

## TRIBOLOGY

# Diamonds are forever — or are they?

The friction and wear of materials is part of our everyday experience, and yet these processes are not well understood. The example of diamond highlights wear processes that result from bumping atoms, showing that the devil is indeed in the details.

Jay Fineberg

**H**ow do you wear down the hardest material known to man? The short answer is that you do not. This is one interesting result of a molecular dynamics study by Lars Pastewka and colleagues<sup>1</sup> in *Nature Materials*. They show that when diamond faces are rubbed against one another an amorphous carbon layer is formed on the contact surface. So although the crystalline structure itself does not wear down, this amorphous layer eventually succumbs to wear. The study additionally shows how and why the layer's thickness is strongly dependent on both the polishing direction and the diamonds' orientations.

The anisotropy in how diamond wears is something diamond polishers have known empirically for hundreds of years. The origin of this behaviour is directly related to the question of how the amorphous layer is formed. The authors suggest that as the crystalline faces of the diamond surfaces rub against each other, a spatially localized, shear-induced phase transition takes place at the atomic scale<sup>1</sup>. The amorphous layer is formed as protruding crystal atoms pluck each other off the opposing surfaces during polishing. The vulnerability of these protruding atoms to this process depends on how they are packed along the exposed diamond surfaces — hence the strong dependence of the efficacy of the polishing process on both the direction of polishing and the orientation of the exposed planes. This process builds up an amorphous carbon layer whose thickness is determined by how difficult it is to pluck an atom off the neighbouring diamond surfaces. The amorphous, diamond-like carbon (DLC) material composing the layer is itself quite hard. Surprisingly, however, despite the fact that its temperature hardly rises in this process, this layer has fluid-like behaviour. These results suggest that this phase transition is an intrinsically non-equilibrium process. The new phase formed is both local and shear driven, with little relation to the physics of solid–liquid transitions in physical systems under equilibrium conditions.



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The wear generated by rubbing two surfaces together is one consequence of the physics of everyday friction. In frictional sliding, a thin layer of metastable tribomaterial<sup>2</sup> is thought to form between the sliding surfaces. Tribomaterials, which are believed to have properties very different from the bulk properties of the materials in contact, have been proposed to play a key role in the determination of both frictional properties and wear management. Tribomaterials are very difficult to study, because they may undergo further phase changes or even disappear once the non-equilibrium conditions necessary for their formation are relaxed. Using atomic potentials previously derived<sup>3</sup> to describe the fracture of carbon bonds, Pastewka and colleagues<sup>1</sup> demonstrated good quantitative agreement with the dependence of experimental wear rates on crystal orientation and polishing direction. Thus, these calculations may provide a 'smoking gun' for the existence and generality of this elusive but critical phase of matter.

A related, fundamental question is that of where friction actually comes from. It has long been known that frictional strength is related to the real contact area of the two interfaces — an area that is generally orders of magnitude lower than the nominal contact area of the two bodies. In nearly every instance of sliding, surfaces are rough on some scale. Recent studies<sup>4–6</sup> have suggested how local roughness could play a key role in determining frictional strength. When a system, however, is atomically flat, as in the study by Pastewka and colleagues<sup>1</sup>, there is no ostensible roughness. Indeed, studies of friction have shown that atomically flat surfaces can sometimes exhibit no friction at all<sup>7</sup>, a phenomenon known as superlubricity. The present study, however, suggests that atomic roughness could be a key culprit in surface wear and, by extension, in determining frictional resistance. Interwoven surface 'bumps' resulting from the intrinsic roughness of an atomically flat surface may be all that is required to cause frictional resistance.

