Frictional Asymmetry and Wear Pattern Formation by Slip and Cleavage Detected at Directional $r\{1\ 0\ -1\ 4\}$ Face of Calcite (CaCO_3)

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Frictional force was measured on directional calcite ($1\ 0\ -1\ 4$) surface, where triangular carbonate ions are all tilted to $[4\ 2\ -1]$ direction. With the normal load $< 49\text{ mN}$, observed frictional asymmetry, $+[4\ 2\ -1] > -[4\ 2\ -1]$, was the same as that measured in nm-scale. In the higher normal load range, a new component was added to the friction in $-[4\ 2\ -1]$ direction, and the asymmetry was reversed. Only in the direction of stronger friction, characteristic triangular deformation patterns were formed. Microscopic observation after indentation experiments revealed that the patterns were formed by slip on $c\ (0\ 0\ 0\ 1)$ faces on one side of the stylus, followed by cleavage on $r\{1\ 0\ -1\ 4\}$ faces. A mechanical model was proposed to explain why the deformation occurs only in one quadrant of the surface. The result of scratch perpendicularly in $[0\ 1\ 0]$ direction, also supports the mechanism of deformation. The results show when and how the contribution of plastic deformation is added to intrinsic surface friction and affects the frictional asymmetry. The frictional force in the $-[4\ 2\ -1]$ scratch increased linearly with the total lengths of the traces of c -slip.

Keywords: frictional asymmetry, CaCO_3 , single crystal, deformation mechanism, slip, calcite

1. Introduction

Friction measurements in nanometer-scale at single crystal surfaces with frictional force microscopy (FFM) [1,2] often show clear anisotropy and asymmetry due to periodicities of atomic arrangements [3,4], surface corrugation [5], and tilts of long-chain molecules [6-8] or chemical bonds [9-13]. In previous measurement of anisotropy at $(0\ 0\ 1)$ surfaces of alkali halide and MgO , for example, the alternate arrangements of different ions in $[1\ 0\ 0]$ direction gave about twice as strong friction as the arrangement of the same atom in $[1\ 1\ 0]$ direction [3]. On the other hand, tilted S=O bonds at $(1\ 0\ 0)$ surface of anhydrite (CaSO_4) pushes the FFM probe horizontally in one direction, giving clear frictional asymmetry [11,12]. Results of frictional anisotropy and asymmetry detected with FFM do not betray our intuition.

On the other hand, attempts of detecting frictional anisotropy in μm -scale using a classical friction apparatus with a stylus [14-16] have given results much less clear and often contradictory with the anisotropy observed with FFM. It is probably because effects of bulk plastic deformation, caused by heavier normal loads applied, overwhelm intrinsic surface friction.

Where, then, do the two regimes merge? We need to

study friction at the same, well-defined surface both in nm-scale and μm -scale. This time, cleaved $(1\ 0\ -1\ 4)$ surface of calcite, shown in Fig. 1(a,b), was chosen. In previous FFM experiments, frictional anisotropy and asymmetry were clearly observed [13]. Tilted carbonate ions gave nearly twice as strong friction in $+[4\ 2\ -1]$ direction as in the $-[4\ 2\ -1]$ direction. In this case, the asymmetry was explained by considering the C=O bonds of carbonate ion as a tilted mass-spring system which supports the normal load mainly by bond bending.

In the present work, we have measured frictional force with Bowden-Leben apparatus in the scratch in $\pm[4\ 2\ -1]$ directions and $\pm[0\ 1\ 0]$ directions. By changing the normal load applied with the stylus, we have studied, at which level of normal load bulk plastic deformation starts to participate in friction and change the friction coefficients. Traces of deformation at the surface and in the bulk were observed with optical microscopy. Indentation experiments were also performed.

Fig. 1 Crystal structure of calcite $r(1\ 0\ -1\ 4)$ surface and a mechanical model of deformation processes.

(a) Sketches of outer shape of a cleaved crystal, $c(0\ 0\ 0\ 1)$ slip surface, and a triangular pattern of plastic deformation formed by indentation at point O. The pattern formation proceeds segment by segment in $[-4\ 2\ -1]$ direction.

