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Friction Anisotropy: A unique and intrinsic property of decagonal quasicrystals

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We show that friction anisotropy is an intrinsic property of the atomic structure of Al-Ni-Co decagonal quasicrystals and not only of clean and well-ordered surfaces that can be prepared in vacuum [J.Y. Park et al., Science (2005)]. Friction anisotropy is manifested both in nanometer size contacts obtained with sharp atomic force microscope (AFM) tips as well as in macroscopic contacts produced in pin-on-disc tribometers. We show that the friction anisotropy, which is not observed when an amorphous oxide film covers the surface, is recovered when the film is removed due to wear. Equally important is the loss of the friction anisotropy when the quasicrystalline

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order is destroyed due to cumulative wear. These results reveal the intimate connection between the mechanical properties of these materials and their peculiar atomic structure.

I. Introduction

Among metallic alloys, quasicrystals[1] are interesting because they exhibit both unusual atomic structure (order without periodicity) and unusual physical properties. The tribological properties of quasicrystals —including low friction, high hardness, low surface energy, and high wear resistance— have attracted much interest during the last 15 years.[2-4, 5, 6, 7] Anomalously low coefficients of friction between quasicrystalline materials and diamond or steel under ambient condition were first reported in 1991 by Dubois et al.[4] In the original observations the experiments had two noteworthy features.[2, 3] First, the environment was air and so the surface of the aluminum-rich quasicrystals was covered by a layer of oxide 2-5 nm thick. Second, irreversible deformation and wear of the sample occurred during sliding.[8, 9, 10, 11] In addition to low friction, a new and remarkable property was discovered recently on clean, oxide-free quasicrystal surfaces. Using an atomic force microscope (AFM) in ultra high vacuum, Park et al. reported a large directional anisotropy of the friction force[12] : friction was found to be 8 times larger when sliding along the periodic direction of the surface than when sliding along the aperiodic one. These experiments were performed under low loads, such that the contact was elastic and reversible (no wear). The anisotropy was attributed to the peculiar structural anisotropy of the surface. It disappeared when an amorphous thin oxide film was formed after exposure to air.

These observations raise the important question of whether the quasicrystalline nature of the material influences its tribological properties in practical situations and environments, including air and loads large enough to produce wear. To address these questions we performed a comparative study of the friction properties of $Al_{72}Ni_{11}Co_{17}$ decagonal quasicrystals using the two-fold symmetric surface (parallel to the 10-fold axis) [13] with both AFM and a pin-on-disk tribometer.

II. Experimental

The sample had dimensions of 1 cm x 1 cm x 1.5 mm and was cut from a large single grain of d-$Al_{72}Ni_{11}Co_{17}$ grown at the Ames Laboratory, Iowa State University[14]. The chemical composition was determined by energy dispersive x-ray analysis in a scanning electron microscope.

Figure 1a shows a schematic of the friction measurement with AFM on the 2-fold Al-Ni-Co surface. The image of the oxidized quasicrystal surface in Fig. 1a shows an amorphous structure although linear topographic features are still visible that are parallel to the 10-fold direction (the periodic direction) of the quasicrystalline material underneath. The aperiodic direction is perpendicular to it.

A commercial ultrahigh vacuum (UHV) RHK microscope[15] was used for the AFM study. The base pressure in the chamber was in the 10^{-10} mbar range. In the present work the AFM cantilever was coated with approximately 50 nm of TiN and had a spring constant of 48 N/m[16]. This relatively high stiffness was necessary to reach loads high enough to produce wear. To determine forces the cantilever spring constant was

calibrated using the method of Sader et al.[17]. To change the scan orientation and measure the angle-dependence of the friction force, the sample was removed from the UHV chamber, rotated in air, and reloaded. The scan direction relative to surface crystallographic directions was determined from atomic-scale STM images of the clean surface, as described previously [6].

