NANOMETER SCALE TRIBOCHEMICAL MODIFICATION OF SURFACES

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ABSTRACT

Tribology shares a number of phenomena with investigations of deformation and fracture. With the advent of the atomic force microscope (AFM), tribological experiments were given the advantage over traditional crack growth studies of allowing intimate access to the interacting surfaces with highly controlled, localized stresses and measurable exposure to chemical stimulation. In the work to be presented here, we describe results of fundamental tribochemical studies of the simultaneous application of chemical agents and mechanical stress applied between a model single asperity and a solid surface at the nanometer size scale. We show the consequences of combining highly localized mechanical stress (due to contact with an atomic force microscope--AFM tip) and exposure to aqueous solutions. In many respects, our results share similar behavior to stress-corrosion crack growth in materials such as silica glass. A number of applications to nanotechnology and to the physics and chemistry of polishing surfaces by Chemical Mechanical Planarization-CMP are accessible by our techniques.

The tribological wear of ceramic and mineral-like surfaces is often greatly enhanced in the presence of a corrosive fluid. Examples are the wear of surfaces associated with joints (biomaterials) subject to and the extremely active application to high density circuit production which requires chemical mechanical polishing (CMP). The physics and chemistry of these enhanced wear rates are needed to reduce wear and to improve and extend CMP to new applications. In both situations, surfaces experience simultaneous tribological loading and corrosive chemical exposure, which together produce high wear rates and altered topography. In CMP, the goal is to efficiently achieve very flat surfaces. As feature sizes diminish further, it is conceivable that atomically flat surfaces will be necessary. In almost all tribological situations, it is the interaction of asperities, often micron and sub-micron in dimensions, that control the wear processes due to the high stresses associated with these small structures.

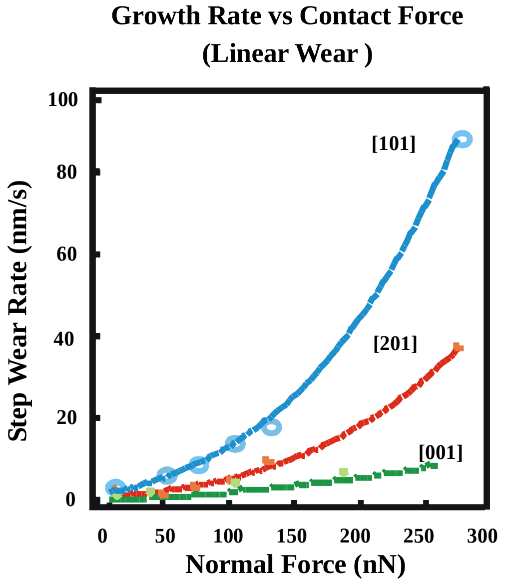
Growth Rate vs Contact Force (Linear Wear)

Fig. 1. Wear rate of atomic steps on brushite with three orientations vs. applied normal force.

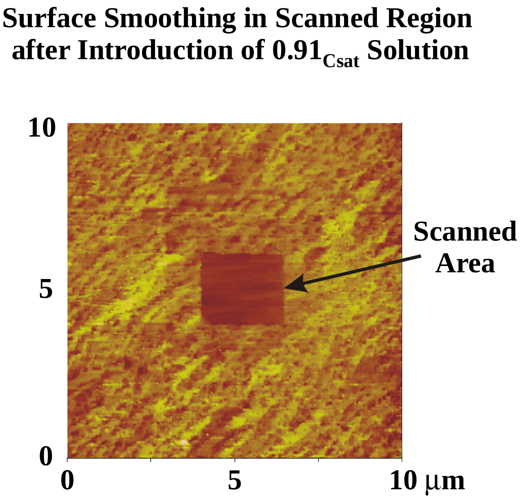
Surface Smoothing in Scanned Region after Introduction of 0.91_{Csat} Solution

Fig. 2. Atomically flat planarization on brushite in a nearly saturated solution of Ca^{++}, HPO_4^{2-} ions.

