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The chemical reactivity of graphite fluoride in conjunction with its use as a solid lubricant

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Interpretation of differential scanning calorimetry (DSC) results suggest that on heating tin/graphite fluoride, cadmium/graphite fluoride and indium/graphite fluoride mixtures to 773 K, chemical reactions occur. Examination of the reaction products from these reactions by X-ray photoelectron spectroscopy (XPS) clearly shows the presence of metallic fluorides. These fluorides are also formed on evaporation of tin, cadmium and indium onto the clean polymer surface. Graphite fluoride flims rubbed on stainless steel, nickel and aluminium counterfaces also form metal fluorides at the interface suggesting a different interpretation of the mode of failure of the lubricant film of this material.

1. Introduction

The recent interest in the use of graphite fluoride $(CF_x)_n$ as a solid lubricant stems from the publication in 1969 of a preliminary study [1] concerning the friction and wear properties of this compound. Results showed that the friction coefficients of $(CF_x)_n$ were comparable or superior to those of MoS_2 and graphite; with greater wear lives under particular experimental conditions than the latter compounds.

For over a century graphite has been known to form chemical compounds by reaction or by intercalation with other substances. The discovery of $(CF_x)_n$ is attributed to Ruff, Bretschneider and Bert [2] who found in 1934 that graphite and fluorine combined without combustion at approximately 693 K to form a grey coloured solid. Other workers [3, 4] have since found that by varying reaction parameters such as temperature and pressure, different fluorine to carbon ratios could be obtained. Products with compositions in the range of $CF_{0.68}$ to $CF_{0.8}$ are nearly black while those of compositions $CF_{0.8}$ to $CF_{0.95}$ and $CF_{0.95}$ to $CF_{1.2}$ are grey and white, respectively.

Graphite fluoride has puckered ring structure with fluorines substituted above and below the rings causing expansion of the inter-layer C–C bond distances. There are, at present, thought to be two possible structures either translinked cyclohexane rings in the chain conformation [5] or as *cis*-translinked cyclohexane boats [6].

Compounds of $(CF_x)_n$ are stable in air up to at least 873 K [4] decomposing at approximately 1073 K or under a high vacuum at 693 to 853 K forming elemental carbon and fluorocarbon containing up to six carbon atoms [7]. Graphite fluorides are chemically inert being stable in acids and alkalis.

Improvements in the wear lives of burnished graphite fluoride films have been achieved by bonding to the substrate with polyimide [8]. Good wear properties are also found using graphite fluoride in both silicate and epoxy–phenolic binders [9]. Graphite fluoride has also been used as an additive in greases, mechanical carbons and carbon fibre-reinforced PTFE [10]. Recently [11], various polymers have been grafted onto the surface of $(CF_x)_n$ resulting in improved adhesion and when used as a suspension in paraffin oil, a better load carrying capacity is obtained.

Atkinson *et al.* [12] have carried out X-ray photoelectron spectroscopy (XPS) studies in conjunction with wear tests of graphite fluoride films rubbed against a stainless steel counterface and have found evidence of metallic fluoride formation.

It has become increasingly apparent (cf. [13]) that in order to realize the full potential of graphite fluoride or any such polymer as a solid lubricant, it is necessary to obtain basic information concerning its chemical as well as frictional properties and, in particular, any interactions with potential metal counterfaces which may occur in its tribological applications [14]. XPS has been used to analyse the products at various metal–$(CF_x)_n$ binary mixtures which have been heated to 773 K in a DSC. A useful technique for studying the reacting species is by metal evaporation onto a clean polymer surface. When carried out under UHV conditions this obviates any possible interference/catalytical effects of surface contaminants and accords further study on the elucidation of the reaction mechanism by XPS examination *in situ* of the metal polymer interface. This work also describes the XPS examination of the interface formed when $(CF_x)_n$ is rubbed against particular metals.

XPS is an important and powerful technique for studying tribochemical processes mainly due to its surface sensitivity. The principle of the technique has been described previously [15, 16] including its application to tribological problems [12, 17, 18].

2. Experimental procedure

A Perkin Elmer DSC 1B was used to search for any thermal transitions occurring during the heating to 773 K (under a N_2 atmosphere – < 1 ppm O_2) of the various metal/graphite fluoride mixtures (volume ratio 1 : 1). The heating took place in aluminium sample pans.