Before and after AFM experiments on the 2-fold decagonal quasicrystal surface, friction was measured on a silicon oxide surface at an applied load of 100 nN, and no change of friction and adhesion forces was found. This indicates that the wear of the AFM tip is negligible during the AFM experiments on the 2-fold decagonal quasicrystal surface.

A schematic of the pin-on-disk measurement is shown in Fig. 1b. Details of the instrumentation have been described elsewhere[18]. Due to its small and brittle nature the sample was embedded in epoxy resin. The specimen was polished using silicon carbide paper down to 2400 mesh size and cleaned in an ultrasound bath with acetone for 10 min, then in ethanol for 2 min. After this it was mounted in a vacuum chamber containing the pin-on-disk tribometer. The following parameters were used: load 1 N, disk velocity 1×10^{-4} m/s, radius of the trace 1.5×10^{-3} m, integration time 1s, and frequency of rotation 0.6 rpm. The vacuum was 10^{-6} mbar and sample temperature was 25-28 °C. The pin was a 6 mm diameter hard steel ball (high carbon Cr-steel, AISI 52100). Due to the fact that the sample surface could not be aligned perfectly horizontal, the pin (when in contact with the sample) oscillated along a vertical direction by a distance of a few micrometers. This was used to follow the angular rotation of the disk with good resolution, although with an arbitrary phase relative to the

angular position of the periodic axis of the decagonal crystal. The run distance in these experiments was a fraction of a meter.

III. Results

III.A. AFM results

Using AFM the friction force along the two crystallographic directions was measured as a function of load by repeatedly scanning the probe tip over a 200 nm line in each direction[19]. A plot of the friction vs load (Figure 2a), shows that there is no noticeable difference in friction force along the two directions up to 1.5 μN. This isotropic behavior is due to the fact that the amorphous aluminum oxide film prevents direct contact of the tip with the underlying quasicrystalline material at low loads.

Interestingly the two friction force curves diverge above 1.5 μN, the point where the oxide film breaks down[20]. This is shown by the images in figure 2, acquired before and after a set of friction measurements along the 10-fold direction. The maximum applied load in this experiment was 3.6 μN, which created a 200 nm long trench at the center of the image (Fig. 2c). A line profile of the trench (Fig. 2d) shows a depth of 2 nm that is much larger the roughness of the oxidized surface (0.2 ± 0.06 nm). The friction curves of Fig. 2a show oscillating features and plateaus once the oxide layer is broken. Because these features are not reproducible, we suppose they are associated with the noise in friction measurement. The resolution of contact AFM imaging is limited by the low force sensitivity of stiff cantilever (spring constant of 48 N/m).

The removal of the oxide layer permits contact of the tip with the quasicrystalline metal substrate and explains the appearance of friction anisotropy between periodic and quasiperiodic directions. The magnitude of the anisotropy, defined as the ratio of friction forces along the 10-fold and 2-fold directions, is 1.2-1.4. This value is lower than that found previously on the clean surface at low load and can be explained by the fact that under the present conditions the tip is in contact with quasicrystalline material after breaking through the oxide film, which contributes an additional isotropic term from wear to the friction force.

III. B. Pin-on-disk results

A similar experiment was performed using a pin-on-disc apparatus (Fig. 1b) on the same quasicrystalline material, again initially covered by an oxide film. On a flat surface perpendicular to the rotation axis the vertical displacement of the pin provides a measure of the wear of sample and pin. In the present experiment however, the small size of the quasicrystal (approx. 1 cm diameter) made it difficult to achieve a perfect perpendicular geometry relative to the pin[21], so that the displacement due to wear is superimposed on a larger up-and-down oscillation during the rotation of the sample. The small tilt gives rise to a lateral force component that varies with 2π periodicity if the friction coefficient is isotropic. If the friction coefficient were *anisotropic* however, with different values along two directions, then the friction force should exhibit a variation with period π. This is indeed what was observed, as shown in Fig. 3a. During the initial part of the test (first two periods in the plot) the friction force (top curve)

oscillates with 2π periodicity (bottom curve). However, after the pin breaks through the oxide layer the period of the friction force changes to π. The pressure in the chamber is low enough ($\sim 10^{-6}$ mbar total) [22] to prevent growth of a new thick oxide layer between successive rotations.

