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Rapid Note

Very low friction for natural diamond in water of different pH values

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Abstract. Very high reductions in the friction coefficient are reported for natural diamond sliding upon natural diamond when water is introduced at the interface of contact. This reduction is found to depend on the pH value of the water, the load and the sliding velocity. The results are interpreted in terms of the reduction of adhesion due to adsorption of the liquid on the surface, and of graphitisation occurring during sliding, with graphite acting as a lubricant.

PACS. 81.40.Pq Friction, lubrication and wear – 46.55.+d Tribology and mechanical contacts – 81.05.Tp Fullerenes and related materials; diamonds graphite

The friction coefficient for natural diamond sliding upon natural diamond depends on the crystal orientation and the direction of sliding but typically has a value in the range 0.05 to 0.15 under ambient conditions when sliding in air. These values are known to be significantly dependent on the environment, being increased by an order of magnitude under high vacuum conditions [1,2]. Two hypotheses have been traditionally put forward to explain the mechanism of diamond friction. The one by Tabor [3] is based on ideas of adhesion: it considers the bonds formed at the interface of contact between the two surfaces and explains friction in terms of the force needed to break them. The second, by Casey and Wilks [4], attempts to explain friction in terms of the force needed to cause sliding of the asperities of one surface over those of the other. Friction in vacuum is successfully explained by the adhesion theory: the high value of the coefficient (typically 1) being due to the attraction of the dangling bonds on the two surfaces which are not terminated by adsorbed species.

Since conventional organic lubricants do not reduce the friction coefficient [5], it had been assumed that adhesion does not play a role and surface roughness has traditionally been taken to be responsible for diamond friction under ambient conditions. However, more recent experiments on the effect of the environment at the interface of contact [6,7] indicated that water reduces the coefficient from its value in air, thus suggesting that adhesion is important. The extent of the lubricating influence of water under different conditions and the question as to which other liquids can act as lubricants in diamond friction are important questions both for clarifying the friction mechanism and for practical applications involving diamond [8,9].

The influence of the environment on the friction of polycrystalline chemically vapour deposited (CVD) diamond has been studied in some detail [8–12] and it has been shown that the presence of water and oxygen containing liquids significantly affect the friction coefficient, and can cause high reductions in its value. The properties of CVD diamond are dependent on the deposition method, and results obtained on particular samples cannot always be generalised. Experiments on the effect of the environment on the friction of diamond-like-carbon (DLC) [13,14] have shown that at very low sliding velocities the friction coefficient for DLC was decreased by 10% by mineral oils, and by a higher extent by water. Wear was instead found to significantly increase in the water environment.

Here, results are reported on friction experiments for natural diamond sliding upon natural diamond, where a very high reduction in the coefficient is observed in a water environment. In these experiments, the friction coefficient in air, both under ambient conditions and when water was introduced at the contact interface, was measured under different loads and sliding velocities. The pH value of the water was also varied to investigate whether the reductions in the coefficient were sensitive to changes in the chemical composition of the liquid.

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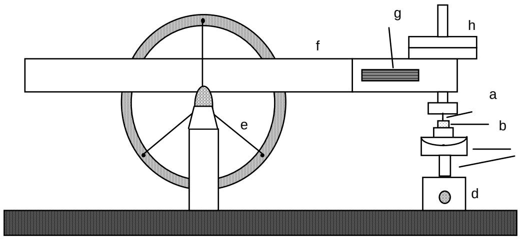

Fig. 1. Experimental apparatus: a) Diamond stylus, b) Diamond surface, c) Goniometers, d) Moving stage, e) Piano wires, f) Arm, g) Strain gauges, h) Weights.

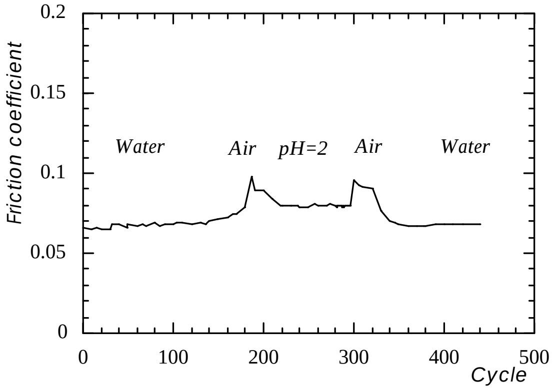

Fig. 2. Friction coefficient in alternating environments for a 1 N load at 0.2 mm/s.

