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Tip-Induced Calcite Single Crystal Nanowear

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ABSTRACT

Wear behavior of freshly cleaved single crystal calcite ($CaCO_3$) was investigated by continuous scanning using the Hysitron Triboindenter in ambient environment as a function of scanning frequency (1 Hz – 3 Hz) and contact load (2 μN – 8 μN). At lower loads below 4 μN, initiation of the ripples takes place at the bottom of the surface slope, which continue to propagate up the slope as scanning progresses. The orientation of these ripple structures is perpendicular to the long scan direction. As the number of scans increases, ripples become fully developed, and their height and periodicity increase with the number of scans. At 6 μN normal load, tip-induced wear occurs as the tip begins removing the ripple structures with increased number of scan cycles. As the contact load increased further, ripples did not initiate and only tip-induced wear occurred on the surface, and saturated after 20 scans. At 1 Hz frequency wear takes place as material slides towards the scan edges when the tip moves back and forth. Material removal rate increased with contact load and it is observed that the number of scans required to create a new surface is inversely proportional to the contact load. Possible mechanisms responsible for the formation of ripples at higher frequencies are attributed to the slope of the surface, piezo hysteresis, system dynamics, or a combination of effects. The wear regime is due to abrasive wear. Single crystal calcite hardness of 2.8±0.3 GPa and elastic modulus of 75±4.9 GPa were measured using nanoindentation and used to determine the wear mode.

INTRODUCTION

The development of the nano-mechanics field over the past few decades produced a significant amount of methods for determination of mechanical and tribological properties of materials at micro and nano scales. Among others, nanoindentation and micro/nanotribology methods have been considerably developed, including depth sensing nanoindentation and Atomic Force Microscopy (AFM)/Scanning Tunneling Microscopy (STM). These are powerful and versatile tools for surface topography characterization and local mechanical properties measurements at small scales. In addition, it is possible to utilize the scanning nanoindenter capable of modifying the materials structure. As the use of coatings constantly increases in the field of nanotechnology, it is important to know the behavior of materials at small scales. In recent years the formation and characterization of nanometer-sized structures have attracted a great deal of interest.

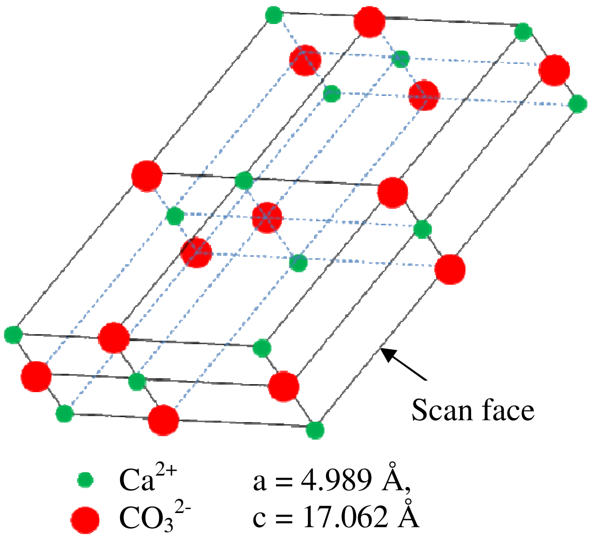
One of the nanotechnology research motivations is the construction of nanosized surface patterns. In a typical wear experiment a hard material is scanned over the tested material surface, resulting in a wear rate measurement in terms of the removed material depth or volume as a function of normal applied load and the number of wear cycles. When applying moderate forces in combination with repeated scanning over the same region, one could observe a periodic ridged pattern, called wear ripples, oriented perpendicular to the tip motion direction. These nanopatterns or ripple structures can also be produced by other methods such as erosion of materials by ion sputtering and by abrasive particles bombardment. Under off-normal ion-beam incidence, a periodic height modulation in the form of ripples or wavelike structures with submicron wavelength develops during low-energy ion bombardment of single crystalline Si (100) [1], single crystalline metals [2] and glasses [3]. Recently, Krok *et.al.* found that ion bombardment of InSb at an oblique angle of incidence led to the formation of wire-like structures on the surface with a diameter of tens of nanometers [4]. Tip-induced nanopatterns or nanowear ripples on the material surface can be produced by scanning it repeatedly for a number of cycles and applying moderate normal forces using AFM or scanning Triboindenter. Although the main AFM function is imaging surfaces, it can also scan them continuously and modify their structure. The Triboindenter is mainly used for measuring hardness and elastic modulus at the nanoscale. Using the Triboindenter scanning feature, one can produce nanowear ripples or nanostructures on the material's surface. The interaction between the tip of the scanning probe apparatus (AFM or the Triboindenter) and tested surface is a complex process, which depends on material properties and the scanning parameters. By varying the applied force and scanning speed, tested material surfaces can exhibit different regimes of wear caused by the tip.