To estimate the friction coefficient the effect of the slope must be subtracted from the measured friction force. As mentioned earlier, the periodic variation of the friction force in the isotropic regime is purely geometric and is due to the pin going "uphill" or "downhill" as the sample rotates. A schematic diagram of the various forces acting on the pin for a fixed external load is shown in Fig. 4a. L is the fixed external load, 1N in this experiment. F_L, N, and f are the observed lateral force, the effective normal force, and the actual friction force respectively. It is easy to show, from simple geometrical considerations that $F_L(\alpha, \mu) = L \times \tan(\alpha + \text{atan}(\mu))$, and $N(\alpha, \mu) = L \times \cos(\text{atan}(\mu)) / \cos(\alpha + \text{atan}(\mu))$, where α is the angle between the direction of advance of the tip and its projected horizontal direction during the circular motion. Likewise, the actual friction force $f(\alpha, \mu)$ for a given α and μ is: $f(\alpha, \mu) = L \times \sin(\text{atan}(\mu)) / \cos(\alpha + \text{atan}(\mu))$. The friction coefficient can then be written as $\mu(F_L/L, \alpha) = \tan(\text{atan}(F_L/L) - \alpha)$. Assuming that α follows a sinusoidal variation, $\alpha = \alpha_0 \sin(2\pi x + \phi)$, μ can be obtained in the isotropic regime by adjusting the parameters α_0 and ϕ so as to compensate the geometric 2π oscillation. The bottom curve of Fig 4b shows the fitting result for α and the top curve the corrected value of the friction coefficient.

The plot clearly reveals the friction anisotropy of the 2-fold decagonal surface in the regime where irreversible removal of the oxide layer occurs. Assuming that the highest friction is along the 10-fold axis, the friction coefficient along this periodic

direction is 0.45 ± 0.06, whereas that along the aperiodic direction is 0.30 ± 0.05, i.e., larger by a factor of 1.5. These results are important because they show that friction anisotropy is not only manifested in nanoscale contacts (with the AFM tip) but also in larger macroscopic contacts (with the tribometer pin). The two values are higher than the single value measured on the oxide (0.26 ± 0.05) film before its removal.

Another and very important question is whether the friction properties of quasicrystals are related to their peculiar crystallographic structure or are simply the result of their unique composition. For example, if the same atomic composition is maintained but with a different order (or disorder), is friction still anisotropic? The following experimental result shows the intimate connection between friction anisotropy and quasicrystalline order. When the friction experiment was continued for sufficiently long times the anisotropy disappeared, as shown in figure 3b. The figure shows how the two initially identical intervals separating the two friction minima in the 2π rotation become increasingly unequal in successive cycles, until eventually only one is left. As can be seen in the figure, after the 17th cycle of this experiment, the period became again 2π. This loss of friction anisotropy is connected with the destruction of quasicrystalline order by wear[23]. The changing interval can be explained by considering the small diameter of the circle described by the pin (3 mm) compared to the width of the wear track (0.3-0.5 mm). It is clear that the inner and outer sides of the contact do not contribute equally to the friction and that this difference should become more important as the width of the track increases due to wear.

IV. Discussion

According to Wittman et al.[24], the Vickers hardness H_{2N} of the decagonal $Al_{62}Co_{15}Cu_{20}Si_{13}$ quasicrystal shows a slight anisotropy, amounting to at most 5%, depending on whether the measurement was made on a surface perpendicular to the 10-fold axis or parallel to it. Reducing the load on the Vickers indenter to 0.5N (the load used in ref. 22) however increased the data scatter, and could not demonstrate a larger anisotropy of H_V. It makes therefore sense to assume that the plowing component $F_{n\ plowing}(x)$ experienced on the thin oxide film is isotropic, as expected from its amorphous structure. The same authors also found an anisotropy in the friction of quasicrystals in scratch test experiments in air[24]. The anisotropy for a spherical diamond indenter of small (but unspecified) radius was 1.4 (±0.3) between the parallel and perpendicular directions of the periodic axis. This value is similar to that found on our sample and points to a similar origin, which however cannot be attributed to the very small hardness anisotropy.