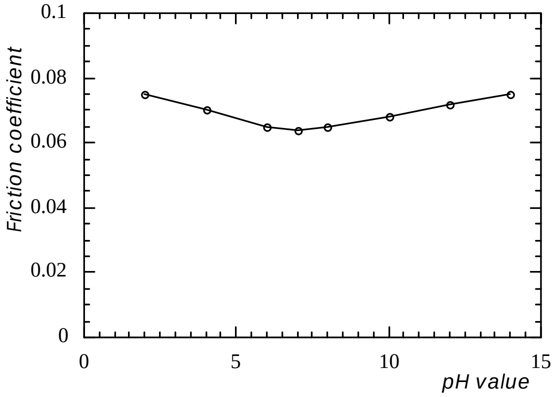

Fig. 3. Friction coefficient *versus* pH value for a 1 N load at 0.2 mm/s.

The apparatus used in these experiments is shown schematically in Figure 1; a detailed description of it can be found in [15]. The stylus with the diamond tip is mounted at the end of a balanced duralumin arm which is free to rotate smoothly and can be lowered onto a moving stage supporting the diamond sample. The stage is driven by a computer-controlled stepper-motor, and performs bi-directional motion of chosen variable velocity and displacement. The levelling of the diamond surface is achieved using a laser beam and adjusting two goniometers positioned at 90 degrees to each other until the surface is horizontal (to within approx. 5×10^{-4} rad.).

During an experiment, a known load is applied to the arm above the stylus, and the lateral force is measured by the deflection of two parallel thin steel strips (on each of which two strain gauges are mounted) which hold the stylus. The gauges are connected into a Whetstone bridge, whose output is fed into a computer which collects and processes the data. A data point is collected every 10 μm along the track, and only the 50% of the data corresponding to the region around the centre of the track are retained and analysed by the computer.

The diamond sample was a Type Ia diamond, polished on a $\{100\}$ surface; traversals were performed in a $< 100 >$ direction. The stylus was a hemispherical diamond tip fixed at the end of a metal holder. The tangent plane to the sphere at the point of contact was $\{100\}$ and the direction of sliding of the stylus was $< 110 >$ to minimise wear. The radius of the spherical tip was 80 μm producing a nominal pressure on the sample of approximately 14 GPa, assuming elastic contact and using Hertz theory. The solutions of different pH values were prepared by mixing deionized H_2O with HCl or with NaOH at the required concentration. To check whether the Na^+ and Cl^- ions had an effect on the coefficient, pure deionized water was used with NaCl at a concentration of 10^{-1} M.

The water solution was introduced by adding a drop with a syringe onto the flat sample at the point of contact. The metal holder was coated in araldyte to avoid corrosion by the acidic solutions. The sample was allowed to perform reciprocating traversals under the stationary stylus with a track length of 1 mm, at an initial sliding velocity of 0.2 mm/s and under a load of 1 N. Since the value of the measured friction coefficient in the different solutions was found to vary only by a small amount, a method which involved alternating the different regimes within one single experiment was used for more accurate comparison of the friction values.

A typical experiment would be started in air, then deionised water be introduced whilst the experiment was still in progress; it would then be blown away using a nitrogen gas flow which is known not to affect the friction coefficient [16] and the regime returned to air; a liquid of a different pH would be introduced, then blown away and finally the experiment ended with deionised water. Care was taken to have the same regime (in this case deionized water), both at the beginning and end of the set of traversals to ensure that if any drifts or errors in measurement were taking place (due either to the measuring apparatus or to changes in the conditions of the track), they would be detected by comparing the first set of traversals with the final ones. Figure 2 shows results for pH = 2, indicating clearly a difference in the friction coefficient from its value in deionised water. The results of a set of experiments at different pH values are summarised in Figure 3.

