

Tribological enhancement of CaCO_3 dissolution during scanning force microscopy

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Abstract – We report scanning force microscope (SFM) observations of enhanced calcite dissolution in aqueous solution due to mechanical stimulation induced by the SFM tip. Images and mechanical treatment were performed in saturated ($\geq 60 \mu\text{M}$) CaCO_3 solution adjusted to pH~9. Small area scans of mono-layer steps significantly increased the step velocity in the scanned area (in the direction corresponding to dissolution) when the applied contact force is above about 160 nN for the tips employed. The step velocity could be increased at least an order of magnitude by scanning at even higher contact forces (e.g., 270 nN). This enhancement is a function of step orientation relative to the calcite lattice. Indentations near pre-existing steps also locally enhance the step velocity. We present evidence that the higher dissolution rates are caused by stress-induced increases in the rate of double-kink nucleation.

I. Introduction

The presence of a chemically reactive environment can dramatically affect materials exposed to mechanical stresses due to “environmentally induced crack growth” and/or “corrosive wear”. The combined attack of a chemical agent and local deformation at a surface often makes irreversible bond breaking much more favorable. Conditions appropriate for corrosive wear are readily attained in scanning force microscopy (SFM), where very high stresses can be applied in liquid environments by the moving SFM tip. With an appropriate choice of substrate, liquid, and scanning conditions, the resulting wear processes can be observed with spatial resolutions on the order of nanometers and time resolutions on the order of a few seconds. In this work, we investigate the corrosive wear of single-crystal CaCO_3 (calcite) in aqueous solution. Calcite was the first material imaged by SFM with unambiguous atomic resolution [1] and is readily imaged in aqueous solutions. In addition, the dissolution and growth of calcite in aqueous solutions are of considerable importance in mineral formation and in the exchange of CO_2 between the atmosphere, ocean, and lithosphere [2-4].

The evolution of calcite surfaces during dissolution and crystal growth have been observed using SFM [2, 4] and optical microscopy [5, 6]. Both techniques

reveal a distinct crystallographic asymmetry in step motion: the rate of dissolution and growth along steps on opposite sides of an etch pit often differ by a factor of 2-4 (Under supersaturated conditions, a similar asymmetry is observed in the deposition rate.). Figure 1 shows a portion of the calcite cleavage surface identifying two parallel steps, one “fast” and the other “slow”, where both growth and dissolution is faster along fast steps than slow steps. The inclination of the lattice along these two types of steps are significantly different (78° and 102° , respectively). The “fast” steps have the more open orientation (102° inclination). These different inclinations apparently affect the activation energy for double-kink nucleation, which is believed to be the rate-limiting step for both dissolution and growth [2, 4]. A similar model was first proposed by Hirth and Pound to describe evaporation from crystal surfaces [7], where double-kink nucleation on step edges was the rate-limiting step. Kinks result in weakly bound atoms (at the kink sites) which are subsequently removed. In the dissolution of calcite, more weakly bound ions at kinks would more readily move into solution.

In previous work, we demonstrated the ability of SFM in humid air to induce corrosive wear at an atomic step in single crystal NaNO_3 [8] where a thin layer of sorbed water present at modest humidities served as the corrosive agent.

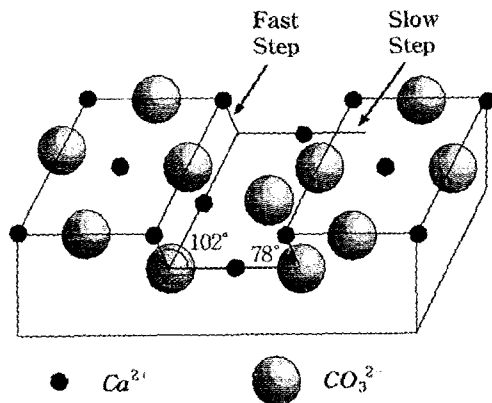


Fig. 1. Simplified molecular model of the structure of fast and slow steps. The removal of the planar CO₃²⁻ ions from fast steps is presumably easier than removal from slow steps, which are “undercut”. The nearest neighbor distance (Ca²⁺-CO₃²⁻) is 3.2 Å; the monolayer step height is slightly less, about 3.1 Å.