In our clean quasicrystal study we proposed that the friction anisotropy is connected with the anisotropy of the thermal and electronic transport properties along periodic and quasiperiodic directions[25, 26]. For example, the phonon dispersion bands in the aperiodic directions might show energy gaps due to the Fibonacci sequence of distances and masses that are not present in the periodic direction[27]. The existence of such gaps would make energy losses by generation of phonon modes less favorable and therefore give rise to a lower friction [28].

Another interesting and feasible experiment would be studying the frictional responses of quasicrystal surfaces with AFM tips having different geometrical structures. For example, the contact between the single crystalline tip and anisotropic quasicrystal surfaces can give rise to the different level of friction anisotropy considering possible effects due to commensurability.

V. Conclusion

In conclusion, we have shown that the unique friction properties of decagonal Al-Ni-Co quasicrystals are an intrinsic property of their peculiar crystallographic structure. The anisotropy, manifested by high and low friction forces along the periodic direction and aperiodic directions, is present not only in clean surfaces prepared in ultra high vacuum but also in crystals exposed to air, and is manifested after the oxide is broken by wear. Equally important is the finding that the anisotropy disappears when the accumulation of wear destroys the quasicrystalline order. By exploiting two widely used tribological techniques, the atomic force microscope involving atomic or nanometer size contacts, and the pin-on-disk tribometer that produces contacts of macroscopic dimensions, we have shown that the anisotropic friction properties of quasicrystals can manifest in practical situations where these materials are exposed to air environments and under loads that lead to wear of the surface films.

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Figure Captions

Figure 1. (Color online) Schematic of the friction measurement on oxidized Al-Ni-Co decagonal quasicrystal surface. (a) friction/atomic force microscopy experiment. (b) pin-on-disk experiment.

Figure 2. (Color online) (a) Friction force measured with the atomic force microscope as a function of applied load. Friction along the periodic (10-fold) direction is higher than that along aperiodic (2-fold) direction after the oxide layer is broken when the load reached 1.5 μN. The unit of a. u. refers to the arbitrary unit. (b) AFM images (1 μm x 1μm) before and (c) after the measurement of friction as a function of the applied load up to 3.6 μN. After the measurement a trench was created due to the plastic deformation on the sample surface. (d) Profile of the trench showing its 2 nm depth and 200 nm length.

Figure 3. (Color online) (a) Friction force measurement (radius, a = 1.5 mm) as a function of the total run distance of the pin (x). Before rupture of the oxide film the friction shows a 2π periodicity due to the tilt effect. After the pin penetrates through the oxide friction anisotropy was observed, with high friction along the periodic quasicrystal direction and low friction along the aperiodic direction. The recorded vertical position of the pin is shown by the bottom trace. (b) Friction force measured with pin-on-disk in the plastic regime (radius = 1.5 mm). The friction force varies with period π. The arrows show that the lengths of the

cycle between adjacent pairs of maxima and minima are not equal and that the short interval decreases with increasing duration of the test. Vertical gray lines mark complete rotations of the sample (i.e., 2π variation).