In our studies we employ scanning probe microscopy (AFM) of single crystal surfaces in mildly corrosive solutions, where the AFM tip provides the mechanical stimulation in a controlled fashion. The tip acts as a single asperity, thus providing the means to apply stresses in a highly localized manner. The applied normal force, the location of the contact, and lateral motion are readily controlled. For simplicity we choose model systems where the corrosive agent is water (properly buffered) and the single crystals are slightly soluble. These include calcite [$CaCO_3$] and brushite [$CaHPO_4$ $2H_2O$] (a model biomaterial). Silicon nitride tips are used with applied normal loads from 0-300 nN, tip radii 30 nm and tip velocities from 1-200 µm/s. Quantitative data on the role of normal force, lateral velocity, surrounding surface topography, and solution chemistry can be obtained from images of the wear of atomic steps. Figure 1 shows the normal force dependence of this wear for three different step orientations on the (010) surface of brushite. The wear rate is a highly non-linear function of applied normal force (essentially exponential). Our results are interpreted in terms of stressed enhanced dissolution of steps, where double kink nucleation is the rate limiting process. We present a model which fits data for all systems examined to date. Careful analysis of step stability explain the observed sensitivity of certain step orientations to the enhanced wear induced by stress. Studies of atomically flat planarization of surfaces produced by controlled scanning are presented. Figure 2 shows an example of planarization on an initially rough (~200 nm roughness), where the central region is made atomically flat.

Tip Induced Nanometer Scale Modification of Solid Surfaces in Chemically Active Solutions. Many biological, geological, and technological processes involve interactions of solid surfaces with chemically active solutions. This includes crystal growth/dissolution and polymer swelling and dissolution. In the case of crystals, the rate of growth and dissolution is controlled by the temperature and chemical composition of the solution on the one hand and the chemical composition, structure, and micro-topography of the crystal surface on the other. In particular, topographical defects (e.g., steps, kinks, and dislocations) and concentration gradients in both the solution and along the solid surface often determine the observed rates. The above scanning force microscope (AFM) observations show that increasing the stress applied by the tip strongly increases dissolution rates along atomic steps in a highly localized fashion on calcite and brushite ($CaHPO_4 \cdot 2H_2O$) cleavage surfaces.[1] We also show how a AFM cantilever tip can also be used to nucleate, accelerate, and control crystal growth and deposition at step edges on brushite crystal surfaces in supersaturated aqueous solutions.[2] We present strong evidence that the tip sweeps ions to nucleation sites, assisting them over a Ehrlich-Schwoebel type barrier.[3] This enhanced growth provides a unique means of generating nanometer scale structures and suggests new methods of controlling biomineralization.

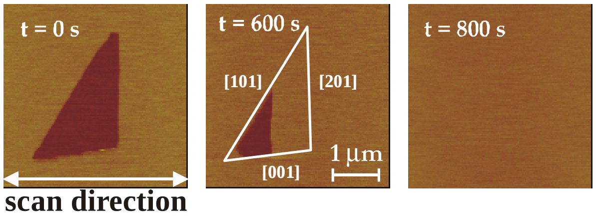

Fig. 3. A sequence of AFM images of a one atomic layer deep etch pit in a brushite (010) surface scanned a total of 23 times at a tip speed of 70 □m/s and normal force of 5 nN.

Although spontaneous dissolution is generally observed at etch pit steps at these supersaturations, localized, directional growth can be induced and propagated by repeatedly scanning over an etch pit at low normal forces ($F_N < 50$ nN). Growth produced by 23 scans at $F_N = 5$ nN and $\sigma = 5.3$ (highly supersaturated) is shown in Fig. 3, eventually producing an atomically flat surface. The growth direction is predominately along and normal to the [201] step. Images of etch pits outside the repeatedly scanned area typically grow larger, proving that deposition is indeed induced by the tip. Scanning at high normal forces (i.e., F_N>60 nN) immediately produces localized wear (dissolution) rather than growth. Spontaneous nucleation of hillocks at on-top sites along the [201] etch pit steps indicates a significant Ehrlich-Schwoebel type barrier. In supersaturated solutions, one expects the nucleation of transient, sub-critical, 3D deposits on the terraces (indirect evidence for these clusters will be presented using cantilever "noise" analysis). If the tip can detach and sweep some of the ions from these clusters over the step, this would increase the concentration of adsorbed ions on the pit surface near the [201] step and promote deposition. To test this hypothesis, we performed linear scans over [201] steps of exactly the same length (1.5 µm), normal force (10 nN), scan frequency (1.0 Hz), and number of scans (32) and supersaturation ($\sigma = 4.3$), but changed the fraction of the scan taking place on the top terrace (i.e., ratios of 1:10 vs. 10:1 in distance on top vs. in the pit). Figure 4 shows the measured growth rates for ten experiments, where we alternated between the two types of scans at 400 nm intervals along a single [201] step. When the majority of the scan took place on the top terrace, the growth rates were 2-3 times higher than when the majority of the scan took place on the lower terrace supporting a "sweeping" mechanism. Extension of these concepts to AFM modification of polymers will also be discussed.