(b) Ionic arrangement at $r(1\ 0\ -1\ 4)$ surface viewed along the a_2 -axis. The c -face is inclined by 44.6 degrees from the r -face.

(c) Normal load applied by a stylus gives tensile stress or compressive stress, respectively, in addition to shear stress, at tilted potential slip interfaces A and B. Actual slip occurs more easily at the interface A.

2. Experimental

Single crystals of calcite were of natural origin. Frictional force was measured with HEIDON 18 LFW, using a sapphire stylus with the cone angle of 60 degrees and the curvature radius of $50\ \mu\text{m}$. At the cleaved $(1\ 0\ -1\ 4)$ surface, the stylus was scanned with the scan speed $24\ \text{mm/min}$ and the scan length of $2\ \text{mm}$ in $+[4\ 2\ -1]$, $[-4\ 2\ -1]$, $+[0\ 1\ 0]$ or $[-0\ 1\ 0]$ directions applying the normal loads of $9.8\text{--}980\ \text{mN}$, and the frictional force was recorded. Only a single scan was performed at one place. After that, wear tracks at the surface and cracks formed inside the crystal were observed with HiRox KH-7700 digital microscope. Indentation experiments were performed using Shimadzu EZ-S universal testing machine with a stainless steel indenter having a cone angle of 60 degrees.

3. Results

Results of frictional force measurement are shown in Fig. 2. With the normal load smaller than $49\ \text{mN}$, observed frictional asymmetry, $+[4\ 2\ -1] > [-4\ 2\ -1]$, was the same with the results obtained with FFM. In this range, the friction may be interpreted as an intrinsic surface phenomenon. Toward the higher normal load range, however, the friction in the $[-4\ 2\ -1]$ direction increased quickly, and reversed asymmetry, $[-4\ 2\ -1] >+[4\ 2\ -1]$, was observed. Something new has occurred.

Fig. 2 Dependence of frictional force on the normal load measured in $\pm[4\ 2\ -1]$ directions at $r(1\ 0\ -1\ 4)$ face of calcite. In the lower normal load range $<49\ \text{mN}$, friction was stronger in $+[4\ 2\ -1]$ direction. In the higher normal load range, new component was added to the friction in $[-4\ 2\ -1]$ direction, and the frictional asymmetry was reversed.

In Fig. 3A, B are shown, optical microscope images along the wear tracks formed in the scratch in $[-4\ 2\ -1]$ and $+[4\ 2\ -1]$ directions, respectively, with the normal loads of 49 and $98\ \text{mN}$. In the $[-4\ 2\ -1]$ scratch, triangular patterns of deformation wider than the actual wear tracks were observed even at the normal load of $49\ \text{mN}$. No such pattern was formed in $+[4\ 2\ -1]$ scratch even with the normal load of $196\ \text{mN}$ (Fig. 3B3). The increase in the friction coefficient in $[-4\ 2\ -1]$ scratch in Fig. 2 is most probably related to the formation of the triangular pattern. Actually, the frictional force increased with the size of the triangles up to the normal load of $700\ \text{mN}$. Triangular pattern formation adds a new component to intrinsic surface friction with the normal load of $49\ \text{mN}$ or larger.

Frictional asymmetry was not observed between the scratch in $+[0\ 1\ 0]$ and $[-0\ 1\ 0]$ direction. However, tracks of deformation as shown in Fig. 3C were formed on the same side of the crystal during the scratch in either direction. With normal load of $98\ \text{mN}$, only traces along the $[0\ 1\ 0]$ direction were observed. With the heavier

normal load of 245 mN, cracks in the $[4\ -4\ -1]$ and $[4\ 8\ -1]$ directions, respectively, were observed in $+ [0\ 1\ 0]$ and $- [0\ 1\ 0]$ scratch. As is seen in Fig. 1(a), the cracks run parallel to the edges of the crystal, suggesting that they were formed by cleavage on other r -faces.

