INFLUENCE OF THE STRUCTURE AND THE MORPHOLOGY ON THE FRICTION PROPERTIES OF FLUORINATED CARBON NANO/MICRO PARTICLES

P. Thomas[1], J.L. Mansot [1], W. Zhang[2], M. Dubois[2],
K. Guérin [2], A. Hamwi[2]

[1]Groupe de Technologie des Surfaces et Interfaces (GTSI EA2432), Université des Antilles et de la Guyane, Faculté des Sciences Exactes et Naturelles, Campus Fouillole, Pointe a Pitre Cedex, Guadeloupe (FRANCE)
[2] Laboratoire des Matériaux Inorganiques, Universite Blaise Pascal de Clermont-Ferrand, UMR-CNRS 6002, 63177 Aubiere (FRANCE)

Introduction

Conventional liquid lubricants are composed of mineral or synthetic oil (base) and additives used to confer to the lubricant specific characteristics such as friction and wear reduction, viscosity improvement, anti-oxidising effect, anti-corrosive properties [1, 2]. The action mechanism of conventional additives is related to the formation, on the sliding surfaces, of a protective tribofilm resulting from chemical reactions between additives molecules and surfaces. The antiwear efficiency is consequently modulated by the reactivity of additives with the sliding materials.

Recent strategies have been investigated, consisting in the introduction, in the lubricant base, of nanoparticles of tribo-active phases or precursors of tribo-active phases [3, 4] subjected to build on the sliding surfaces the tribofilm without any chemical reactions with the substrates.

Fluorinated carbons are well known to present good friction properties and are conventionally used as solid lubricants [5, 6]. The reactivity of carbon structures with fluorine depends on the graphitization and the hybridization state of the carbon atoms, the resulting C-F bonding being either ionic or covalent [7]. The good friction properties of fluorinated carbon species let suppose the possible use of fluorinated carbon nanoparticles as efficient "nano additives".

In this work, the friction behaviour of various new nano fluorinated carbons, respectively carbon nanofibres, amorphous and graphitized carbon nanodiscs and nanocones, was investigated, the fluorination process and temperatures being adjusted to obtain various fluorine contents.

Experimental

High purity carbon nanofibres (MER Corporation) noted CNFs were fluorinated in F_2 atmosphere at temperatures (T_F) ranging between 380°C and 472°C for a reaction time of 16h. This allowed us to achieve fluorination contents, expressed as atomic F/C ratio, in the range 0.04-1.0. The second type of starting carbonaceous nanoparticles was a mixture of carbon nanodiscs, carbon nanocones and amorphous carbon (70/20/10 weight percent composition). These original materials were used as delivered (sample called CNDs) or after graphitization by high temperature (2700°C) under argon treatment (sample called CND2700s). Two series of fluorinated carbon nanodiscs/nanocones were prepared (3h in fluorine atmosphere) from CNDs and graphitized CND2700s. The fluorination temperatures were selected (T_F in the range 280-380°C and 450-520°C for CNDs and CND2700s respectively) to obtain similar fluorine contents for the two series of compounds.

The tribologic properties of the compounds were evaluated using an alternative ball-on-plane tribometer consisting of an AISI 52100 steel ball rubbing against an AISI 52100 steel plane on which the tested material was deposited. The sliding speed was 6 $mm.s^{-1}$ and the normal applied load of 10N leads to a contact area diameter of 140 μm (according to Hertz's theory) and a mean contact pressure of 0.65 Gpa. The friction coefficient was measured with a computer-based data acquisition system. Powdery nanofibres or nanodiscs were deposited on the plane surface. After ball on plane contact, a drop of pentane (boiling point 36°C) was added in order to improve the particle feeding of the sliding contact and the establishment of the tribofilms. The pentane evaporation allowed us to investigate the intrinsic tribologic properties of the various fluorinated carbon nanoparticles in air.