Figure 4. (Color online) (a) Schematic diagram showing the force balance for fixed external load on a tilted plane. L is the external load, F_L, N, and f are the observed lateral force, the effective normal force, and the actual friction force respectively. The tangent of the angle between N and the broken line gives the friction coefficient. (b) The top curve shows the friction coefficient obtained from Fig. 3b (see the text for details). The bottom curve shows the fitting result of α ($=\alpha_0 \times \sin(2\pi x + \phi)$). Friction anisotropy is clearly visible in the corrected friction coefficient after the oxide is broken through.
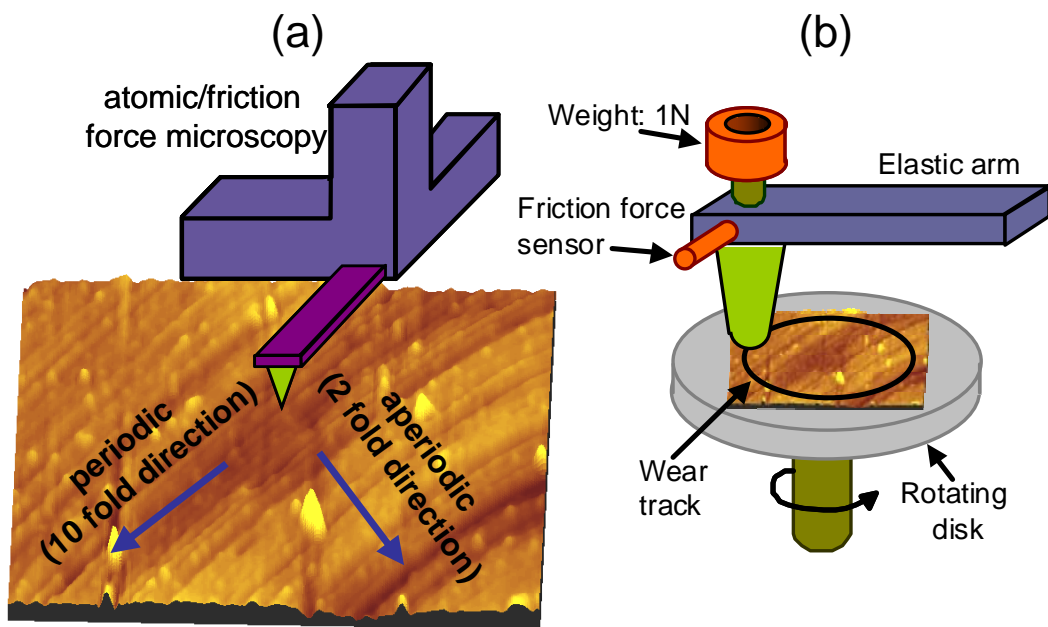
(a)

atomic/friction force microscopy

periodic (10 fold direction)

aperiodic (2 fold direction)

(b)