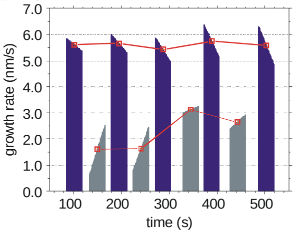

Fig. 4. Growth rates showing the increase when tip is sweeping on the top terrace vs. primarily in the pit.

These types of experiments have been repeated on single crystal calcite in saturated Ca^{++}, CO_3^{2-} solutions.

Tip induced interfacial fracture. We are also interested in the problems associated with removing adhering nanoparticles to surfaces. When an AFM tip encounters a sufficiently large particle, the lateral force applied by the tip can produce significant shear stresses. If this stress is great enough, the particle can be literally fractured from the substrate. However, the required stress can be prohibitive in the absence of a chemically active ambient environment. In this work, we study a model particle substrate system involving salt particles bonded to soda lime glass. Modest partial pressures of water vapor dramatically lower the lateral force required to fracture the salt-glass bond as the SFM tip is drawn across the particle. Particle size also affects the interfacial shear strength, presumably due to variations in the size of interfacial flaws relative to the total interface area.

Submicron-sized NaCl crystals were deposited on soda lime glass substrates by dissolving a few grains (~ 1 mm^3) of commercial salt in a drop of de-ionized water on a clean microscope slide. The solution was spread across the slide with a cotton swab and allowed to evaporate to dryness. Both evaporation and sample storage were under ambient laboratory atmosphere conditions—typically 20-40% relative humidity (RH).

Particle observation and manipulation were performed on the stage of a scanning force microscope mounted in a closed chamber. The humidity was adjusted by introducing a controlled mixture of dry and humidified air. The RH in the chamber was continuously monitored with a BioForce Laboratory humidity sensor. Humidity variations in the course of an experiment were controlled to ± 1% absolute RH, with an estimated uncertainty of ± 2% absolute RH. This work employed triangular, 115-µm long, “wide” Si_3N_4 cantilevers from Digital Instruments of Santa Barbara, CA.

Images taken before and after particle detachment are shown in Fig. 5. A suitable particle was located in a high scan rate (typically 42 µm/s), low contact force image (5-20 nN). After zooming in on the chosen particle [Particle A in Fig. 6(a)], the scan rate was reduced to 0.20 µm/s. Scanning was continued until the tip was positioned to cross the center of the chosen particle [the white line in Fig. 5(b)]; then the contact force raised to a high value (≤ 320 nN). After a single, high contact force sweep across the particle, the contact force was lowered and the scan rate increased to normal values for imaging. Finally, large area scanning was resumed to search for the detached particle, marked A' in Fig. 5(b). At higher relative humidities, locating the detached particle was often difficult. Circumstantial evidence suggests that the absorbed water film can bind the detached particle to the SFM tip, which then drags the particle across the surface.

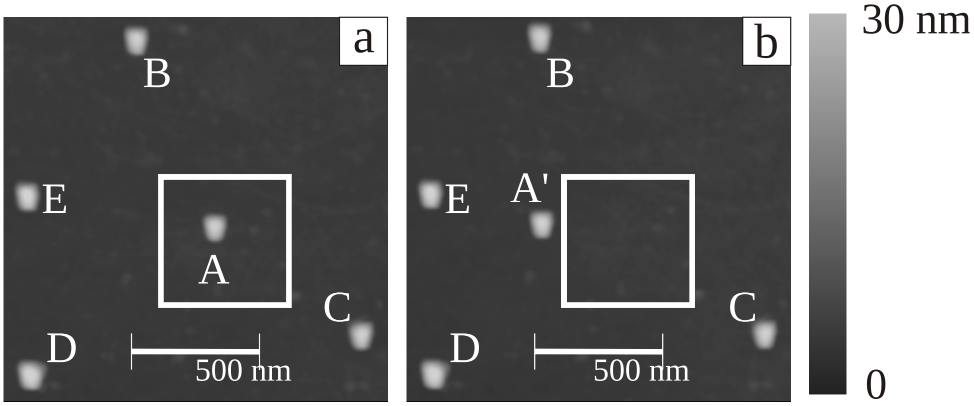

Fig. 5. Low contact force images of NaCl particles (a) before particle detachment, and (b) after particle detachment. The line in (b) shows the orientation of the linear scan used to detach Particle A, which was subsequently found at Position A'.