The effects of load and sliding velocity were investigated, since when chemical processes are involved these

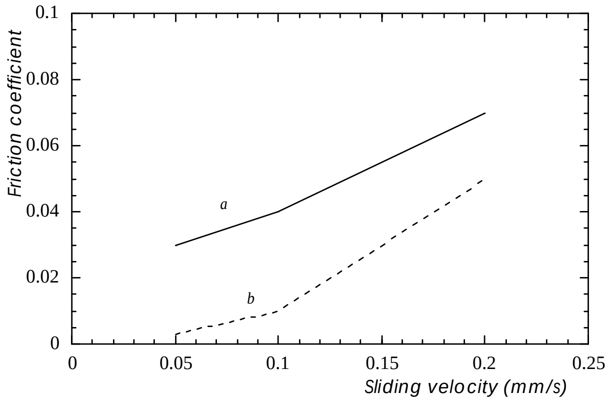

Fig. 4. Friction coefficient in water as a function of sliding velocity, at a load of (a) 2 N and (b) 0.5 N.

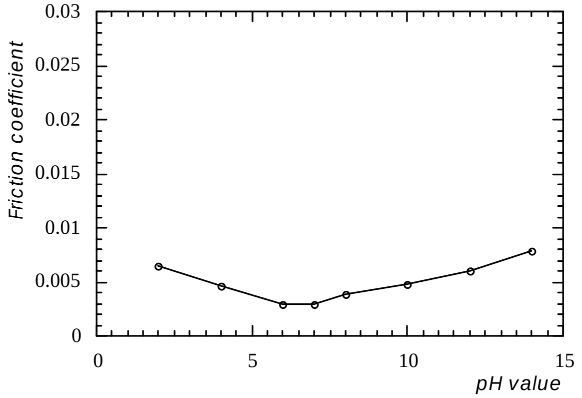

Fig. 5. Friction coefficient *versus* pH value for a 0.5 N load at 0.05 mm/s.

parameters can be important. In air, as expected from Amonton's law, no significant change took place, but in the presence of water the coefficient of friction is dependent on these parameters, and in particular friction was found to decrease drastically with decreasing sliding velocity. The results are shown in Figure 4. Experiments on the dependence of friction on the pH value were performed at low load and sliding velocity, and the results are summarised in Figure 5.

The reduction in the friction coefficient has been shown to be sensitive to the chemical composition of the liquid used; the lower coefficients being recorded at pH values of between 6 and 8. The lubricating effect of water is highly dependent on the sliding velocity, with the highest reductions observed at the lowest sliding velocity studied of 0.05 mm/s. A small dependence on load was also observed, with friction decreasing slightly for smaller loads. The observed trends are qualitatively similar to those observed for CVD diamond friction [9].

The results show that adhesion plays a significant role for natural diamond friction in air under ambient conditions (and not only in vacuum as was previously known), since high reductions in the friction coefficient are obtained in the presence of an appropriate lubricating environment. Water is the main adsorbed species, since the hydrogen or hydroxide concentration is extremely low even for the extreme cases of pH = 2 and pH = 14. Surface studies [17–19] suggest that oxygen forms the bond to the diamond surface. This is in agreement with results on ketones and aldehydes [8], which, unlike conventional organic lubricants, were found to significantly decrease the friction coefficient. The effect of the pH value can be explained either by the fact that some active sites are occupied by hydrogen and hydroxide ions, which would allow a residual attractive field to remain despite the adsorption, or that layers above the first adsorbed one are affected by the presence of hydrogen and hydroxide ions. This would weaken the effect of these layers in reducing the attractive field. A more detailed discussion of the analogous phenomenon observed for polycrystalline CVD diamond can be found in [9].

The high dependence of the coefficient on sliding velocity can be interpreted in terms of the recombination time for molecules to re-adsorb on the surface during each cycle (after removal when the stylus traverses the surface). Calculations based on diffusion theory [12] indicate that the recombination time is between 10 s (the period for a cycle at 0.2 mm/s), and 40 s (the period for a cycle at 0.05 mm/s) and hence that at the lower sliding velocity a greater proportion of molecules from the liquid drop have time to re-adsorb on the surface during each cycle.