Initially tip-induced wear patterns were observed in InSb crystals using atomic force microscope in the ultra high vacuum environment (UHV-AFM) [5]. Few tens of nanonewtons of normal load were applied to scan repeatedly over the 1x1 μm^2 InSb (100) surface, which resulted in a creation of ripples perpendicular to the scan direction. Ripple patterns were not observed when repeated scanning was performed in the ambient environment with AFM. Similar experiments have been conducted on KBr and Al single crystals in the ambient environment using a nanoindenter [6]. Ripples were observed on KBr after 20 scan cycles at 3 Hz scan frequency over a 5x5 μm^2 surface area with a 2 µN normal force. The height of the ripples was 100 nm, and they were spaced 1 µm apart. Tip-induced wear ripples were also reproduced on gold samples in the presence of water using the Hysitron Triboindenter [7].

In this work, we made an effort to produce tip-induced nanowear ripples on calcite single crystals using a diamond Berkovich tip of the Hysitron Triboindenter in ambient environment. The objective was to replicate the nanowear ripples observed in the UHV-AFM and to determine the mechanism responsible for the formation of these ripples.

EXPERIMENTAL DETAILS

Freshly cleaved natural calcite single crystal was scanned repeatedly in the ambient environment using a Hysitron Triboindenter. This tool has the ability to continuously scan the material surface, while producing surface topography images. The piezo scanner of the Triboindenter can scan 80x80 μm^2 or less square area using a rigidly fixed diamond tip. Tip-induced wear patterns were observed as a function of scanning frequency (1 - 3 Hz) and normal load (2 - 8 µN). Scanning speed of the tip depends on the frequency and the scan size. For 20x20 μm^2 scan size, the velocity of the tip will be 120 µm/sec at 3 Hz scanning frequency. Tip-induced wear was achieved by repeated scanning of 20x20 μm^2 areas of the calcite surface at varying loads and frequencies. At 3 Hz scanning frequency wear ripples started initiating during the first scan and propagated as the number of scans increased. Similar results were obtained on KBr and Al single crystals [6] in the ambient environment using the same system as well as using UHV-AFM on InSb semiconductor surface [5]. As the contact load increases beyond 6 µN, material started moving to the scan edges and ripple structures were never initiated. Similarly, at 1 Hz scanning frequency, a ripple structure was not initiated and wearing of the surface layer took place.



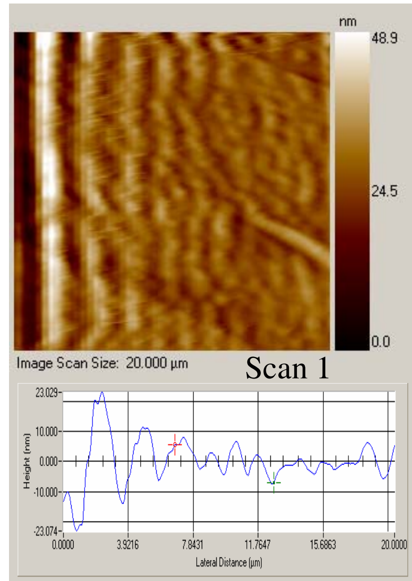


Figure 2. Calcite crystal structure. Adapted with permission from "Calcite: structure". Encyclopedia Britannica Online.

Figure 2. Topography of the calcite surface at 3 Hz frequency and 2 µN normal load and its profile taken at the center.

