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Friction properties of fluorinated carbons

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1. Introduction

In boundary lubrication regime, friction reduction and antiwear processes are associated to the presence of additives in the lubricating oils or greases [1]. These processes are due to the formation of protective tribofilms resulting from chemical reactions between the additives and the sliding surfaces, in the physico-chemical conditions of the sliding contact.

Conventional antiwear additives mainly consist of transition metal organo phosphate or thiophosphates which present a remarkable efficiency in the case of contacts between ferrous alloys [2]. In the case of non reacting surfaces, these additives become inactive.

Recently developed lubrication strategies consist in the use of dispersion in oils of nano additives able to build the protective tribofilm in the sliding contact without reaction with the surfaces [3,4]. Carbon fluorinated phases, due to their lamellar structure and their high chemical stability even at relatively high temperature (400°C) represent interesting candidates as lubricant nano-additives subjected to present friction reduction, anti wear and anti corrosion actions.

This work presents the tribologic behaviour of some carbon fluorinated derivatives such as graphite fluorides, fluorinated carbon nanofibers, fluorinated carbon nanodiscs and fluorinated carbon blacks. The influence, on the tribologic performances, of the structure of the initial carbon phases, of the fluorination rate ($0 < F/C < 1$) and the structure of the fluorinated compounds is discussed.

2. Experimental

2.1. Materials

Graphite fluorides synthesis results from bi-fluorination processes (room temperature synthesis of graphite intercalation compounds with fluorinated species and high temperature post-treatment under fluorine atmosphere) allowing us to control the nature of the C-F bonding (evolving from semi-ionic to covalent) and consequently the friction properties. Graphite intercalation compounds were prepared from Madagascar natural graphite powder at room temperature under F_2 atmosphere with a gaseous mixture of HF and a volatile fluoride to improve the

reactivity of fluorine with graphite [5]. The volatile fluorides MF_n used were BF_3 and ClF_3, leading to the fluorinated materials noted B and C respectively. The reaction time was 14h. The synthesis method is precisely described elsewhere [5, 6]. The compounds were then treated under fluorine atmosphere at temperatures, noted T_{FPT}, ranging from 150 to 600°C leading to two series of compounds, named $B(T_{FPT})$ and $C(T_{FPT})$. The corresponding fluorination rates, expressed as atomic F/C ratio are given in Table 1.

Table 1   Evolution of the fluorine content (atomic F/C ratio determined from weight uptake) as a function of T_{FPT} for B (synthetized with HF-BF_3 catalysts) and C (synthetized with HF-ClF_3 catalysts) series

Fluorination post-treatment temperature (T_{FPT})	$B(T_{FPT})$ F/C ratio	$C(T_{FPT})$ F/C ratio
Room temperature	0.47	0.42
150°C	0.39	-
250°C	0.40	0.41
300°C	0.41	0.43
350°C	0.63	0.45
400°C	0.85	0.51
450°C	0.93	0.80
500°C	0.99	0.93
550°C	1.01	0.94

In the case of nanocarbons, 2D (graphitized carbon nanodiscs CNDs), 1D (carbon nanofibers CNFs) and 0D (graphitized carbon blacks GCBs) materials were fluorinated in F_2 atmosphere. The selection of the fluorination temperatures (T_F) and reaction time allowed us to achieve fluorination contents, expressed as atomic F/C ratio, in the range 0.08-1.0 [7-9].

2.2. Tribologic tests

The tribologic properties of the compounds were evaluated using a ball-on-plane tribometer consisting of an AISI 52100 steel ball describing an alternative motion on a static 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 theoretical contact area diameter of 140 μm (according to Hertz's theory) and a mean contact pressure of 0.65 Gpa. The friction coefficient μ was measured with a computer-based data acquisition system..

In the case of graphite fluorides, the studied materials were deposited on the planes in the form of films by the burnishing method consisting in the crushing of few milligrams of powdery of fluorinated material between two planes leading to the formation of an adherent surface film of 1-2 μm thickness.

The experimental procedure was different in the case of nanocarbons. Powdery compounds 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 accelerate the establishment of an homogeneous film constituted of the particles.

The friction coefficient was determined after three cycles (three cycles after pentane evaporation in the case of nanocarbons) corresponding to the intrinsic tribologic properties of the deposited films, i.e. before structural transformations induced by the friction process.

2.3. Raman spectroscopy investigations

Structural studies of the initial compounds and the corresponding tribofilms were performed by means of Raman spectroscopy, 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 a 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. In order to determine with a high precision Raman bandshifts resulting from structure evolutions, the samples were simultaneously illuminated with a vapour mercury lamp. Emission lines appearing at 1464 cm^{-1} and 1527 cm^{-1} were used as internal spectral references and allowed us to deduce the Raman band position with a precision of ± 1 cm^{-1}.

3. Results and discussion

Figure 1 presents the evolution of friction coefficient as a function of post treatment temperature for B(T_{FPT}) and C (T_{FPT}) graphite fluorides. Whereas the friction coefficient remains stable for partially fluorinated compounds, it increases for the highest fluorination contents corresponding to the highest post treatment temperature.