Structural studies of the initial compounds and the corresponding tribofilms were performed by means of Raman spectroscopy and Scanning Electron Microscopy analyses. Raman spectroscopy investigations were performed with a HR 800 Horiba multi channel spectrometer using a Peltier cooled CCD detector for signal recording. The exciting line was the 532 nm wavelength radiation delivered by Nd YAG laser. The laser power at the sample level was 30 mW and acquisition time was in the range of 10 to 60 seconds depending on the sample thickness. Secondary electron images were obtained using a Hitachi H600 microscope running at 4 kV with a LaB_6 cathode. For film structure investigations, the tribofilm was scratched with a sharp iron needle allowing to study the extracted particles maintained on the iron planes.

Results and Discussion

The tribologic properties of CNFs, CNDs and CND2700s, as a function of F/C ratio are presented in Fig.1. In both cases, fluorination improves the friction performances as fluorinated nano/micro particles present lower friction coefficients than pristine ones.

In the case of carbon nanofibres, the friction coefficient decreases from 0.13 for pristine CNFs down to 0.08 for F/C = 0.15 and does not evolve any more when increasing the fluorination rate (0.2-0.8 F/C range). The influence of friction is less visible in the case of graphitized carbon nanodiscs (CND2700 samples). The friction coefficient remains close to 0.08 whatever the fluorination content was. The friction behaviour is drastically different for amorphous CNDs. In this case, the influence of fluorination is important as μ decreases from 0.21 for pristine CNDs down to 0.10 for higly fluorinated ones (F/C = 0.9).

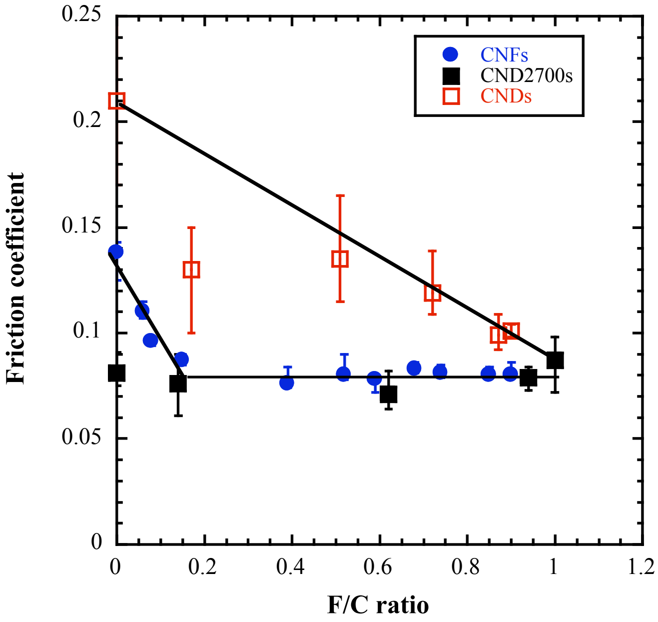

Fig. 1 Evolution of the friction coefficient in air of CNFs, CNDs and CND2700s as a function of F/C ratio.

