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Invited Review

# Chemical, mechanical and tribological characterization of ultra-thin and hard amorphous carbon coatings as thin as 3.5 nm: recent developments

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## Abstract

Diamond material and its smooth coatings are used for very low wear and relatively low friction. Major limitations of the true diamond coatings are that they need to be deposited at high temperatures, can only be deposited on selected substrates, and require surface finishing. Hard amorphous carbon (a-C), commonly known as diamondlike carbon (DLC), coatings exhibit mechanical, thermal and optical properties close to that of diamond. These can be deposited with a large range of thicknesses by using a variety of deposition processes, on variety of substrates at or near room temperature. The coatings reproduce substrate topography avoiding the need of post finishing. Friction and wear properties of some DLC coatings can be very attractive for tribological applications. The largest industrial application of these coatings is in magnetic storage devices. Recent developments in the chemical, mechanical and tribological characterization of the ultra-thin coatings are reviewed in this paper. The prevailing atomic arrangement in the DLC coatings is amorphous or quasi-amorphous with small diamond ( $sp^3$ ), graphite ( $sp^2$ ) and other unidentifiable micro- or nanocrystallites. The mechanical and tribological properties of the DLC coatings are dependent upon the deposition technique. Thin coatings deposited by filtered cathodic arc, ion beam and ECR-CVD hold a promise for tribological applications. Coatings as thin as 5 nm in thickness provide wear protection. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Amorphous carbon; Diamondlike carbon; Friction; Mechanical properties; Wear

## 1. Introduction

Carbon is an unusual material in that it exhibits both metallic and nonmetallic characteristics. Carbon exists in both crystalline and amorphous forms [1,2]. Crystalline carbon includes graphite, diamond and a family of fullerenes, Fig. 1. The graphite and diamond are infinite periodic network solids with a planar structure, whereas the fullerenes are a molecular form of pure carbon with a finite network with a nonplanar structure. Graphite has a hexagonal, layered structure with weak interlayer bonding forces, and exhibit excellent lubrication properties. The graphite crystal may be visualized as infinite parallel layers of hexagons stacked 0.34 nm apart with a 0.1415 nm interatomic distance

between the carbon atoms in the basal plane. The atoms lying in the basal planes are trigonally coordinated and closely packed with strong  $\sigma$  (covalent) bonds to its three carbon neighbors using the hybrid  $sp^2$  orbitals. The fourth electron lies in a  $p_z$  orbital lying normal to the  $\sigma$  bonding plane and forms a weak  $\pi$  bond by overlapping side to side with a  $p_z$  orbital of an adjacent atom to which carbon is attached by a  $\sigma$  bond. The layers (basal planes) themselves are relatively far apart and the forces that bond them are weak van der Waals forces. These layers can align themselves parallel to the direction of the relative motion and slide over one another with relative ease, thus providing low friction. Strong interatomic bonding and packing in each layer is thought to help reduce wear. Operating environment has a significant influence on lubrication, i.e. low friction and low wear, properties of graphite. It lubricates better in a humid environment than a dry one which results