In indentation experiment, with a stainless steel indenter with 60 degrees cone angle under a heavy normal load of 40 N, a single triangular deformation structure, illustrated as $\triangle OPQ$ in Fig. 1(a), was formed. The normal load was applied at point O. The shape was quite similar to the pattern observed in Fig. 3A2. Dense slip lines run in the $[0\ 1\ 0]$ direction, that is, the a_2 -direction in Fig. 1(a). The direction of the slip surfaces giving the lines were checked by observing the inner structure of the indented crystal with the optical microscope in horizontal direction. The slip surfaces observed corresponded to the $c(0\ 0\ 0\ 1)$ faces which make an angle of 44.6 degrees with the indented $(1\ 0\ -1\ 4)$ surface. The slip lines in $[0\ 1\ 0]$ direction in Fig. 3A2 were formed by the slip on $c(0\ 0\ 0\ 1)$ surface in $+a_3$ or

$-a_1$ directions shown in Fig. 1(a). At the indented surface, the compressed point O was at the lowest level, and upward steps were observed toward the $-[4\ 2\ -1]$ direction.

4. Discussion

Two shorter sides of a triangle in Fig. 3(A2) run in $[4\ -4\ -1]$ and $[4\ 8\ -1]$ directions which are parallel to the edges of a cleaved calcite crystal. It suggests that these sides were formed by cleavage or slip on $r\{1\ 0\ -1\ 4\}$ faces parallel to the side faces of the crystal shown in Fig. 1(a). Since the traces in these directions were only occasionally observed, they were probably formed by the cleavage, not by the slip. Origin of the densely populated lines in Fig. 3(A2) along the $[0\ 1\ 0]$, or a_2 -direction, making the bases of the triangles, has several possibilities including slip on $f\{-1\ 0\ 1\ 2\}$ or $c(0\ 0\ 0\ 1)$ surfaces, and twinning on $e\{-1\ 0\ 1\ 8\}$ or f surfaces reported in literature [17,18]. However, only the slip on $c(0\ 0\ 0\ 1)$ face, reported to occur at high temperature, agrees with the result of microscopic observation after the indentation experiment.

Traditionally, frictional force was considered to have two components, namely, shearing term (surface effect) and deformation term (bulk effect) [14,15]. The former does not participate in the indentation experiment. We consider that the triangular patterns obtained in our experiments were formed mainly due to the deformation caused by the normal load. In the friction experiment, however, the triangular patterns were formed under normal loads much smaller than in the indentation experiment. The horizontal scanning of the stylus greatly enhances the deformation effect on the front side of the stylus.

The next question is, why were the slip lines observed only in quadrant I in Fig. 1(a)? It can be explained by Fig. 1(c). Let us consider two tilted potential slip interfaces A and B on either side of the compressed point. At the interface A, the normal load applied by the stylus is decomposed in two directions giving shear stress and tensile stress, respectively. While the slip is caused by the shear stress, the tensile stress helps the slip at the interface A by elongating the distance between the ionic planes on either side. At the interface B, on the other hand, the normal load gives a compressing stress which prevents the slip. This way, the slip on the c surface occurs in quadrant I, but not in quadrant III.

The slip on the c surface for calcite was reported to occur at elevated temperature [17,18]. If we interpret the effect of higher temperature as lattice expansion, the slip mechanism explained above, working at room temperature, does not contradict with the reported results on the slip systems of calcite.

The next question is why the triangular pattern terminated along the lines OP and OQ in Fig. 1(a), and did not extend to quadrants II or IV. We consider that the observed plastic deformation proceeds strip by strip in

Fig. 3 Optical microscope images of wear tracks observed after scratching with a stylus.

A: $-[4\ 2\ -1]$ direction; B: $+ [4\ 2\ -1]$ direction; and C: $+ [0\ 1\ 0]$ direction, with the normal loads of (A1, B1) 49 mN, (A2, B2, C1) 98 mN, (B3) 196 mN, and (C2) 245 mN. Scan directions of the stylus are indicated by arrows. The broken lines in B1 and B2 are guides showing the directions of nearly invisible wear tracks. In the scan in $-[4\ 2\ -1]$ direction, triangular deformation patterns wider than actual wear tracks were formed. No such pattern was formed in the scans in $+ [4\ 2\ -1]$ direction with the same normal loads. In the $+ [0\ 1\ 0]$ scan with the lower normal load, slip lines in the $[0\ 1\ 0]$ direction were formed only on one side of the wear tracks. Traces of r -cleavage in $[4\ -4\ -1]$ direction were added on the same side under heavier normal load.

