An AFM study of the tribological properties of NaCl (100) surfaces under moist air

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Abstract

Water molecules in the air play a very important role in the modification of the physical and chemical properties of NaCl surfaces. In this paper, we report on the dependence of the friction force between this alkali halide and a Pt-coated tip on the external load at different humidity levels. The results clearly demonstrate that the tribological properties of the surface are modified by water adsorption. We also found that at high humidity and below a certain threshold load, the water layer can act as a lubricant. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The condensation of water on alkali halide surfaces under ambient conditions is an important environmental process that has been studied for a long time. NaCl, the most common salt in the environment, is the subject of numerous studies. Below 76% relative humidity (RH), the deliquescence point of NaCl, a layer of water molecules is adsorbed on the NaCl surface. The adsorbed molecules can induce chemical reactions, such as that of HNO_3 with NaCl [1]. It was found with atomic force microscopy (AFM) that, at a RH of ~52%, the surface steps become mobile [2]. To eliminate

the possible influence of the contact forces between the AFM tip and the NaCl surface, Dai et al. used a non-contact technique called Scanning Polarization Force Microscopy (SPFM) [3]. They found that, even in the absence of contact, the steps began to move at ~45% RH. At a higher humidity (73% RH), they found that the steps are no longer stable and disappear abruptly due to dissolution. They concluded that a uniform layer of water is formed above ~35% RH, whereas at a lower RH, water adsorbs primarily at step edges. Their results agree with those from surface conductivity measurements [4] that indicate that a monolayer of water is completed at ~40%.

In this paper, we present our studies on the humidity dependence of friction and adhesion between a Pt-coated AFM tip and a freshly cleaved NaCl(100) surface. As we shall see, there is a clear correlation between the earlier structural findings and the tribological properties of NaCl.

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2. Experimental

The experimental setup consists of a home-made AFM head inside a humidity-controlled chamber. All the experiments are carried out at room temperature (~ 22–$23°C$). Humidity is reduced by flowing dry nitrogen through the chamber (RH could be lowered to below 5%), and increased by vaporizing deionized water (RH could be increased up to 90%). An RH-20C Omega hygrometer is used to measure the humidity with an accuracy of $\sim 2\%$.

We used silicon nitride cantilevers (Digital Instruments, Santa Barbara, CA) with a nominal spring constant of 0.58 N m^{-1}. The tip and lever are coated with a 50-nm-thick layer of Pt to make the tip conductive for our electrostatic force measurements (not reported here). The Pt-coated tips are also found to be more hydrophobic, which reduces capillary effects during scanning. The friction results used for comparison at different humidity levels were obtained with the same tip to eliminate the variation of spring constant in different levers and the influence of the tip shape. The typical radius of the tip is ~ 50–60 nm.

The NaCl crystal was cleaved along the (100) surface under ambient conditions (~ 40–45% RH), and mounted on the scanner. All experiments were conducted within the first few hours after cleavage to minimize contamination. In most cases, contamination effects were unobservable.

To study the correlation between friction and topography, normal and lateral lever deflection images were acquired simultaneously. The dependence of the friction force on load was determined in a different imaging mode, which is described in detail elsewhere [5,6]. Briefly, the normal lever deflection and the friction force are measured simultaneously while the tip is scanned repeatedly along the same x-line (except for the drift). The load is kept constant in each line but increased stepwise from one line to the next. To acquire a complete friction force curve, the load is first increased up to a maximum value and then decreased until the pull-off point. The average value of the friction force in each scan line is used in the construction of the friction vs. load curves during the loading (approaching) and unloading (retracting) parts of the cycle. The scanning speed is ~ 100 nm s^{-1}.

3. Results

3.1. Structural effects

In order to study the dependence of friction on humidity, contact AFM images are acquired together with friction images. We did not observe, even at a very low humidity, any increase of friction at the step edges relative to that on the flat terraces, as was reported by Meyer et al. [7], which is probably due to the difference in imaging conditions. Their sample is cleaved in vacuum and transferred to a dry N$_2$ environment. Therefore, during their sample preparation process, there should be no water condensed on the NaCl surface. However, in our case, water condenses preferably at the steps at low humidity and completely covers the surface at higher humidity, as shown by Dai et al. [3], and this could explain the different observations.