Cadmium was evaporated onto the polymer surface in an Edwards evaporator (10^{-5} Torr pressure) but the tin and indium evaporations were performed in an UHV preparation chamber (base vacuum 10^{-10} Torr) directly attached to the photoelectron spectrometer [9]. Prior to evaporation the polymer surfaces were cleaned by abrasion with a razor blade. XPS examination showed that this method produced a very clean surface (less than 5% of a monolayer impurities at UHV) although in the external evaporation of Cd, some contamination by surface oxygen and carbon is to be expected. Several attempts to evaporate cadmium under UHV conditions in the preparation chamber were not successful for inexplicable reasons.

Graphite fluoride $(CF_{1.0})_n$ was obtained from Ozark-Mahoning Co and the metal powders were B.D.H. laboratory reagents of particle size 10 to 20 μm. The metal wires were obtained from Goodfellow Metals (99.99% purity). Indium used in the DSC experiments was in the form of wire finely cut into small pieces.

The mixtures obtained from heating metal/graphite fluoride mixtures in the DSC were pressed (10 ton in.$^{-2}$) to form suitably sized samples for XPS examination. The graphite fluoride substrates used in the evaporations and rubbing experiments were pressed in the same way.

Samples of stainless steel, nickel, aluminium and copper were cleaned with emery paper and immediately rubbed by hand (pressure approximately 1 Nm^{-2}) for 1 to 2 min with clean $(CF_{1.0})_n$ under atmospheric conditions. These samples were then examined by XPS. After subsequent withdrawal from the instrument, the samples were next scraped with a razor blade to partially remove the transferred polymer adlayer from the surface and then were re-examined by XPS. This cycle was repeated as required.

The X-ray spectrometer used was an A.E.I. E.S. 200A using Mg$K\alpha$ X-ray radiation.

3. Results

The results from heating mixtures of graphite

TABLE I Binary system containing metal and graphite fluoride heated in the DSC

Metal	Thermal events	Comments
Ag	None	No reaction up to 773 K
Al	None	No reaction up to 773 K
Cd	Exotherm 683 K m.p. Cd	Reaction at 683 K; Black residue
Cr	None	No reaction up to 773 K
Cu	None	No reaction up to 773 K
Fe	None	No reaction up to 773 K
In	Exotherm 573 K m.p. In	Reaction at 573 K; Black residue
Ni	None	No reaction up to 773 K
Pb	Pb m.p.	No reaction up to 773 K
Sn	Exotherm 733 K m.p. Sn	Reaction at 733 K; Black residue
Zn	Zn m.p.	No reaction up to 773 K

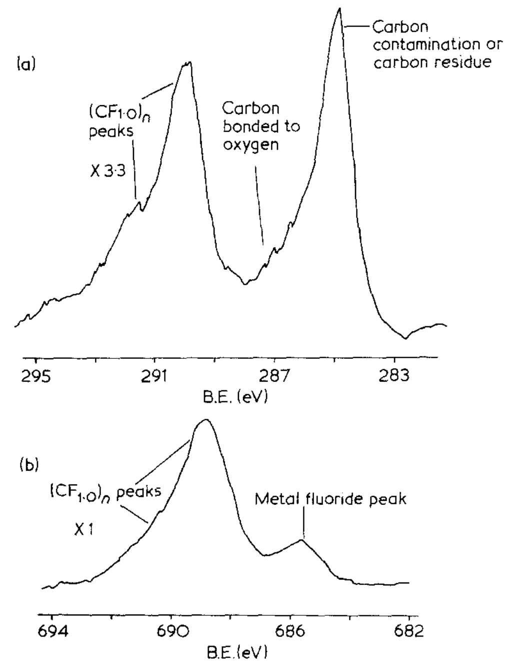

Figure 1 XPS examination of Cd-$(CF_{1.0})_n$ DSC residues (a) C(1s) spectrum. (b) F(1s) spectrum.

fluoride with a number of individual metals to 773 K in the DSC are presented in Table I. Of these metals, cadmium, indium and tin all appear to react with $(CF_{0.1})_n$ exhibiting exothermic peaks at temperatures below 733 K.