Although CaCO₃ has virtually the same crystal structure as NaNO₃, it is significantly harder (Moh hardness 3 vs 1.5-2 for NaNO₃) [9]. Thus much higher contact forces are required to produce corrosive wear in CaCO₃ than in NaNO₃. Secondly, the corrosive effect of water is also much weaker in CaCO₃ than in NaNO₃: the solubility of CaCO₃ in water is almost 6 orders of magnitude lower than NaNO₃. Whereas corrosive wear was readily observed in NaNO₃ in air at modest humidities, comparable wear in CaCO₃ requires that the material be immersed in aqueous solution. Under these conditions, the resulting corrosive wear can be alternatively described in terms of mechanically enhanced dissolution.

II. Experimental Section

Thin slices of single-crystal calcite were cleaved from optically clean material from Ward Scientific (Iceland spar, Chihuahua, Mexico). SFM images were obtained with a Digital Instruments Nanoscope III SFM using commercial Si₃N₄ tips with nominal radii of curvature of 40 nm and a cantilever force constant of 0.06 N/m. All images shown were performed in the attractive mode, thus minimizing surface modification. Their hardness and chemical inertness make these tips ideal for wear studies, especially in corrosive environments where mechanical stimulation can be performed either by localized contact mode scanning

or by indentation. In spite of their large tip radius, we are able to routinely achieve atomic resolution on calcite (not shown here), presumably due to a tip asperity interacting with the lattice.

Experiments were performed in a solution cell (Digital Instruments) with a volume of ~20 μL, sealed with a soft O-ring, and filled with a saturated CaCO₃ solution adjusted to a pH of about 9. Saturated CaCO₃ solution was prepared by adding reagent grade CaCl₂·2H₂O and NaHCO₃ to deionized water to yield calcium and carbonate ion concentrations of 60 μM and adjusting the pH to about 9 with NaOH. At this high pH, the carbonate in solution appears principally as CO₃²⁻, rather than HCO₃⁻, simplifying the solution chemistry. With respect to preexisting steps, this solution is somewhat undersaturated; nevertheless, the step velocities associated with dissolution (<1 Å/s) were quite low relative to the mechanically-induced enhancements described below.

III. Results

Effects of Scanning. Monolayer cleavage surfaces of optical grade CaCO₃ scanned in ambient air (RH ~30%) of average height 3.1 Å were readily observed and found to be totally resistant to tip-induced wear. Figure 2 shows an SFM image taken immediately after three consecutive small area scans in the central

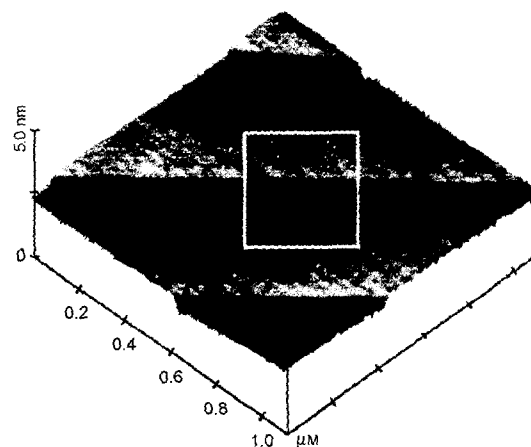


Fig. 2. SFM image (1 × 1 μm²) of a CaCO₃ cleavage surface imaged in ambient air, taken immediately after three small area scans (400 × 400 nm², location outlined in white) across the central step. The applied normal force during the small area scans was 270 nN.

portion of the figure marked by the white box at a high contact force of 270 nN. The monolayer step running along the central portion of Fig. 2 was not affected by the small area scans. Thus, at this relatively high contact force, scanning in air at modest humidities produces no wear features.