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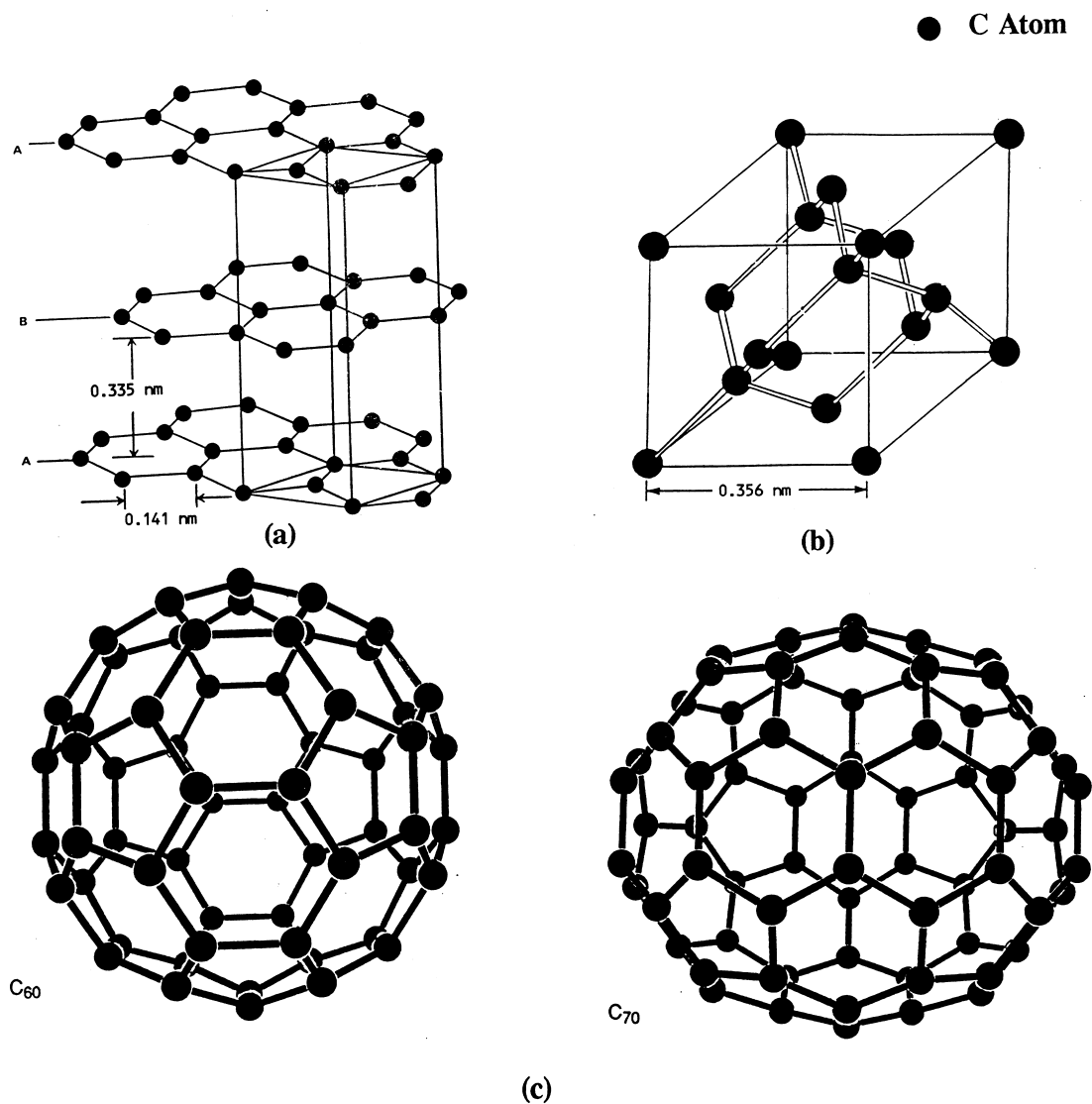


Fig. 1. The structure of three known forms of crystalline carbon: (a) hexagonal structure of graphite; (b) modified face-centered cubic (fcc) structure, two interpenetrating (fcc) lattices displaced by one-quarter of the cube diagonal, of diamond (each atom is bonded to four others that form the corners of the pyramidal structure called tetrahedron); and (c) the structure of two most common forms of fullerenes — soccer ball  $C_{60}$  and rugby ball  $C_{70}$  molecules.

from adsorption of water vapor and other gases from the environment which further weakens the interlayer bonding forces, resulting in easy shear and transfer of the crystallite platelets to the mating surface. Thus transfer plays an important role in controlling friction and wear. Graphite oxidizes at high operating temperatures and can be used up to about  $430^{\circ}\text{C}$ .

One of the fullerene molecule is  $C_{60}$ , commonly known as Buckyball. Since the  $C_{60}$  molecules are very stable and do not require additional atoms to satisfy chemical bonding requirements, they are expected to have low adhesion to the mating surface and low surface energy. Since  $C_{60}$  molecules with a perfect spherical symmetry are weakly bonded to other molecules,  $C_{60}$  clusters get detached readily, similar to other layered-

lattice structures, and either get transferred to the mating surface by mechanical compaction or are present as loose wear particle which may roll like tiny ball bearings in a sliding contact, resulting in low friction and wear. The wear particles are expected to be harder than as-deposited  $C_{60}$  molecules because of their phase transformation at high asperity contact pressures present in a sliding interface. The low surface energy, spherical shape of  $C_{60}$  molecules, weak intermolecular bonding, and high load bearing capacity offer potential for various mechanical and tribological applications. The sublimed  $C_{60}$  coatings and fullerene particles as an additive to mineral oils and greases, have been reported to be good solid lubricants comparable with graphite and  $\text{MoS}_2$  [3–5].

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