XPS analysis of the black residues showed that for each sample there was a peak in the F(1s) spectra (Figs. 1 and 2) which could be attributed to metallic fluoride formation. The other peaks in the F(1s) spectra have concomitant C(1s) peaks; the splitting of 399 eV between F(1s) and C(1s) and respective stoichiometries [20, 21] of $(CF_{1.0})_n$ indicates that they originate from the unreacted graphite fluoride. The twin $(CF_{1.0})$ F(1s) peaks for the cadmium mixture Fig. 1b arises from $(CF_{1.0})_n$ species present in differing electrical environments (i.e. charging effects [22] are occurring). The low binding energy (B.E.) C(1s) signal present for every sample arises partly from carbonaceous residue formed in the reaction and partly from contamination sources. The high B.E. shoulder on this principle peak is attributed to carbon bonded to oxygen containing contaminants. It is not possible to detect fluoride shifts in the metal spectra because of contaminant oxidation of the metals.

All the samples showed similar behaviour on argon etching (30 min, 5×10^{-5} Torr; Fig. 3).

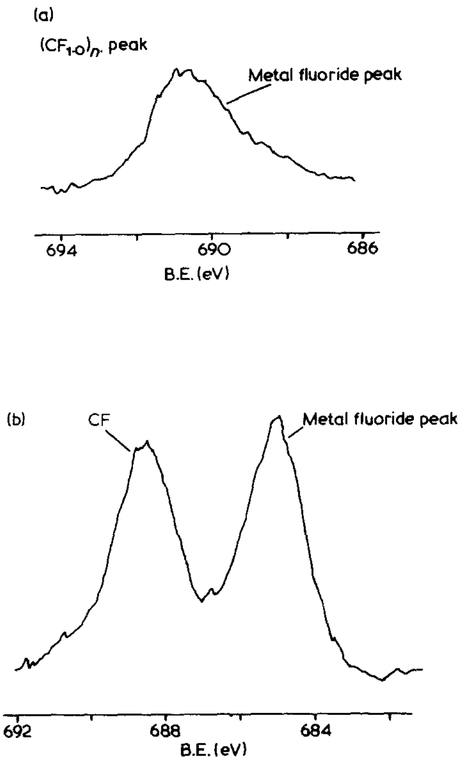

Figure 2 (a) XPS examination of In-$(CF_{1.0})_n$ DSC residue, F(1s) spectrum. (b) XPS examination of Sn-$(CF_{1.0})_n$ DSC residue.

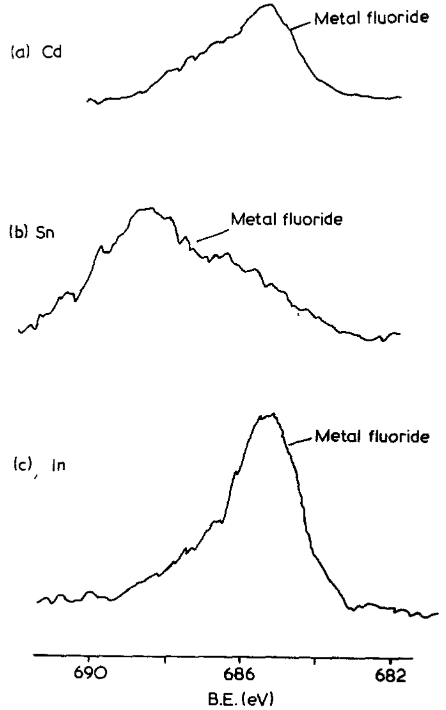

Figure 3 XPS examination of argon-etched metal-DSC residues, F(1s) spectra.

Argon bombardment diminished the graphite fluoride peak intensities by preferential removal of the fluorine atoms leaving residual carbon chemically shifted at 284.7 eV. The metallic fluoride signals were enhanced in intensity as a result of the argon ions forming more fluoride ions, probably as metallic fluoride.

3.1. Evaporation of tin onto graphite fluoride

After evaporation of tin onto the polymer substrate at 10^{-8} Torr, XPS examination showed that there was a doublet peak in the F(1s) spectrum (Fig. 4b). The part at high B.E. can be ascribed to the polymer substrate while the peak at 684.7 eV B.E. can be assigned to metal fluoride formed at the interface during the evaporation. The Sn(3d) spectrum has correspondingly changed into two sets of doublets (Fig. 4a).