Weight: 1N

Elastic arm

Friction force sensor

Wear track

Rotating disk

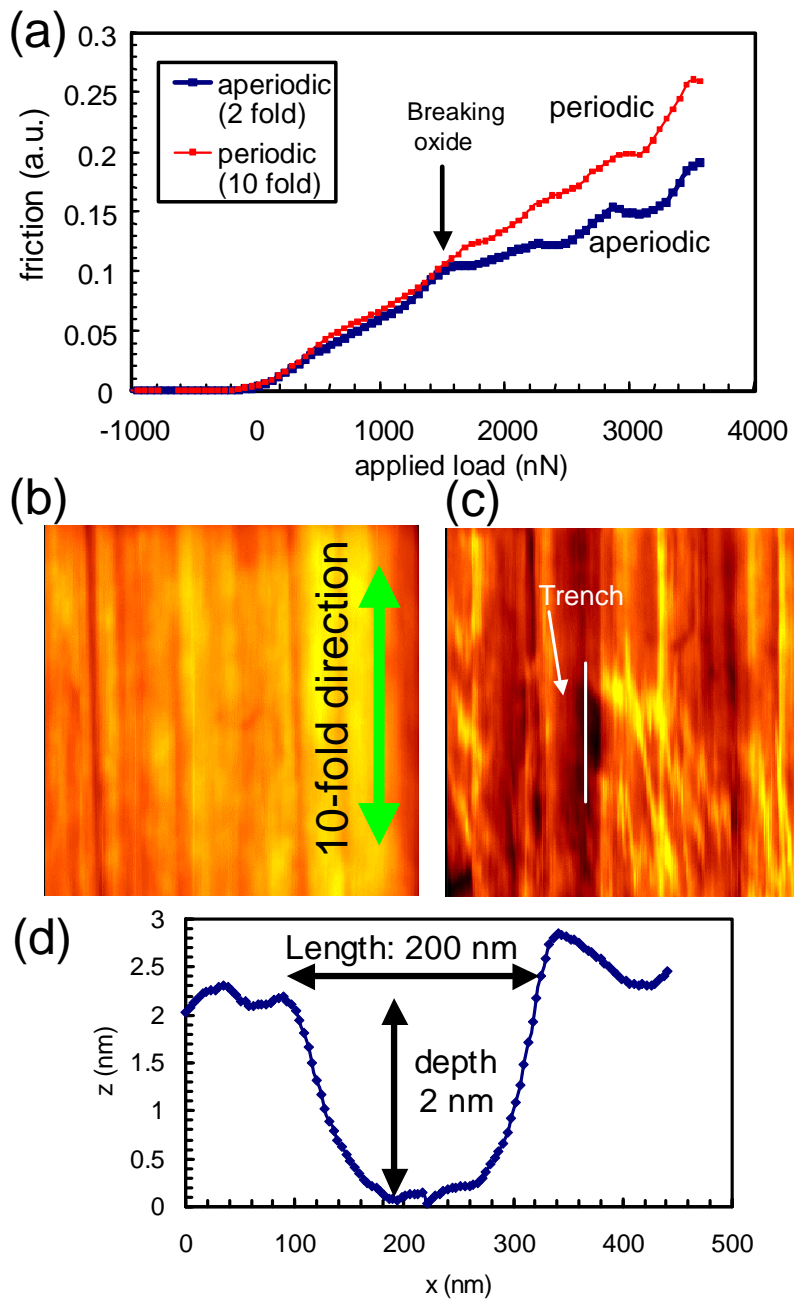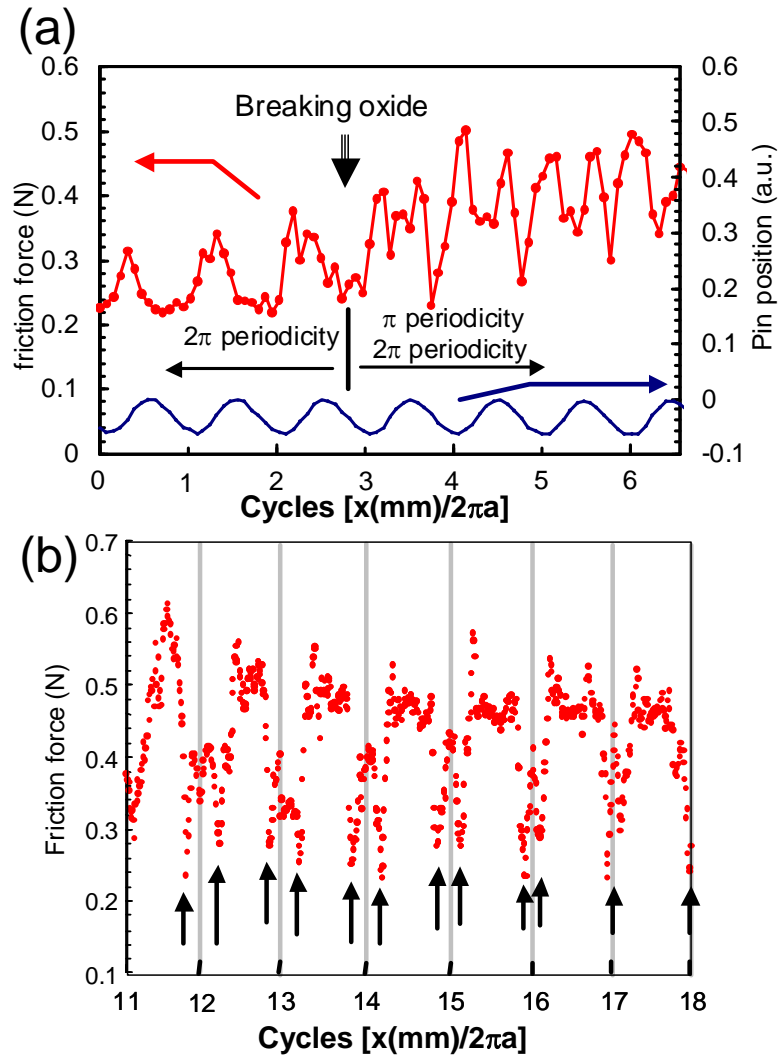**Figure 1. J. Y. Park et al.**