Calcite has a chemical formula of $CaCO_3$, and is one of the most widely distributed minerals on the Earth. Figure 1 shows the true unit cell (2[$CaCO_3$]) of the acute rhombohedron calcite crystal structure.

Figure 2 shows the topography image and the line profile of the calcite single crystal after the first scan. Here, the surface horizontal slope is ~200 nm over a 20 µm scan length. Ripples initiated at the bottom of the surface slope during the first scan. As scanning continued, ripples propagated towards the other end of the scan edge, and the ripples orientation was perpendicular to the long scan direction.

RESULTS AND DISCUSSION

Figure 3 shows a series of calcite topography images after repeated scanning at 3 Hz frequency, 2 µN and 6 µN normal loads at the intermittent scans. At 2 µN normal load, ripples started initiating during the first scan and propagated as scanning progressed. One could see ripples on the surface with a periodicity of 2.3 µm after 10 scan cycles. They merged together after 10 scans and the rms surface roughness increased as the ripples height increased from 30 to 145 nm at the end of 130 cycles. Even after 130 scans, ripples with higher periodicity can be seen and the top layer of the surface was not completely removed. At 6 µN, no ripples were initiated during the first scan, while they started to appear after five scans at the bottom of the surface horizontal slope and propagated towards the other scan edge as scanning continued. The initial ripple height was 55 nm and as scanning continued, the ripples height decreased to 42 nm due to surface wear. As the number of scans increased, the tip started removing the ripples on one end, while propagating them at the other end of the scan edge. One can clearly see material removal from the surface as the scanning progressed with ripples periodicity decreased from 3.4

to 2.5 µm. After 28 scans, next surface layer of the calcite appeared and all the ripples were swiped away to the scan edges. When normal load increased above 6 µN, ripples were not initiated on the crystal surface and the tip started removing the calcite surface layer, and material wear took place. A trench, 10-15 nm deep is observed after 30 cycles, which corresponds to about 10 top unit cells of calcite removed.

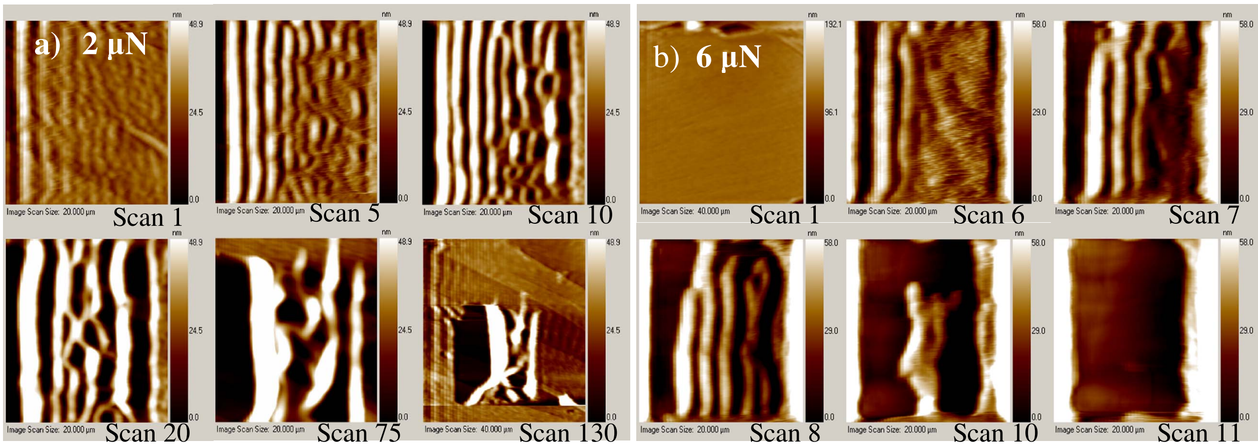


Figure 3. Topography images of calcite after repeated scanning, showing ripple initiation and propagation as scanning progressed at a) 2 µN and b) 6 µN normal load.

