2$$

is very small, we get the zero

$$r_0 = \frac{2C}{\sigma}. \quad [\text{S3}]$$

Evolution of Rate Profiles During Superimposition of Stepwaves from Multiple Sources

In addition to Fig. 3, we show a sequence of rate profile data that illustrates outward motion of rate pulses that get partially disturbed by a neighbored source of pulses (Fig. S4, *Left*). The regular motion and decay of a pulse is reported. This picture is, however, significantly altered into an interference pattern of pulses in Fig. S4 (*Right*). Here, the outward motion of a single pulse is no longer constant. Additionally, the rate-amplitude distribution is significantly altered, thus resulting in an unexpected distribution of surface rates.

On a larger spatial and temporal scale, this result is confirmed (Fig. S5). After a reaction time of 12 h, the reacting ZnO surface shows the evolution of large single-rate pulses and the formation of complex patterns that reflect locally enhanced reactivity. Such surface areas with a diameter of about 10 μm and greater are the starting point of the porosity pattern within the crystalline material.

Fig. S6 illustrates the basic surface building blocks of a reacting crystal surface at a screw dislocation. The resulting surface step consists of step atoms. Here, the kink sites are the preferred positions for reactions because of their coordination number. Removal of kink-site atoms is a self-replicating process, that is, the removal of a kink atom results in a new kink-site position on the surface.

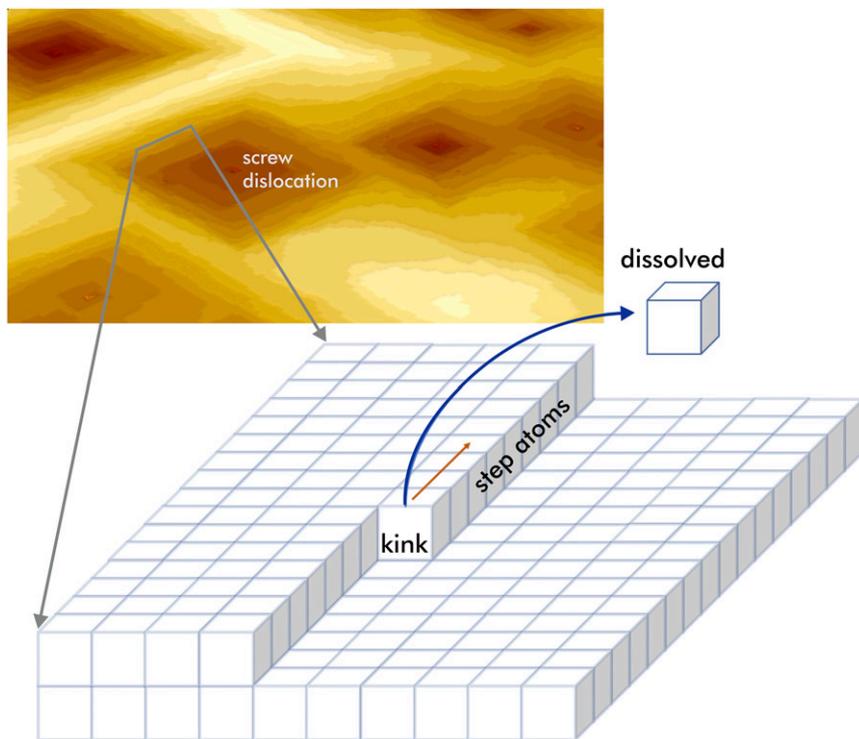


Fig. S6. Illustration of crystal-surface building blocks at a screw dislocation. The removal of step atoms at kink sites during dissolution is a self-replicating process.