In our experiment, we find that, at a critical point of $\sim 45\%$ RH, many of the surface properties changed. At an RH below 45%, contact images are repeatable, and no wear effects could be detected at loads less than 100 nN. Under those conditions, atomic lattice resolution is routinely obtained, and the steps are stable. At $\sim 45\%$ RH, however, we observed mobility of the surface steps, similar to the observations already reported by Dai et al. [3].

3.2. Friction and adhesion measurements

The results of our measurements of friction vs. load for several values of RH are shown in Fig. 1. The x-axis is the externally applied load (lever bending), which is positive (lever bending away from the surface) for $x > 0$ and negative (lever bending towards the surface) for $x < 0$. This is due to the adhesion, mostly from capillary forces. The first trend that can be observed among these curves is that, for a given load, the friction force increases with humidity. When the RH is equal or less than 45%, the approach and retract curves overlap each other. This shows that the interaction between the AFM tip and the NaCl(100) surface is predominantly wearless. Above 45% RH, the approach and retract curves have different slopes, and the
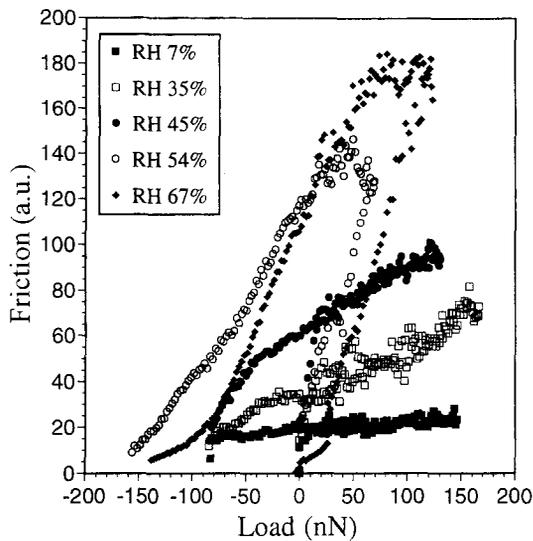
Fig. 1. Friction force vs. load at different humidity levels between a Pt-coated tip and a NaCl (100) surface. The loading and unloading curves overlap at positive loads when RH is equal or less than 45%, whereas a strong hysteresis is observed when RH is over 45%. Except at the lowest loads, the curves tend to become straight lines as the load increases.

two curves do not overlap. This hysteresis indicates that structure modification processes are taking place. It also suggests that the coverage of water molecules reached a critical value. It was argued by Hucher et al. [4] that, at ~40% RH, a monolayer of water is completed. This is close to the 45% value where we observe the transition from reversible to hysteretical friction–load behavior. However, even in the latter case, large area images acquired after the friction measurements did not reveal any modification of the scanned area, such as holes or wear tracks. This indicates that the damage heals very rapidly or is too small to be observed. For comparison, we followed the recovery of a deep hole (~10 nm in depth) on the NaCl surface produced by the tip at a very high load (>100 nN) and found that, at ~60% RH, this hole disappears in about 2 or 3 min due to refilling.

It is known that in many cases, the friction force F_f for an elastic single asperity contact (such as an AFM tip scanning over a flat surface) is proportional to the contact area $F_f = \tau A$, where τ has the dimensions of a shear strength. (For a review of the application of these models to AFM,

see Ref. [8].) However, the relationship between contact area, A, and load is complicated. In the elastic regime, several models have been proposed to explain the variation of A with load. The JKR model is suitable to describe short-range adhesion between soft materials, whereas the DMT model is more appropriate when long-range forces are responsible for the adhesion between hard materials [7]. Under dry conditions, i.e. NaCl crystal cleaved in a vacuum chamber and never exposed to air, Meyer et al. [7] found that the JKR model adequately described the friction behavior of NaCl(100). However, if water is adsorbed on the NaCl surface, the physical and chemical properties of the surface may change. We found that, even at the lowest humidity achieved in our chamber, the curves do not fit with any of the models mentioned above. Instead, at each humidity and at sufficiently high load, friction increases nearly linearly with load. This can only be explained by a strong dependence of τ on pressure. Although this dependence is negligible under dry conditions [7], it becomes much more important when a water layer is adsorbed on the NaCl surface, and is even dominant at high humidity.