Considering the structure evolution of the compounds as a function of fluorination post-treatment temperature presented in Figure 2, the tribologic results show that very low friction coefficients (close to 0.06) are obtained if the planar initial structure of the graphene sheets is maintained The increase of the post-treatment temperature leads to the formation of armchair type structure (associated to the removal of

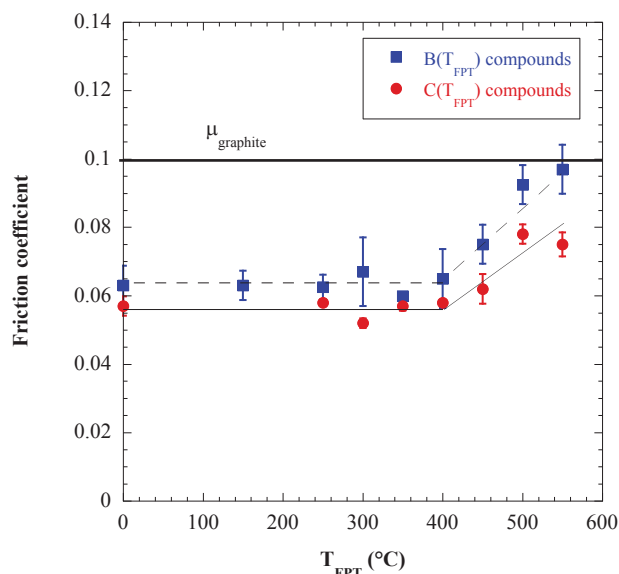intercalated species and the C-F covalent bonding) resulting in a degradation of the friction performances.

Figure 1 Evolution of friction coefficient (recorded after three cycles) as a function of fluorination post-treatment temperature for B(T_{FPT}) and C(T_{FPT}) materials
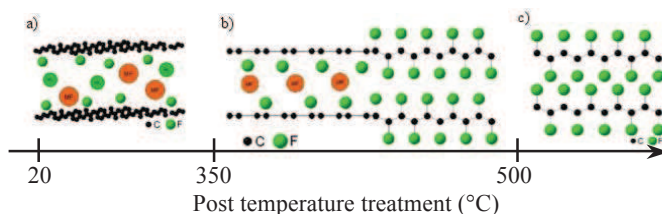

Figure 2 Evolution of the structure of graphite fluorides as a function of post-treatment temperature T_{FPT}

In the case of fluorinated nanocarbons, the C-F bonding is covalent for all the compounds. Figure 3 presents the evolution of intrinsic friction coefficient (recorded at three cycles) as a function of F/C ratio for fluorinated carbon nanodiscs, nanofibers and carbon blacks. In the case of CNFs and GCBs, the intrinsic friction properties are strongly improved by fluorination. Starting from μ > 0.1 for pristine materials, the friction coefficient decreases to raise an asymptotic value close to 0.08 for F/C ratios superior to 0.15 and 0.6 for CNFs and GCBs respectively. In the case of CNDs, the friction coefficient does not depend on the fluorine content (0.07 < μ < 0.08).

These different tribologic behaviors can be interpreted considering the fluorination process of the compounds. In the case of fluorinated carbon nanofibers and carbon blacks, TEM analyses show that the external layers are firstly fluorinated and then the fluorination process progresses towards inner ones [8, 9]. The decrease of the friction coefficient is associated to the decrease of surface free energy of the particles during the fluorination of external carbon layers. The stability of μ after the complete fluorination of the surface of the materials strongly suggests that the friction reduction

mechanism is associated to interparticles interactions [10]. In the case of graphitized carbon nanodiscs fluorinated derivatives, the fluorination process occurs via the edge of the nanodiscs. The stability of the friction coefficient as a function of the fluorination rate strongly suggests friction reduction mechanisms resulting from bulk structure effects.
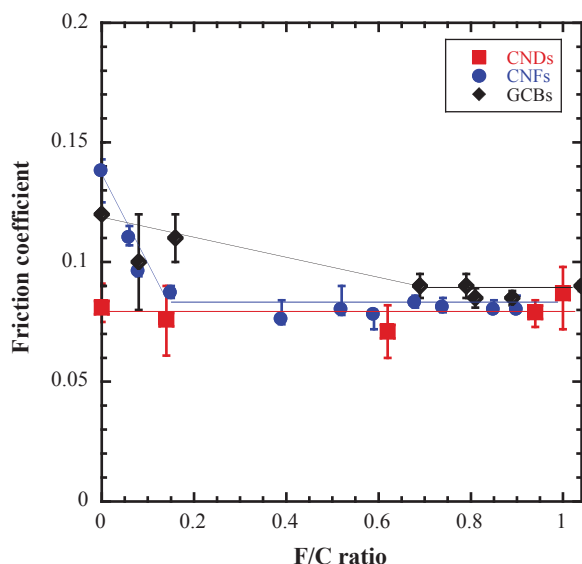

Figure 3   Evolution of friction coefficient (recorded after three cycles) of fluorinated carbon nanodiscs, nanofibers and carbon blacks as a function of fluorination fluorine content

4. Conclusion

The investigations of the friction properties of pristine and fluorinated carbon phases show that fluorinated derivatives present improved tribologic properties compared to pristine compounds.

In the case of graphite fluorides, the bi-fluorination process (room temperature synthesis and post-treatment under fluorine atmosphere) allows us to control the nature of the C-F bonding and as a consequence the friction properties.

The tested carbon nanostructures appear as promising new nano-additives. Here again, the control of the fluorination conditions allows us to achieve optimized friction properties. The advantages of fluorinated nanocarbons are their sizes and geomeries, well adapted for a good feeding of the sliding interface, their high chemical and temperature stability and the possibility to obtain stable dispersions in liquid or gel lubricants.

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