The fluoride separation of the Sn(3d$\frac{5}{2}$) fluoride peak from that of the metal is 2.8 eV which is larger than the value [6] found for SnO_2 (1.7 eV). The stoichiometry of the concomitant Sn(3d) and F(1s) peaks is approximately SnF_2. The B.E. of the Sn3d$\frac{5}{2}$ metal peak was found to be 484.9 eV compared to a previous value [6] of 484.5 eV. Argon etching (5×10^{-5} Torr, 15 min, Fig. 4c) causes the diminution of the $(CF_{1.0})_n$ and tin metal peaks whereas the intensity of the fluorine (in the tin fluoride) is enhanced giving a final stoichiometry of approximately SnF_3.

3.2. Evaporation of indium onto graphite fluoride

The sample of graphite fluoride was coated with indium at 10^{-8} Torr as above. Two peaks were found in the F(1s) spectrum Fig. 5b. The higher B. E. peak with its concomitant C(1s) peak (stoichiometry $CF_{1.0}$) is again ascribed to the graphite fluoride substrate. At lower B.E. the peak at 684.8 eV was assigned to the metallic fluoride produced by the metal on evaporation. The B.E. of the In(3d$\frac{5}{2}$) metal peak of 443.6 eV is exactly the same as a recently published value [22]. The shift of 1.5 eV to higher B.E. of the In(3d) spectra (Fig. 5a) caused by the fluoride compares with 1.1 eV for indium oxide [22]. Also present in the In(3d) spectra were two peaks at energies of 11.7 eV higher than the metal In(3d) peaks. These have been previously identified as plasmon peaks [23].

Argon-ion bombardment (5×10^{-5} Torr, 100 min; Fig. 5c) caused the intensity of the polymer and the indium metal peaks to diminish but increased the concentration of the fluorine in metal fluoride. The stoichiometry changed from $InF_{1.3}$ before etching to $InF_{1.8}$ after the etch. The B.E.s of the concomitant In(3d$\frac{5}{2}$) and fluoride

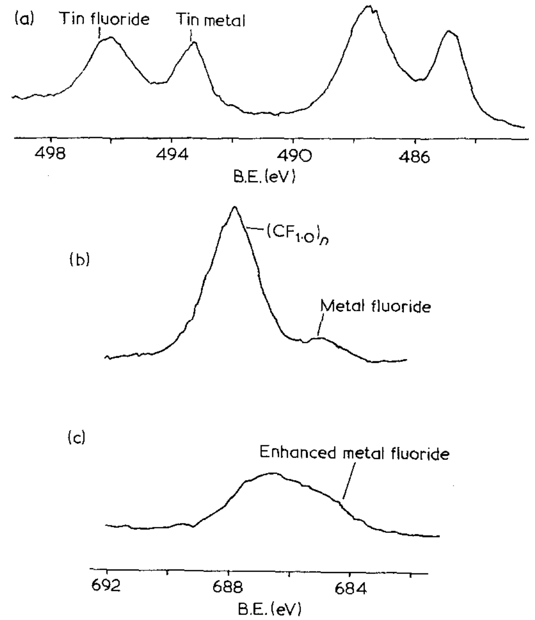

Figure 4 XPS examination of Sn evaporated onto $(CF_{1.0})_n$ (a) Sn(3d) spectrum, (b) F(1s) spectrum, (c) argon-etched sample, F(1s) spectrum.

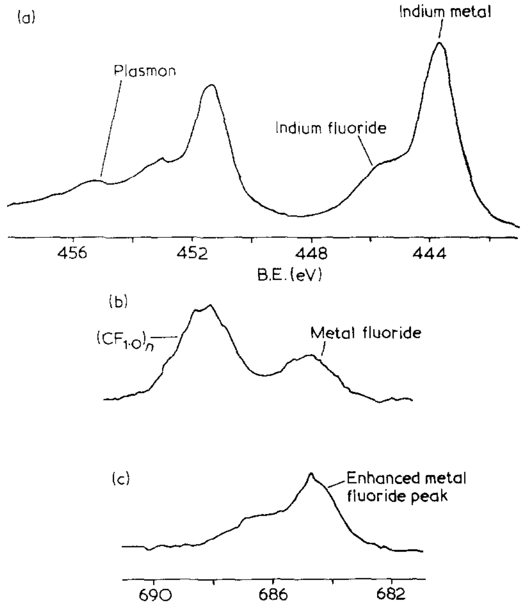

Figure 5 XPS study of In evaporated onto $(CF_{1.0})_n$. (a) In(3d) spectrum, (b) F(1s) spectrum, (c) argon-etched sample, F(1s) spectrum.