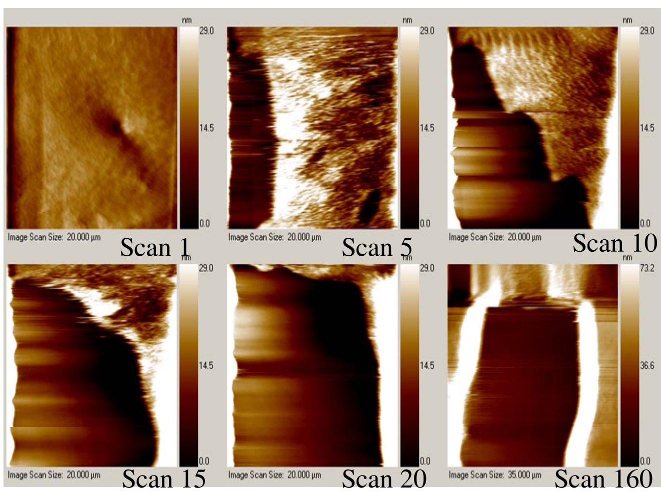


Figure 4. Topography images of calcite after repeated scanning at 1 Hz scanning frequency and 2 µN normal load.

Figure 4 shows series of topography images of the calcite surface at 1 Hz scanning frequency and at 2 µN normal load. In this case, calcite surface topography has a horizontal slope of 280 nm over 20 µm. Ripple structures were not initiated at these scanning parameters and as the scanning continued, the tip started removing the material from the bottom of the slope instead of forming ripples on the surface. The top surface calcite layer was completely removed after 20 scans without forming the ripples.

A trench, 15 nm deep can be seen after 20 scans at this frequency and normal load. As the load increased to 6 µN, the tip started removing the calcite surface at a faster rate and no ripples were initiated. A new surface layer could be seen with less number of scans when compared to the previous case and a trench of 15 nm deep can be seen after 10 scan cycles. From the initial surface topography images, it is clear that the surfaces had a horizontal slope in the range between 100 nm and 200 nm for the 20 µm scan length. It was observed that in all cases ripples initiated and started propagating at the bottom of the slope, i.e. at the left side of the scan edge, which is attributed to the sample tilt. Similar behavior was seen in KBr in the ambient environment using Hysitron Triboindenter [6] and on the InSb semiconductor surface in the

UHV-AFM [5]. A possible mechanism for the initiation of ripples is due to piezo hysteresis and surface slope. While the indenter is moving up along the surface slope, the piezo will work against gravity. Since the indenter scans the surface with constant velocity, the piezo takes little time to respond when indenter is in transition motion from forward to backward direction and vice-versa. This response time in the piezo could cause digging effect of the tip into the sample, which causes initiation of the ripple structure. As the ripple pattern behavior was observed at a relatively high frequency of 3 Hz, and removal of surface material occurred at a lower frequency of 1 Hz, the self-excited vibration of the tip could have caused the ripples to propagate along the surface of the crystal. This phenomenon is equivalent to chatter observed at the macroscopic scale [8, 9].

Figure 5 shows the wear behavior of the calcite single crystal at 1 Hz frequency and 2 μN normal load. Tip-induced wear in the negative z direction linearly increased for 6 cycles, removing approximately 15 calcite unit cells, and then saturated as scanning progressed further. This might be attributed to the hardening of the surface or dislocation density increasing during scanning. Tip-initiated material removal along the scan edge from the bottom slope increased as scanning continued. This lateral wear removal is approximately linear with the number of scans.

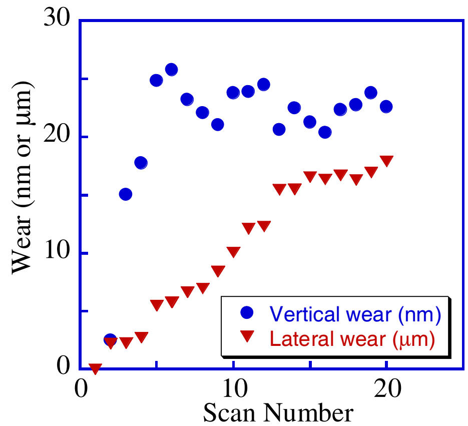


Figure 5. Wear behavior of the calcite single crystal at 1 Hz frequency and 2 μN load.