When a cleavage surface is immersed in 60 μM CaCO_3 solution, the surface features initially evolve rapidly due to dissolution. This initial dissolution is consistent with the observations of Hillner *et al.* [2], who report that supersaturations of about 170% (100 μM) are required for a neutral dissolution/deposition environment in the presence of steps and pits. In the present work, the 60 μM CaCO_3 solution was allowed to remain on the surface (no flow) until it reached equilibrium with the underlying material, and the velocity of steps along the etch pits was $<1 \text{ \AA/s}$.

Under ideal conditions, dissolution pits in CaCO_3 form parallelograms with sharp corners. However, the etch pits in this work typically displayed one rounded corner, as shown in Fig. 3. The rounded corner has been attributed to the presence of impurities which hinder kink propagation toward the intersection of the fast steps.

The effect of scanning across the monolayer high step edges of an etch pit at high contact force of about 270 nN. The recess in the central region of the small area scans. As noted above, the step velocity associated with dissolution alone (without small area scanning) is less than 1 \AA/s . In terms of a wear "rate",

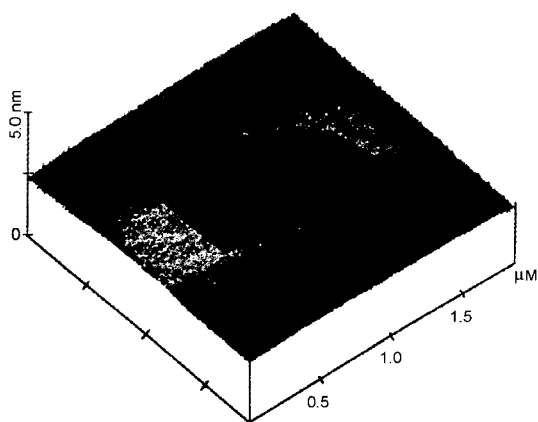


Fig. 3. SFM image of a "spontaneous" dissolution pit in CaCO_3 . The two straight edges are "slow steps" and are aligned parallel to the edges of the cleavage rhombohedron. The two "fast steps" intersect along a curve.

we observe here a removal of $\sim 30 \text{ nm}$ per scan (12 \AA/s). Note that the terraces above and below the step remain flat; wear is localized along the step and does not affect material along the flat terraces above and below (This is in contrast to the corrosive wear observed on the much softer NaNO_3) [8]. Further, the wear pattern along the step extends somewhat beyond the small area scan. Thus it appears that the stresses applied during scanning to have enhanced dissolution in the region where scanning has occurred and that this dissolution has propagated out beyond the scanned region.

We therefore propose the following mechanism: high contact forces nucleate double kinks along the step, and these kinks propagate (through dissolution) in and near the small area scan. Subsequent images of similar steps show that the affected step gradually straightens out. This is consistent with the propagation of kinks nucleated in the small area scan toward the corners of the etch pit.

Similar experiments were performed in which the direction of scanning was varied $\pm 45^\circ$ with respect to the direction in Fig. 4 (normal to the fast step). No change in the shape of the induced recess or the step velocity as a function of scan direction was observed. This suggests that the frictional forces applied by the tip on the step (which should depend strongly on scan direction) do not significantly affect the dissolution

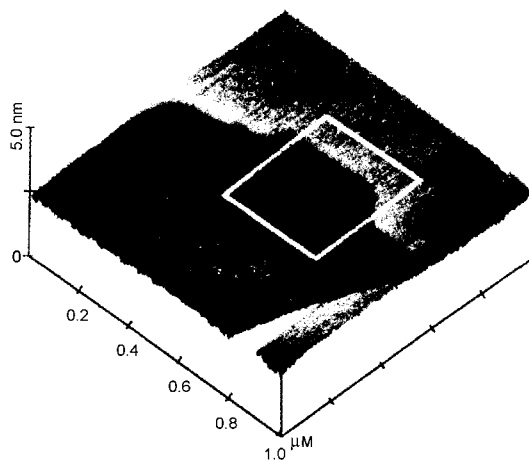


Fig. 4. SFM image of a typical fast step along an dissolution etch pit after three small area scans at a contact force of 270 nN. The location of the small area scans is outlined in white; the tip encountered the step at a 90° angle during scanning.