F(1s) peaks increased by 2 eV with the increasing fluoride content in the compound.

3.3. Evaporation of cadmium onto graphite fluoride

XPS examination of $(CF_{1.0})_n$ samples coated with cadmium in an Edwards evaporation again showed the presence of a doublet peak in the F(1s) spectra (Fig. 6a). The higher B.E. line is identified as of graphite fluoride origin. The peak at 684.4 eV is attributed to cadmium fluoride formed at the interface.

Transfer of the sample through air in this case before the XPS examination contributes to high contamination levels. The Cd(3d) doublet peaks were broadened by surface oxidation shifting the peaks to higher B.E.

Argon-ion etching (5×10^{-5} Torr, 30 min) preferentially removed the surface oxide causing the half-width of the Cd($3d\frac{5}{2}$) to decrease from 2.4 eV to 1.1 eV. There was no evidence for a shift in the Cd(3d) spectrum due to fluoride formation.

The polymer peaks were also removed by the etching procedure leaving the metallic fluoride (Fig. 6b) and residual carbon behind as before.

3.4. Graphite fluoride rubbed against various metals

XPS examination of metals rubbed with graphite fluoride showed only the presence of the transferred graphite fluoride adlayer either in the form of single or doublet peaks depending on the presence of charging effects. Initial scraping with a razor blade diminished the intensity of the polymer peaks especially those at higher B.E. For the stainless steel (Fig. 7), nickel (Fig. 8a) and aluminium (Fig. 8b) samples, there emerged peaks at lower B.E. which can be attributed to fluoride signal and are formed at the polymer–metal interface during the rubbing. There was no evidence of fluoride formation for the copper sample. Further scraping of the samples initially enhanced the fluoride intensities but eventually they also diminished. With the removal of the polymeric adlayer there was a corresponding increase in the substrate signals. Argon etching (5×10^{-5} Torr, 30 min) removed all traces of graphite fluoride F(1s) peaks but the metal fluoride peaks still remained (Fig. 8c).

4. Discussion and conclusion

A reaction between tin and graphite fluoride giving a metal fluoride was first reported in 1934 [2]. More recent work [24] using a combination of differential thermal analysis and thermogravimatric analysis has found that heating graphite fluoride with alkali halides such as KI, KBr, KCl, NaI, NaBr and NaCl results in the formation of gaseous

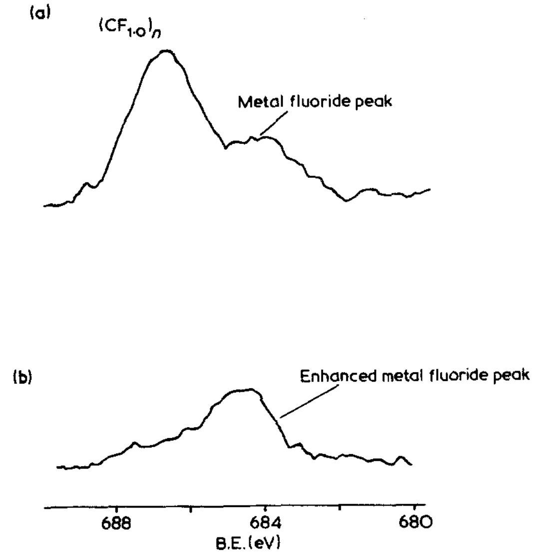

Figure 6 XPS study of Cd evaporated onto $(CF_{1.0})_n$. (a) F(1s) peaks prior to etching, (b) F(1s) peaks after etching.