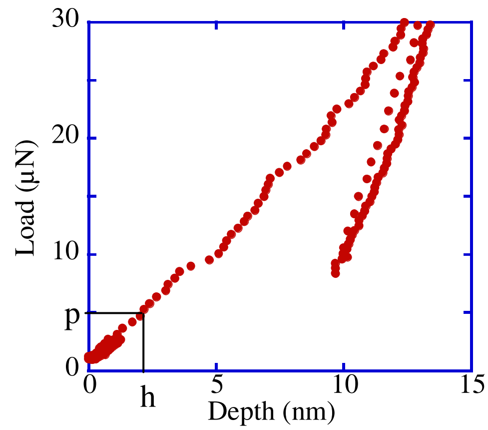


Figure 6. Load-displacement curve of calcite single crystal showing contact depth determination.

Single crystal calcite hardness and elastic modulus were measured using the Hysitron Triboindenter with the diamond tip. In this measurement, partial loading and unloading cycle was used to evaluate these properties as a function of contact depth. Figure 6 shows part of the partial loading and unloading load-displacement curve. The contact pressure under the tip surface was measured from the normal load applied while scanning over the corresponding contact area. Contact area was calculated from the geometry of the tip and contact depth corresponding to the normal loads. Figure 7 shows the hardness (2.8±0.3 GPa) of the calcite single crystal as a function of the contact depth and the values corresponding to the horizontal lines show the contact pressures applied by the tip during the scanning at various normal loads. At small loads, it is evident that contact pressure is greater than the hardness of the calcite single crystal and tip-induced plastic wear of the material takes place during scanning. Figure 8 shows the calcite single crystal elastic modulus of 75±4.9 GPa, which does not vary significantly with the contact depth.

CONCLUSIONS

Formation of tip-induced nanowear ripples was studied on the surface of single crystal calcite in the ambient environment using a Hysitron Triboindenter. Ripple structures were observed at different contact loads and at different frequencies by scanning the surface repeatedly with a Berkovich diamond tip. At 3 Hz scanning frequency, ripples initiated at the bottom slope of the scanned surface and propagated as the number of scans increased at lower loads below 6 μN. At 1 Hz scanning frequency, only material removal on the surface was observed and ripples did not initiate. Similar experiments were also conducted on InSb, Si, GaAs, and Quartz single crystals, and polycrystalline Bismuth. It was observed that nanoripples did not initiate in these materials.

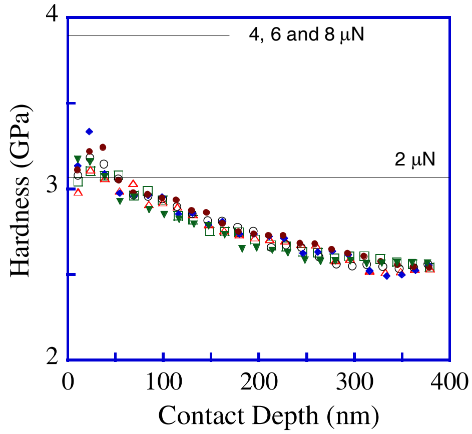


Figure 7. Calcite hardness and contact pressure under varying normal loads.

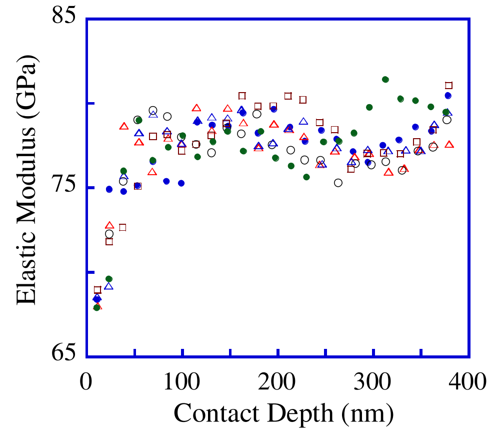


Figure 8. Elastic modulus of the calcite single crystal.

ACKNOWLEGDEMENTS

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