To explain the extreme reduction in the coefficient observed under given conditions of load and sliding velocity, we consider further the transformation of material on the diamond surface which is known to take place during sliding in polishing experiments [12,20] and in friction experiments which were performed using the same apparatus as that employed in the present work [21]. The wear debris produced during sliding was analysed using EELS (Electron energy loss spectroscopy) in the STEM (Scanning transmission electron microscope) and was found to contain graphitic carbon. A model based on stress-induced graphitisation has been proposed and supported by calculations [22]. A similar transformation of sp^3 to sp^2 carbon sites was observed for DLC [23] during friction experiments in a water vapour environment. The extremely low resistance to sliding of the basal planes in graphite can thus explain the high reductions in the friction coefficient that has been observed. This hypothesis is further supported by the fact that the only other similarly low friction coefficient have been obtained for molybdenum disulphide [24,25], and were explained in terms of its layered structure. Water vapour and oxygen have been shown to have a lubricating effect on sp^2 carbon materials [26], thus accounting for the effect of the environment. This is in agreement with research on the effect of ketones and aldehydes on diamond friction [8].

In conclusion, very high reductions of the coefficient of friction for natural diamond sliding upon natural diamond have been measured in water of different pH values under given conditions of load and sliding velocity. The results show that adhesion plays a significant role in the friction mechanism even under ambient conditions. The hypothesis has moreover been put forward that the graphitic material, which is known to be produced during sliding, is responsible for the more extreme reductions of friction in some sliding directions.

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References

1. F.P. Bowden, J.E. Young, Proc. Roy. Soc. London A **208**, 311-325 (1951).
2. F.P. Bowden, A.E. Hanwell, Proc. Roy. Soc. London A **295**, 233-43 (1966).
3. D. Tabor, in *The properties of diamond*, edited by J.E. Field (Academic Press, London, 1979), Chap. 10.
4. M. Casey, J. Wilks, J. Phys. D, Appl. Phys. **6**, 1772-81 (1973).
5. M. Seal, Proc. Roy. Soc. London A **248**, 379-393 (1958).
6. Z. Feng, J.E. Field, *Proc. 1st European Conf. on Diamond and Diamond-like Films* (Crans Montana, Switzerland, 1990), 17-19.
7. Z. Feng, J.E. Field, Surf. Coat. Techn. **47**, 631-636 (1991).
8. S.E. Grillo, J.E. Field, Diamond Related Mater. (in press).
9. S.E. Grillo, J.E. Field, J. Phys. D, Appl. Phys. (in press).
10. Y. Tzeng, Z. Feng, S.E. Grillo, J.E. Field, in *Proc. 3nd Int. Conf. on New Diamond Science 9.3*, (1992).
11. Y. Tzeng, Appl. Phys. Lett. **63**, 3586-3588 (1993).
12. S.E. Grillo, Ph.D. Thesis, University of Cambridge, 1995.
13. D.S. Kim, T.E. Fischer, B. Gallois, Surface Coatings Technology **49**, 537-542 (1991).
14. H. Ronkainen, S. Varjus, K. Holmberg, Wear **222**, 120-128 (1998).
15. Y. Enomoto, D. Tabor, Proc. Roy. Soc. London A **373**, 405-417 (1981).
16. Z. Feng, Y. Tzeng, J.E. Field, J. Phys. D, Appl. Phys. **25**, 1418-24 (1992).
17. T.E. Derry, C.C.P. Madiba, J.P.F. Sellshop, Nucl. Instr. and Meth. **218**, 559-562 (1983).
18. J.O Hansen, R.G. Copperthwaite, T.E. Derry, J.M. Pratt, J. Colloid Interface Sci. **130**, 347-353 (1989).
19. S. Evans, C.E. Riley, J. Chem. Soc. Faraday Trans. **82**, 541-550 (1986).
20. S.E. Grillo, J.E. Field, J. Phys. D, Appl. Phys. **30**, 202-209 (1997).
21. F.M. van Bouwelen, L.M. Brown, J.E. Field, Ind. Diam. Rev. **57**, 21-26 (1997).
22. M.R. Jarvis, Pérez Ruben, F.M. van Bouwelen, M.C. Payne, Phys. Rev. Lett. **80**, 3428-3431 (1998).
23. T. Le Huu, H. Zaidi, D. Paulmier, P. Voumard, Thin Solid Films **291**, 126-130 (1996).
24. Y. Tsuya, H. Shimura, J. Jap. Sol. Lub. **19**, 855-861 (1974) [in Japanese].
25. J.M. Martin, C. Donnet, T. Le Mogne, T. Epicier, Phys. Rev. B **48**, 10583-10586 (1993).
26. B.K. Yen, Wear **192**, 208-215 (1996).