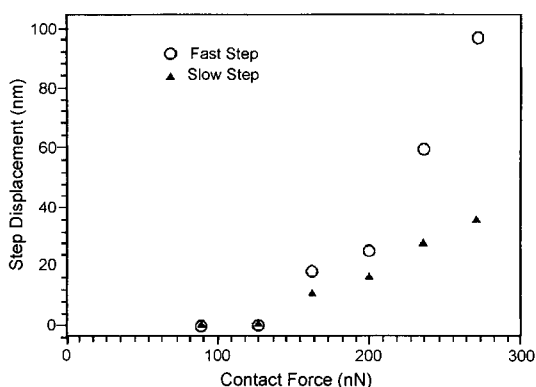


Fig. 5. Increase in step velocity as a function of contact force for fast and slow step.

process.

The step velocity enhancement (the velocity in the scanned region minus the velocity well outside the scanned region) is, however, a strong function of the normal force applied to the tip. Figure 5 shows the velocity enhancements measured for both the “fast” and “slow” steps vs normal force. For both types of steps, the velocity enhancements are clearly nonlinear. As might be expected, the fast-step velocity increased more rapidly with increasing contact force than the slow-step velocity. A more detailed study with significantly more values of F_N indicate a continuous (no threshold), exponential increase with applied force. This strong dependence of step velocity on normal force rules out enhanced material transport (e.g., due to mixing of the solution by the SFM tip) as the mechanism for enhanced dissolution. Mixing effects would be quite insensitive to the normal force applied by the tip for the same scanning motion.

We tested the consequences of high contact force scans on broad flat terraces, many hundreds of nanometers from any steps. In such regions at contact forces up to 270 nN and scan sizes larger than about $100 \times 1000 \text{ nm}^2$, repeated scanning had no effect on the CaCO₃ surface. Likewise, repeated indentations with the tip at these normal forces generated no visible feature. However, repeated scanning with very small scans ($10 \times 10 \text{ nm}^2$) and high contact forces (270 nN) reproducibly nucleated dissolution pit on broad, flat terraces. The growth of a dissolution pit initiated by a sequence of three $10 \times 10 \text{ nm}^2$ scans at 270 nN is shown in Fig. 6. This scan area is not much larger than the expected tip -