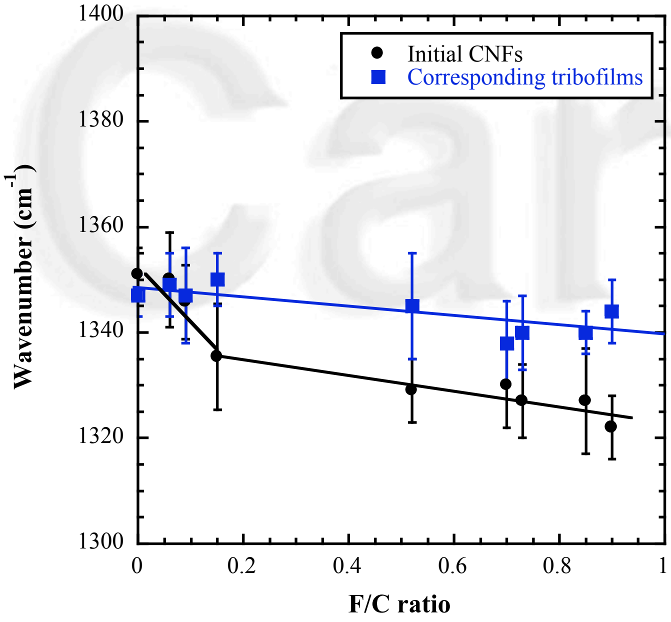

Fig. 2 Evolution of the D band position as a function of F/C ratio for the initial CNFs and the corresponding tribofilms.

Raman spectroscopy analyses were performed on the initial compounds and on their corresponding tribofilms. All the spectra exhibit the characteristic D, G and D' bands associated to the presence of graphitic domains in the tested fluorocarbonaceous structures [8]. In all cases, the increase of the F/C ratio leads to a downshift of the D band for initial compounds, as evidenced in Fig.2 for CNFs. This downshift is attributed to the increase of the C-F bonds content and the size reduction of the graphitic domains due to fluorination. In the case of the corresponding tribofilms, the D band is shifted towards the high wave numbers compared to the initial compounds, whatever the fluorination rate was. This phenomenon points out a partial transformation of the nanoparticles into ill-organized phase during the friction process.

This partial transformation was confirmed by SEM experiments. The study of particles extracted from the wear scars shows that in the case of carbon nanofibres, the tribofilms are mainly composed of individual fibres covered by a thin amorphous layer. Contrarily to CNFs, the structure of the tribofilms is mainly amorphous in the case of carbon nanodiscs. The presence of some individual nanodiscs can be observed for CND2700s.

Conclusions

The study of the tribologic properties of fluorinated carbon nanofibres and nanodiscs shows that fluorination improves the lubricating performances of the compounds. CNFs and graphitized CND2700s present adequate properties to be uses as new nano-additives.

The fibrous nature of the tribofilms observed in the case of CNFs suggests that individual nanofibres are involved in the friction reduction process. The interfibres interactions are lowered for low fluorine contents (F/C < 0.15) because of the fluorination of the external graphene layers leading to the lowering of surface free energy. The interfibres interactions do not evolve any more when the fibres surfaces are completely fluorinated (F/C > 0.15) resulting in a stabilization of the friction coefficient.

In the case of carbon nanodiscs, the evolution of friction properties, regarding their initial structure, points out that initial long range order (graphitic structure) is a parameter of first order. Contrarily to CNFs and as for fluorinated graphite, the improvement of friction properties seems to result from bulk effects and are obtained for low fluorine contents.

References

[1] Booser, E.R.: Tribology data handbook, CRC Press, New York 1997.
[2] Georges, J.M.: Frottement, usure et lubrification: la tribologie ou science des surfaces, CNRS editions, Eyrolles 2000.
[3] Mansot, J.L., Martin, J.M., *Nanolubricants*, Wiley, New York 2008, Chapter4.
[4] Mansot, J.L. Martin, J.M., Bercion, Y., Romana, L., Brazil. J. of Phys.2009, 39, 53.
[5] Fusaro, R.L.: Mechanisms of graphite fluoride $(CF_x)_n$ lubrication. Wear 1979, 53, 303-323.
[6] Tsuya, Y.: Tribology of graphite fluorides. in T. Nakajima (Ed), Fluorine-carbon and fluoride-carbon materials, Marcel Dekker, New York 1995, 355-380.
[7] Hamwi, A., Daoud, M., Cousseins, J.C.: Graphite fluorides prepared at room temperature. 1. Synthesis and characterization. Synhttic Metals 1988, 26, 89-98.
[8] Delbé, K., Thomas, P., Himmel, D., Mansot, J.L., Dubois, M., Guérin, K., Delabarre, C., Hamwi, Tribol. Lett. 2009, 37(1), 31-41.