$-[4\ 2\ -1]$ direction starting at the compressed point O. Let us consider a narrow strip of the surface, the hatched area in Fig. 1(a). When the middle part of the strip was pressed down by the normal load and slipped against the neighboring strip, strong tensile stress, then, arises within the strip in horizontal a_2 -direction. Cleavage at r surfaces, shown by broken lines in Fig. 1(a), parallel to the side faces of the crystal occurs at the narrow intersection of the slipped strip with lines OP and OQ. It is because, along the lines, that is, along the potential r -cleavage face indicated by the broken lines, the normal load applied at O constantly gives additional tensile stress between quadrant I and II and between quadrant I and IV. The whole slipped strip is, then, pushed down permanently. The process continues on to the outer strips. This explains why the cleavage proceeds along the lines OP and OQ, finally forming a triangle.

Results shown in Fig. 3C give additional evidence to the above discussion. When only a small normal load was applied in $\pm[0\ 1\ 0]$ scratch, only the slip on the c -surface occurred. And it occurred only on one side of the crystal in accordance with the mechanism of deformation shown in Fig. 1(c).

With the higher normal load, the r -cleavage occurred together with the c -slip. However, the traces of r -cleavage run either in $[4\ 8\ -1]$ or $[4\ -4\ -1]$ direction depending upon the scan direction. We consider that the cleavage occurs only in the areas already segmented into narrow strips by the c -slip. Tensile stress given by the horizontal scanning of the stylus works on each strip and causes the cleavage only on the rear side of the stylus. Since nearly the same thing occurs in scratches in $\pm[0\ 1\ 0]$ direction no frictional asymmetry is observed in this direction.

Now we discuss the effect of scanning a stylus on the surface. If only the normal load was concerned with the deformation, the same triangular pattern would be formed upon scanning the stylus both in $+ [4\ 2\ -1]$ or $- [4\ 2\ -1]$ direction. The results shown in Fig. 3 tell that the triangular deformation patterns were formed only on the front side of the stylus during the scan in $- [4\ 2\ -1]$ direction, but not on the rear side of the stylus during the $+ [4\ 2\ -1]$ scan. The plowing with the stylus markedly enhances elastic surface deformation on the front side and caused the slip. Compared with the static indentation experiment, much smaller normal load was required to form the triangular pattern in the friction experiment.

Finally, we have checked if the friction data in Fig. 2 are quantitatively explained by the formation of the c -slips. When we calculated the total lengths of the traces of c -slips observed in optical microscope images like the ones shown in Fig. 3A, the frictional force increased in proportion to the total length with the normal load from 49 mN up to 700 mN. The increased friction in the $- [4\ 2\ -1]$ direction is explained by the c -slips formed at the outermost layer of the surface.

5. Conclusions

By analyzing deformation patterns formed at highly directional calcite surface, mechanisms of plastic deformation were clarified. At certain levels of the normal load, slip and/or cleavage, two forms of energy dissipation processes, are added to intrinsic surface friction. Reversal of frictional asymmetry at the calcite surface, depending upon the normal load, was explained by this mechanism. Plowing with a stylus greatly enhances deformation on the front side.

Acknowledgements

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ERRATA

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Title: Contribution of Slip and Cleavage in Friction and Wear at (10-14) Surface of Magnesite (MgCO_3) Crystal

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	Appearing	Corrected
p.318 Ordinate of Fig. 2	Frictional force [mN]	Frictional force [gf (=9.81 mN)]
p.318 right column, line16	0.0085	0.085
p.320 right column, lines 2-3 from bottom	0.010 and 0.016	0.10 and 0.16
p.321 left column, line 4	0.060	0.60
left column, line 15	0.0085	0.085

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Title: Frictional Asymmetry and Wear Pattern Formation by Slip and Cleavage Detected at Directional r {10-14}
Face of Calcite (CaCO_3)

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	Appearing	Corrected
p.9 Ordinate of Fig.2	Frictional force [mN]	Frictional force [gf (=9.81 mN)]

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