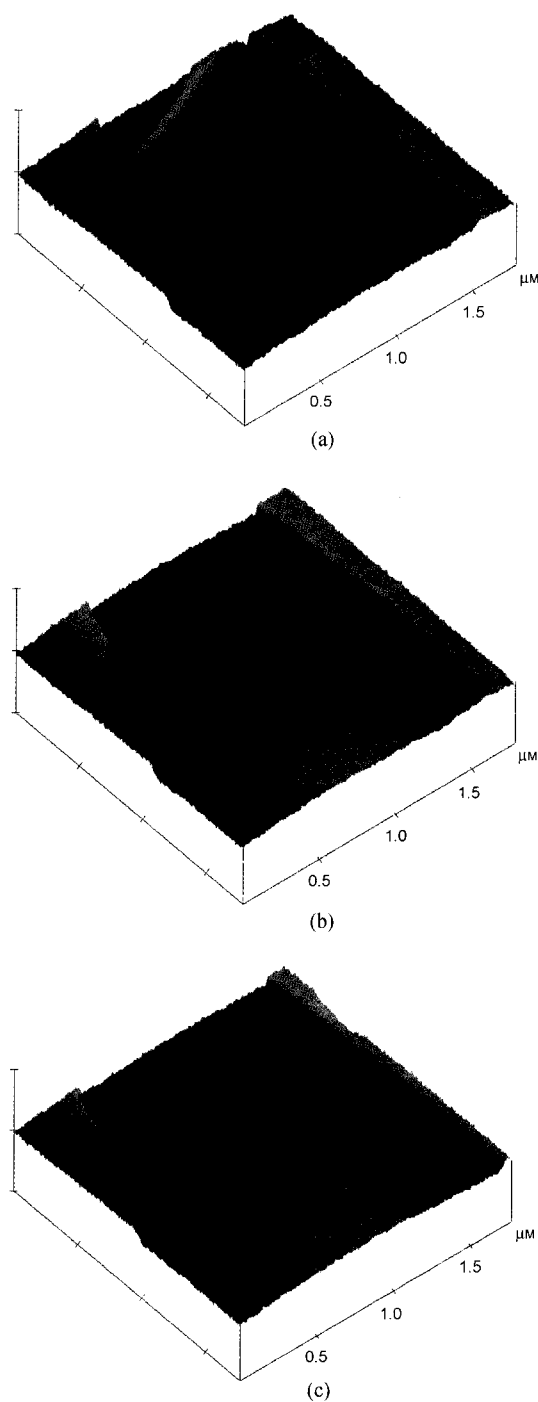


Fig. 6. SFM scan showing (a) a large flat region along the bottom of an etch pit, (b) a small dissolution pit nucleated by three extremely small SFM scans ($10 \times 10 \text{ nm}^2$) at a contact force of 270 nN, and (c) the same etch pit after 6 min, showing normal growth.

substrate contact area at these high contact forces. Once the pit is nucleated, growth continues in a fashion similar to that of randomly nucleated pits. Pits nucleated by this "nanoscratching" typically reach about three monolayers deep. The nucleation of a pit on a flat terrace requires significantly more energy than the nucleation of a double kink along a step—and therefore requires a correspondingly stronger mechanical stimulus (The Madelung energy of an ion in a terrace site is ~10% higher than a step site).

IV. Conclusions

We have shown that scanning across the edges of dissolution pits at high contact forces can increase the local dissolution rate by over an order of magnitude. Similar enhancements are observed when the SFM tip is used to produce an indentation near the edge of a dissolution pit. We attribute the dramatic difference in step velocities due to high contract force scanning to an increase in the rate of double-kink nucleation by elastic strains, Enhanced dissolution along steps adjacent to indents may also involve plastic strains as well.

In this work, double-kink nucleation by contact mode scanning also enhanced dissolution outside the scanned area, until the kinks reached a natural obstacle (the edge of the pit). Enhanced wear was not observed during scanning on board flat terraces, except at the smallest scan sizes. In the contest of cyclic wear, one would therefore expect little "corrosive wear" on atomically flat surfaces. As might be expected, surface roughening enhances not only normal mechanical wear but also the corrosive effect of chemically aggressive environments. Depending on the nanostructure of the surface roughness, enhanced corrosion may continue for many seconds after successive passes of a cyclic loading device. In the present context, delayed corrosion (during the "unloaded" portion of the wear cycle) may in principle be minimized by the addition of impurities which hinder kink motion.

Another clearly observed effect was the ability of step edges formed by chemical etching to promote the formation of nearby pits by indentation. In the context of corrosive wear, a chemical effect (corrosion) has enhanced a primarily mechanical effect by relieving the constraints against deformation on the perfect surface. Although sufficiently strong mechanical stimuli

(here $10 \times 10 \text{ nm}^2$ scanning at high contact forces) can nucleate etch pits at arbitrary positions on the surface, much weaker stimuli serve in the presence of nearby steps.

SFM is a valuable tool for the study of corrosive wear processes. Using the SFM tip to mechanically stimulate the surface allows for rapid, *in situ* observations of wear and corrosion on spatial scales of tens of nanometers and time scales of tens of seconds. This allows for the observation of corrosive wear on practically relevant time scales. No fundamental barrier would prevent similar studies in lubricants, for instance. Provided with suitably hard, chemically resistant SFM tips, such work may also be readily extended to much more corrosive environment.

Acknowledgments

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