Investigation of tribochemical reactivity of DLC coatings by combining electronic spectroscopies (XPS/AES/REELS) and microscopy (FIB/TEM/EELS)

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ABSTRACT
Solid and liquid lubrication have a significant impact to control friction and wear phenomena omnipresent between moving parts in mechanical systems, responsible for major energy losses and reduced system life in industrial applications, such as automotive and power generation. Therefore, the use of diamond-like carbon (DLC) films with solid-like lubricant character is mostly preferred. For DLC films, carbon and hydrogen are known to have a high chemical inertia under static conditions towards their environment. On the contrary, in a lubricated sliding contact, a kind of complex "chemical reactor" operating under severe dynamic conditions, these materials can interact with the surrounding molecules. The possibility of breaking of C-H and C-C bonds under the shear effect, which leads to the emergence of C° free radicals or "dangling bonds" at the contact zone, gives rise to a wide variety of tribochemical reactions with the lubricant. It was recently showed that very rigid sp3 hydrogen-free amorphous carbon (ta-C) lubricated in the presence of the ZDDP (zinc-dialkyldithiophosphate) additive shows significant wear, associated with the absence of phosphate-based tribofilm formation. The wear is related to a preferential reactivity between the sulfur atoms released by the ZDDP and the reactive carbon atoms formed on the ta-C surface. In contrast, the softer, hydrogenated DLCs and a-C, show lower wear rates and the formation of ZDDP-derived tribofilms with higher coefficients of friction. Thus, the decomposition of ZDDP appears to be governed by contact pressure at the bearing asperities, but the surface and subsurface sulfur transport depends on both stiffness and surface chemistry [1]. Thus, the objective of this study is to investigate the tribochemical reactivity of four different DLC coatings: aC, a- C:H(20), a-C:H(40), ta-C. First, tribological experiments are performed with DLC coated-steel flat and ball in Ultra-High Vacuum (UHV) conditions in environmentally controlled analytical tribology platform (figure 1). After that, gas phase lubricated experiments were performed by introducing dimethyl sulphide (DMS) and dimethyl disulphide (DMDS) molecules in the tribometry chamber to evaluate the surface reactivity of these different DLCs. Various surface analyses combining *in situ* XPS/AES/REELS and *ex situ* FIB/TEM/EELS are performed on the tribofilms formed on the rubbed DLC surfaces.

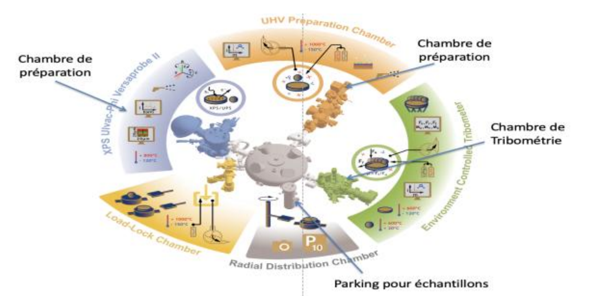

Fig.1 Platform ECAT « Environmentally Controlled Analytical Tribology»

Thereby, it is targeted to understand the interplay between mechanical/chemical contributions in the tribochemical reactions of DLCs with the existence of additives. A special attention will be paid to the modifications of the chemical hybridization state (sp2/sp3) undergone by the DLC coating in extreme surface under shear, key parameter of the tribochemical mechanisms. *Ex situ* observations by analytical transmission electron microscopy (EF-TEM) will complete these analyses to investigate the phenomena in depth (1-100 nm). Ultimately, this study is targeting to improve the way for the optimization of "multi-functional DLC surfaces", combining mechanical properties and surface chemistry, in order to better control friction and wear properties of DLC films.

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REFERENCES

[1] V. R. Salinas Ruiz, et *al.*, *Nature Communications* (2021) *12*(1) 4550.