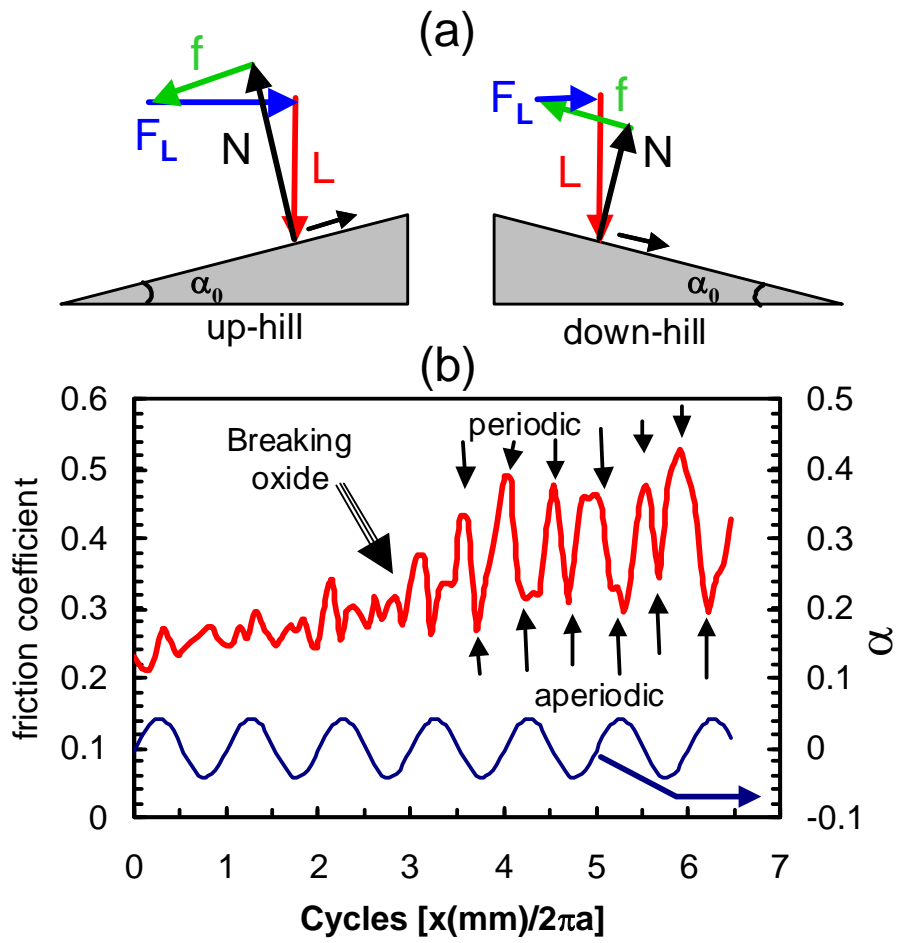
(a)

(b)

(c)

(d)

Figure 2. J. Y. Park et al.

Figure 3. J. Y. Park et al.

Figure 4. J. Y. Park et al.