There is also the possibility that, at a high load, the contact is no longer single-asperity, but multi-asperity, as proposed by Putman et al. [9], when they studied the friction–load dependence on mica. Under this case, the friction force could increase linearly with load.

If we measure the slope of the linear part of the friction–load curves, we find that it increases with humidity (Fig. 2a). There is a jump in the value of the slope at ~45% RH, which also indicates that a significant change in surface properties occurs at this point.

The adhesion force between the Pt tip and NaCl, as measured by the pull-off force, shows two different regimes as well: below 45% RH, it is ~80–100 nN and, above 45% RH, it jumps to ~140–160 nN (Fig. 2b). This sudden increase can be explained as being due to an increase in the capillary force when a water monolayer is completed.

One unexpected observation is the very slow increase in friction at very small loads in the loading process when the RH is 67%. At this low-
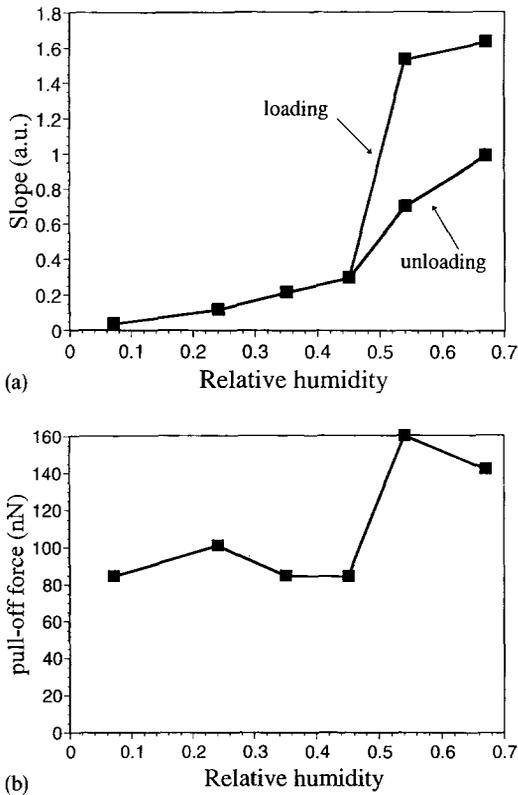
Fig. 2. (a) Slope of the linear part of the friction curves as a function of relative humidity. (b) Pull-off forces vs humidity. A clear change can be observed when RH is more than 45%.
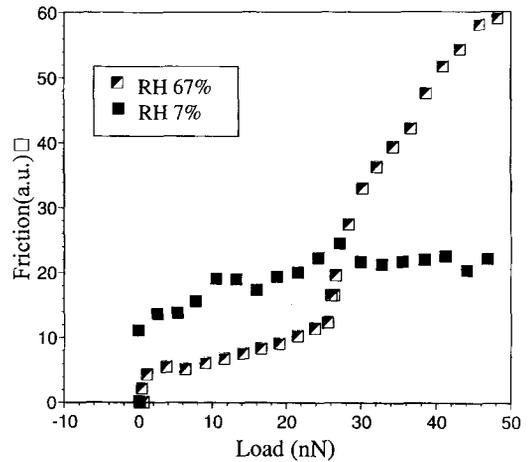

Fig. 3. Expanded view of the low-friction curve region obtained at 67% RH in Fig. 1. The friction–load curve at 7% RH is also plotted for comparison. Note the rather abrupt change from a low-friction region to the higher one at ~26 nN.

load regime, the friction is even lower than that in the drier cases (Fig. 3). It is possible that this is due to the presence of a liquid film several molecules thick and containing hydrated ions. Such a film may start to form when the RH is above 45%. Then, the unusually low friction force at low load can be explained by the tip sliding over this layer of liquid, which acts as a lubricant. It is possible that the tip contacts the liquid surface at low loads without penetrating it. In this model, the critical load for the tip to penetrate the liquid layer is ~26 nN for the 50–60 nm tip radius at 67% RH. Above this load, friction increases much more quickly.

