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TRIBOLOGY OF CARBON-BASED COATINGS: PAST, PRESENT, AND FUTURE

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ABSTRACT
During the last three decades, carbon-based coatings have enjoyed a growing interest in several industrial applications. By tuning the C sp³-to-sp² bonding ratio and by alloying the carbon with other elements, the researchers have been able to tailor unique physical, mechanical, and tribological properties in order to satisfy an increased technological demand. For instance, the low-friction coefficient in graphitic coatings, which were already in use as solid lubricants prior to the industrial revolution, arise from their sp²-layered structure with a weak interlayer bonding. In the other hand, high hardness carbon coatings, discovered in the mid 1950s and know presently as “diamond-like coatings” (DLC), are the result of a microstructure with a high amount of sp³-C bonding. A combination of high hardness and low friction carbon films has resulted in coatings with long-term wear resistance which reduces material and energy loses [1].

Nitrogen doping, metal, and other alloying additions have also been developed to improve mechanical, optical, and electronic properties of DLC coatings. Metal doping or carbide doping has been developed in the mid 1980s to try to improve DLC films by enhancing adhesion, thermal stability and toughness. These new tribological films can be considered to have a nanocomposite structure and offer improved hardness and elastic modulus with a certain ductility. Carbide doped hydrogenated DLCs prepared by physical vapor deposition (PVD) methods are commercially available, in particular tungsten carbide doped (WC/C) DLC, a chemically inert film with high elasticity and good wear resistance. Another example is Ti-C nanocomposites deposited by PVD methods [2].

The introduction of Si in carbon films has been used to suppress the formation of aromatic structures and to promote the diamond-like character of the films by forming tetrahedral bonds with hydrogen and CHₙ groups. In terms of the resultant properties, incorporating silicon into the DLC structure reduces residual internal stress, improves the adhesion to most
substrates, including various metal alloys, steels and glasses, increases hardness, increases thermal stability, results in a low friction coefficients independent of relative humidity, and decreases the wettability [2].

The experimental work regarding the doping of carbon films with nitrogen was sparked when, in 1989, a theoretical calculation from Liu and Cohen predicted that the hypothetical single crystal $\beta$-C$_3$N$_4$ would have a bulk modulus higher than diamond. The result was misinterpreted by some researchers, who thought that this carbon nitride material would be “harder than diamond”. So far, all attempts to synthesize this phase resulted in other crystalline structures or amorphous and short-range ordered CN-allotropes, like the “fullerene-like” carbon nitride discovered at Linköping University in 1994 (Figure 1). During the last decade, other “fullerene-like” coatings incorporating P and F have also been discovered (Figure 2) [3]. These fullerene-like compounds, obtained by self-organization of nano-curved sp$^2$-hybridized carbon features, have unique tuned mechanical and surface energy properties. They consist of bent and intersecting hexagonal basal planes, fabricated by the incorporation of odd-member rings. Cross-linking enables the material to extend the strength of the covalently 2-D hexagonal graphene network into 3-D [1]. From the tribological point of view, the fullerene-like films have lower friction coefficient, lower wear rate, and a surface energy that can be tailored according to the application [1-3].

![Figure 1: Plan view high-resolution transmission electron micrograph of the curved and intersecting fullerene-like sheets in CN$_x$ for a film grown by reactive magnetron sputtering from a carbon target in mixed Ar/N$_2$ discharge at 450°C with an N$_2$ fraction of 0.5 and a bias voltage of -25 V. The inset illustrates the buckling of the graphene sheets by pentagon-incorporation obtained from ab-initio calculations [2].](image)
In the 1990’s carbon-based coatings enabled the operation of fuel injectors in gasoline and diesel engines, providing necessary protection against wear, scuffing and other adverse effects of lubricant-lean friction. Nowadays, carbon-based thin films are found in most facets of our daily lives, from the protective coatings in the hard disks of computers to the lubricious coating in the blades of a disposable shaving machine. They are used in the chemical, food and packaging industries (valves and cutting hardware), semiconductor processing equipment (wafer handling and mechanical drives of cluster tools), compressors and pumps, and automotive industry (piston rings, camshafts, gears), etc. All the emerging applications of carbon-based coatings are originated in the great variety of crystalline and disordered structures that are possible to obtain by many different deposition techniques [4].

In this talk, the development of carbon-based coatings will be reviewed. The most recent findings in the synthesis, characterization and application of carbon-based coatings will be highlighted. Future perspectives of new fullerene-like carbon-based tribological coatings will be discussed. Novel applications of fullerene-like CNx, CPx, and CFx will be envisioned.

REFERENCES