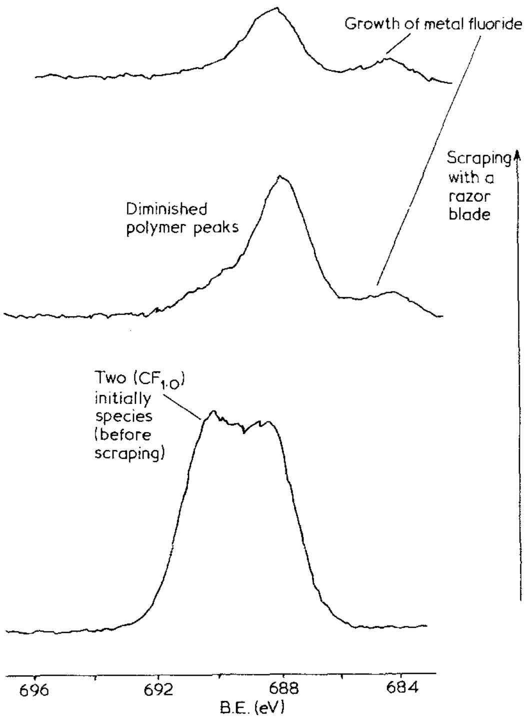

Figure 7 XPS study of stainless steel rubbed with $(CF_{1.0})_n$.

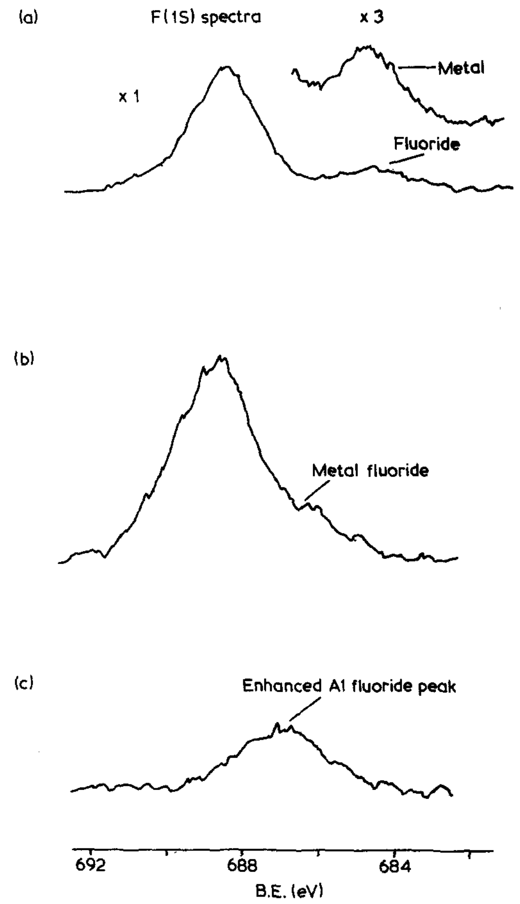

Figure 8 XPS study of nickel and aluminium rubbed with $(CF_{1.0})_n$. (a) Ni rubbed with $(CF_{1.0})_n$ and scraped with a razor blade. (b) Al rubbed with $(CF_{1.0})_n$ and scraped with a razor blade. (c) Al sample alone argon–ion etched.

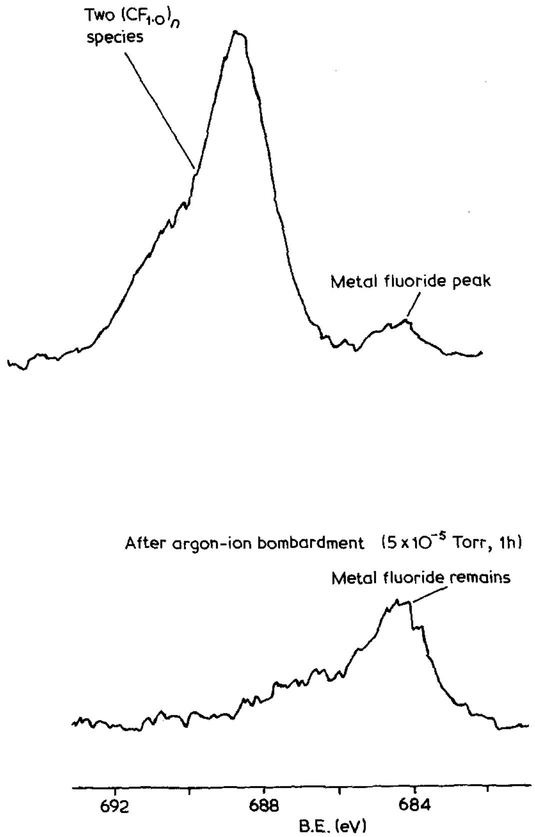

Figure 9 XPS studies of Sn-CF sample heated under pressure.