There is also a low-friction regime in the unloading process at 67% RH (Fig. 1). Here, the transition from a low- to higher-friction regime is relatively smooth compared with that in the load-

ing process. This can be explained as a result of capillary effects. Close inspection of the unloading force–distance curve (Fig. 4) shows that, at a RH higher than 60%, the pull-off is not a simple jump-out. Instead, a couple of stages are observed that can be interpreted in the following way. First the tip detaches from the solid part of the substrate but still forms a water bridge (point A to point
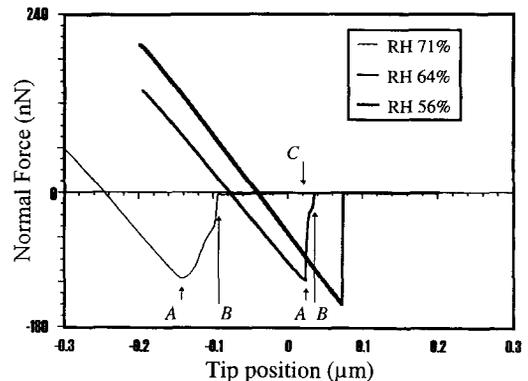

Fig. 4. Force–distance curve during the unloading process at different humidity levels. At 64% RH, the pull-off occurs in two stages. The first, marked by A, corresponds to the rupture of the tip–solid NaCl contact. This is followed by the extension of a liquid bridge due to the capillary effects. This bridge breaks at point B. At 71% RH, a third break-point C is observed at a much greater distance (>100 nm).

B), and then the bridge ruptures (point *B*). When the RH is as high as 71%, the meniscus may extend up to 40 nm. Sometimes, the neck of the bridge can suddenly reduce its diameter during the retraction of the tip, and the narrower neck can extend to more than 100 nm (point *B* to point *C*). Under these conditions, the tip is out of contact with the NaCl surface, and friction is consequently reduced.

The difference in friction behavior between 54 and 67% RH in the low-load regime could be due to the structural effects of the adsorbed water film. To explain the existence of the low-friction region in the loading process (Fig. 3), we propose that the hydrated ions on the NaCl surface play a very important role. The water film hydrates ions from the NaCl that become mobile on the surface, and these ions induce a repulsive force (structural hydration force [10]) on the AFM tip during the scan. At small separations of the tip and NaCl surface, the hydration repulsive pressure should increase exponentially with decrease of distance. This force is often observed between two surfaces in solution. When the water layer is sufficiently thick, this repulsive force may be strong enough to support the tip at a low load, and the tip can slide on the liquid film. As a result, at a low load, we may measure the friction on the liquid film that is acting as a lubricant. In our experiment, this critical density seems to be achieved between 64 and 67% RH. Recently, Shindo et al. [11] observed a steep increase of the speed of monatomic step motion at ~63–66% RH. They proposed that, beyond this point, water adsorbs on NaCl in a 3D manner, whereas below this point, the adsorption is in the form of 2D water clusters. Whereas our data cannot determine the growth mode of water, they clearly indicate that, at an RH within this range, a particularly stable structure of hydrated ions is achieved.

4. Conclusions

We studied the influence of humidity on the tribological properties of NaCl (100) surfaces, and found that friction forces increase with humidity. The friction–load curves are the same during loading and unloading (except, of course, in the negative load region) at humidity levels below 45%.

However, they are highly hysteretic at a higher humidity. The critical humidity separating the two regimes, ~45% RH, is close to the 40% value found in previous studies corresponding to the completion of the water monolayer.

A new, unexpected phenomenon was observed. At low loads during the loading process, below 26 nN in the present study, a region of unusually low friction is detected at ~67% RH. We propose that this low friction is due to the tip sliding on top of a trapped layer of hydrated ions in the water film. This film acts as a lubricant under these conditions.

Acknowledgements

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