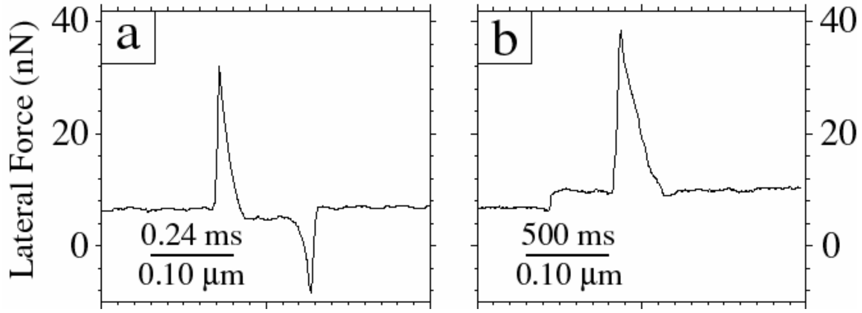

Fig. 6. Lateral force signals during (a) a low contact force scan while aligning the tip on the particle, and (b) the slow, high contact force scan used to detach the particle from the substrate. In (b), the stepwise increase in lateral force coincides with the increase in normal force (not shown), and the sharp peak corresponds to the completion of crack growth along the particle-substrate interface.

The lateral force signal during a typical scan prior to particle detachment at 10% RH is shown in Fig. 6(a). This scan was acquired at a low normal force (10 nN) and high scan rate (42 μm/s). The lateral force as the tip passes over the salt particle is significantly lower than the lateral force as the tip passes along the glass, reflecting salt's lower coefficient of friction. At 3% RH, the ratio of the lateral force measured along the salt to that measured along the glass ranges from 0.20 to 0.25. As the RH is increased to 68%, this ratio increases to 0.7. This increase is related to the high affinity of water for NaCl; at high RH, capillary forces may contribute to the measured lateral force along the salt.

Dividing the peak lateral force measured during detachment by the particle area, A, yields the nominal shear strength of the interface, σ_c. Nominal shear strengths determined for a large number of particles are displayed in Fig. 7(a) as a function of particle area for several relative humidities. We have scaled the failure stress for 3% RH (reduced by a factor of ten) for presentation purposes; the smallest particle at 3% RH failed at $\sigma_c = 55$ MPa! Raising the humidity from 3% to 11% dramatically lowers the interfacial shear strength. Increasing the particle size also tends to reduce σ_c. Both effects impose experimental limits on the size of particles amenable to study at the lowest humidities, where the SFM tip may break before a large particle will be detached. This is consistent with anecdotal reports of the difficulty of removing small particles under dry conditions. Importantly, increasing the humidity beyond 50% has little additional effect on the shear stress at failure. Similarly, the particle-size dependence becomes weak for particles with contact areas larger than about 3000 nm^2.

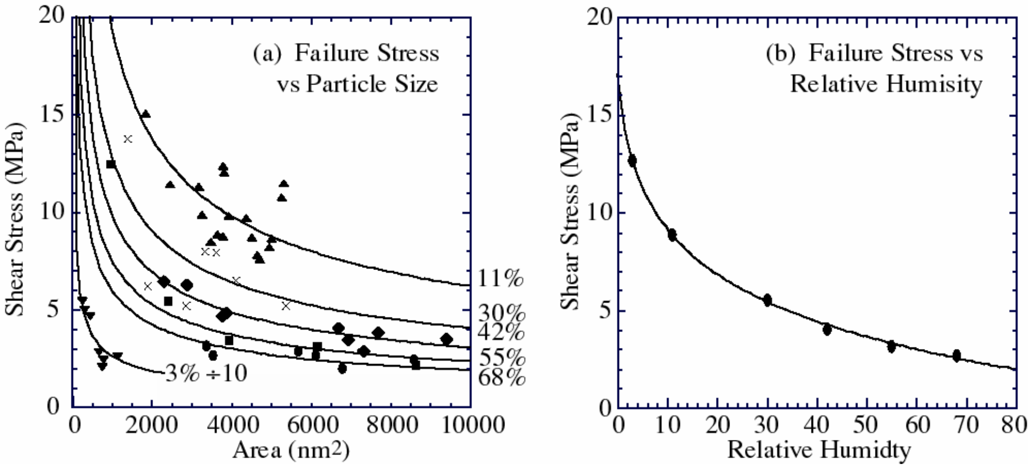

Fig. 8. Nominal shear stress at failure as a function of (a) particle/glass contact area at relative humidities ranging from 3% to 68%, and (b) relative humidity for a fixed particle size of ~5000 nm^2. The dark lines in (a) represent one-parameter, least squares fits to the data of the form $\sigma_c \sim A^{-1/2}$.

Figure 7(b) shows the nominal shear strength as a function of humidity for a set of particles with contact areas of ~5000 nm^2. The failure stress drops rapidly with increasing RH at the lower humidities, and falls more gradually at higher humidities. The dark line represents a least squares fit of the data to a model based on the expected dependence of interfacial binding energy on humidity.

References

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