halogens and alkali fluorides. Another product of these highly exothermic reactions was carbon. Graphite fluoride reacts similarly with potassium carbonate giving potassium fluoride and carbon dioxide [24]. Pure graphite fluoride alone has been found to decompose at about 873 K giving only a mixture of carbons and low molecular weight fluorine compounds such as CF_4, C_2F_4, C_3F_6 etc. The carbon was found to be sooty and completely amorphous from X-ray diffraction studies.

From this work it is concluded that tin, cadmium and indium also react on being separately heated with graphite fluoride giving a reaction product of metal fluoride and amorphous carbon. Although the temperatures at which these reactions take place in the DSC are not likely to be reached under normal conditions of use, increased mechano-chemical effects such as pressure and catalysis could provide a pathway for these reactions to occur at lower temperature. For example, reaction has been found to occur between tin and graphite fluoride forming a metal fluoride (Fig. 9) on heating the powdered mixture for 10 min at 523 K under 10 ton in^{-2} pressure.

The study of these metal evaporations onto the virgin polymer surfaces supports the DSC results suggesting that reactions are occurring at the metal polymer interfaces with consequent fluoride formation. It is probable that this fluoride formation is enhanced on argon bombardment of the coated samples by releasing more fluorine from the polymer capable of bonding to the metal atoms.

Rubbing $CF(_{1.0})_n$ against metal causes the polymer to transfer to the counterface and so effectively graphite fluoride is rubbing against itself. The occurrence of single or doublet peaks depending on the presence of charging effects is also one of the salient features of PTFE transfer to metals [19, 25].

This recent work [25] has also shown that metal fluorides have been formed at the interface when PTFE is rubbed in a similar manner against stainless steel and nickel in air.

The process of rubbing stainless steel, nickel and aluminium on to a graphite fluoride surface with very little applied pressure resulted in a chemical reaction occurring at the interface forming metal fluorides, these fluorides being discovered by careful removal of the $(CF_{1.0})_n$ overlayer with a razor blade. For copper, the small fluoride peak (if present) would lie underneath the low B.E. graphite fluoride F(1s) peak. Due to its small chemical shift [25] and this peak is, therefore, indistinguishable from covalent F(1s).

Atkinson *et al.* have investigated the mode of failure of graphite fluoride films on stainless steel using XPS. They showed that films of graphite fluoride run to failure in air show only metallic fluoride peaks in the XPS spectra. From this evidence they postulate that the destruction of the graphite fluoride lattice at the polymer–metal interface is responsible for film failure in wear tests. The wear rate of the polymer thereby being related to the formation of this metallic fluoride and its subsequent removal from the surface region thereby causing more polymer to be exposed and hence further wear.

An alternative explanation, however, is that film failure occurred simply due to the removal of the lubricant (graphite fluoride) from the interfacial region. This loss of polymer simply allowed the discovery of the metal fluoride which had been formed at the beginning of the rubbing procedure and was now exposed on the metal surface. This is analogous to the exposure of metal fluorides by removing the polymer overlayer with a razor blade in the experiments described in this work.

Toy [27] has utilized fluoride films on metal substrates under anhydrous conditions as *in situ* catalysts for surface polymerization of tetrafluoroethylene. Other workers [28] report that rare earth fluorides are also good surfaces for film formation on certain metals. It seems extremely likely, therefore, that the initial formation of metal fluoride, far from decreasing the lubricant near life would, in fact, impose the near properties by strengthening the adhesion of the polymer to the metal counterface.

The relative importance of chemical reactions in the adhesion/wear properties of bearings involving graphite fluoride is still uncertain but their occurrence and possible influence should at least be considered as these results show that such reactions do occur.

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