With this knowledge, how can we get rid of friction? It is known that when hydrogen is bound to DLC surfaces used to coat metals, friction and the resulting wear nearly disappear<sup>8</sup> as long as the surfaces are not too rough. When surfaces are sufficiently rough, however, friction suddenly becomes substantial. What might be happening? Hydrogen atoms covalently bound to the tough DLC surfaces will electrostatically repel one another. We surmise that as long as the repulsion distance is greater than the scale of the surface roughness, friction will become negligible. Once the surface roughness surpasses this repulsive scale, the coefficient of friction of these materials becomes very large<sup>8</sup>, as frictional resistance is then governed by the interaction of surface protrusions<sup>4–6</sup>. Hydrogenated DLC coatings are used not only in laboratory systems under special, controlled conditions: they are currently implemented in some commercial

automobile engines and their use is expected to increase considerably in future.

Given the enormous importance of friction and wear to fields ranging from nanotechnology to earthquake dynamics, it is surprising that our understanding of them is so unclear. The difficulty lies precisely in what is demonstrated here: the phenomena that we know on large scales as friction and wear are governed by seemingly insignificant microscopic or even atomic details at the interface<sup>1,2,9</sup> that separates the two sliding materials. Both friction and wear are very sensitive to the conditions at the sliding interface. This sensitivity results from the fact that the load-supporting contacts that compose the interface are both discrete and relatively few in number. The resulting huge (limiting) values of the stresses felt by the contacts effectively change the material properties, transforming the material at the interface and locally driving each point

of this tribomaterial to very near a critical state of matter<sup>10</sup>. □

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## TROUBLE ON THE SILK ROAD

No one really knows how China (the Middle Kingdom, *Zhongguo*) came to be so-called in the West, although there is no shortage of theories: perhaps it is from *Qin*, the first dynasty of Imperial China, or maybe from *Cin*, the Persian word for the region. But Ji-Huan He of the Modern Textile Institute in Shanghai argues for another derivation: beginning with *si*, the Chinese word for silk, we get 'Sino', then 'Cina' and finally 'China'<sup>1</sup>.

That etymology is significant because, for He, it links China's national identity with its claim to be the cradle of sericulture, the production of silk. That of course is the traditional picture; after all, the Silk Road commences at the ancient Chinese capital of Xi'an. The science and technology of silk manufacture is still afforded dedicated research institutes in China, where surely more is known about this ancient craft than anywhere else in the world. So it is not surprising that a recent suggestion by Irene Good of the Peabody Museum at Harvard and her colleagues that silk production might have begun independently in the Harappan culture of the Indus Valley (now in east Pakistan) has been greeted with some dismay in China. Good and colleagues identified the Harappan silks in an archaeological project

conducted in 1999–2000 through a US–Pakistan collaboration<sup>2</sup>.

The claim is challenged by He, who says that the Harappan silk fragments dated by Good *et al.* to the mid-third-millennium BC far postdate evidence for Chinese sericulture from around 5000 BC<sup>1</sup>. But that evidence is partly circumstantial: it comes from engraved drawings on ivory that have been interpreted, but not conclusively, as silkworms. Some samples of silk have been found in the Yangtze delta in Zhejiang province in association with a bamboo basket dated to 3500–2700 BC, but Good *et al.*<sup>3</sup> say that the presence, at the same site, of items such as peanuts that must stem from a much later period raise questions about the silk's age. Silk from Qingtai in Henan province is associated with cultural artefacts from 4000–3500 BC, but the textile itself lacks a radiocarbon date. So Good and colleagues argue that there are no clear examples of Chinese silk before around 2500 BC.

The debate doesn't just rest with the archaeological dating. Good *et al.* also pointed out that, on the basis of microscopic morphology of the threads, their samples of early Harappan textiles were made from the silk of wild silkmoths indigenous to southeast Asia, not the domesticated



PHILIP BALL

silkworm *Bombyx mori* used in China<sup>1</sup>. They stress that nothing in their findings threatens the notion that the domestication of silkworms first happened solely in China. Domesticated silk does not start to appear outside China until around two millennia ago.

It's unlikely that this is the end of the story. Ji-Huan He may of course be right that sericulture had a unique origin in China. But because definitive proof of that is likely to be very hard to come by, it seems risky to develop too much emotional attachment to the idea. □

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