JOURNAL OF MATERIALS SCIENCE 14 (1979) 2672–2678

The chemical interaction of metals with polytetrafluoroethylene

P. CADMAN, G. M. GOSSEDGE
Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth, UK

Chemical reactions of cadmium, indium and tin with PTFE have been found to occur when mixtures of the metal and polymer were heated in a differential scanning calorimeter to 773 K. Analysis of the residues by X-ray photoelectron spectroscopy (XPS) showed the presence of fluoride ions. The evaporation of a metal film on to the clean polymer surface has also been found by XPS to produce metal fluoride for nickel, cadmium, tin, indium and lead but not silver or gold. The rubbing of aluminium on to PTFE also produces reaction to give fluoride. The PTFE polymer molecules have been found to diffuse to the surface of metal/polymer composites at a significant rate. This latter process may be important in the use of this polymer in bearing materials.

1. Introduction

Following the realization that PTFE has a low coefficient of friction [1, 2] against most materials, its mode of action has been much investigated. Transfer films [3–5] (of thickness 3 to 10 nm) of PTFE have been found to occur when the polymer is slid against many metals and therefore at the interface PTFE is effectively sliding against itself with a resultant low friction coefficient. Repeated sliding under certain conditions continually removes and replenishes this transferred film of polymer and as a result large polymer wear rates often occur. This wear is usually greater under aqueous conditions. Tanaka *et al.* [4] have shown that the wear rates of PTFE and high-density polyethylene (HDPE) are 100 times greater than those of other polymers. These large wear rates are probably caused by weak adhesion of the transfer film to the counterface and in this process the chemical nature of the PTFE–metal interface may play an important role. Such chemical aspects have previously received scant attention and are therefore examined in this work.

Various fillers have been added to PTFE to achieve the desired properties of longer wear life. Pratt [6], investigating filled PTFE composites rubbed against steel counterfaces, initially suggested that the fillers helped PTFE bond physically to the metal surface. More recently [7] he has proposed that this process is chemical in nature in lead bronze/PTFE composites. Above 573 K a reaction is thought to occur between PTFE and the lead (or lead oxides) during sintering. The DSC work of Pocock and Cadman [8] has indicated the occurrence of such reactions between certain metals and PTFE and drawn attention to their possible importance. Studies of Brainard and Buckley [9, 10] using Auger photoelectron spectroscopy (AES) have shown that strong adhesion occurs under ultra high vacuum (UHV) conditions between clean PTFE and metal surfaces which may be chemical in nature. They suggest that such adhesion may be caused by metal–carbon bond formation.

This work is concerned with the elucidation of the nature of this bonding between PTFE and metal surfaces under various conditions, especially those in a tribological context. Polymer–metal interactions have been studied by heating mixtures of the polymer and various metals (both in a powder form) in a differential scanning calorimeter (DSC) and examining the residue by X-ray photoelectron spectroscopy (XPS) for possible chemical reactions. Metals have also been evaporated on to the clean polymer surface under ultra high vacuum (UHV) to minimize the effect of surface contamination. The resultant interfaces have been examined by XPS. The metal–polymer inter-

0022–2461/79/112672–07 $02.70/0

face has also been examined by XPS after aluminium was slid against PTFE. The principles of XPS and its application to tribological processes as a result of its surface sensitivity has been described previously [5, 11, 12].

2. Experimental details

Various polymer–metal mixtures (volume ratio 1:1) were heated in a DSC using an aluminium sample pan to 773 K and scanned for thermal transitions. This was carried out in a Perkin Elmer DSC 1B using a nitrogen atmosphere (< few ppm O_2). The PTFE was Fluon L 169B powder. The metals and metal oxides were B.D.H. Ltd laboratory reagents of particle size 10 to 20 μm. After heating the residues were removed from the pans, examined and then cold-pressed into pellets (10 ton in^{-2}) suitable for XPS examination

Tin, indium and gold were evaporated on to a clean PTFE surface in a UHV preparation chamber (base vacuum 10^{-10} Torr) directly attached to the photoelectron spectrometer [5]. The evaporation of nickel, cadmium and silver was performed external to the spectrometer in an Edwards Evaporator (at 10^{-5} Torr). The metal wires used were obtained from Goodfellow Metals (99.99% purity). Indium used in the DSC experiments was in the form of finely divided wire. Samples of solid PTFE used in the evaporations were cleaved before use and cleaned by abrasion with a stainless steel razor blade. Similar cleaning was done prior to the argon etching and rubbing experiments. This technique has been shown by XPS to produce a very clean surface (< 5% of a monolayer of surface contaminants under UHV). In the argon ion etching experiments, the polymer was etched with argon ions (5×10^{-5} Torr pressure, 700 V) in the actual spectrometer and immediately examined by XPS. It was left at 10^{-8} Torr for various periods of time up to a maximum of 12 h and then re-examined. This cycle was repeated as required.

Aluminium metal was cleaned with various grades of emery cloth and then rubbed by hand under atmospheric conditions (pressure approximately 1 N m^{-2}) for several minutes against the surface of PTFE. After XPS examination, the sample was scraped with a razor blade to partially remove the polymer transfer film and expose the interfacial region before re-examining by XPS.

The X-ray photoelectron spectrometer used in all the experiments was an A.E.I. ES200A with a sample preparation chamber and fitted with an Mg*K*α X-ray anode.

3. Results

3.1. Differential scanning calorimetry

Several reactions have been found on heating binary mixtures of PTFE to 773 in the DSC. The results of these experiments are presented in Table I. Thermal events which could not be assigned to phase transitions were the exotherms found for cadmium–PTFE mixtures at 683 K and tin–PTFE mixtures at 533 K. In addition indium–PTFE mixtures heated to 773 K produced a black carbonaceous residue similar in appearance to that found with the cadmium and tin mixtures and hence suggesting reaction had taken place. Experimental difficulties prevented the temperature of the reaction exotherm being determined. Recent work by Meadows [13], in these laboratories, has confirmed these results and shown that the exotherm occurs at 723 K in these indium–PTFE mixtures.

The fluorine F(1s) spectra (Figs. 1 and 2) obtained by XPS analysis of these black residues

TABLE I Binary systems containing metal and PTFE heated in the DSC

Metal	Thermal Events	Comments
Al	PTFE transition	No reaction up to 703 K
Cd	Cd m.p. + PTFE transition exotherm at 683 K	Reaction at 683 K; black residue
Cr	PTFE transition	No reaction up to 703 K
Cu	PTFE transition	No reaction up to 703 K
Fe	PTFE transition	No reaction up to 703 K
Ni	PTFE transition	No reaction up to 703 K
Mg	PTFE transition	No reaction up to 703 K
Sn	Sn m.p. PTFE transition. Exotherm at 733 K	Reaction at 733 K; black residue
Zn	Zn m.p. PTFE transition	No reaction up to 703 K
In	–	Black residue on heating to 733 K

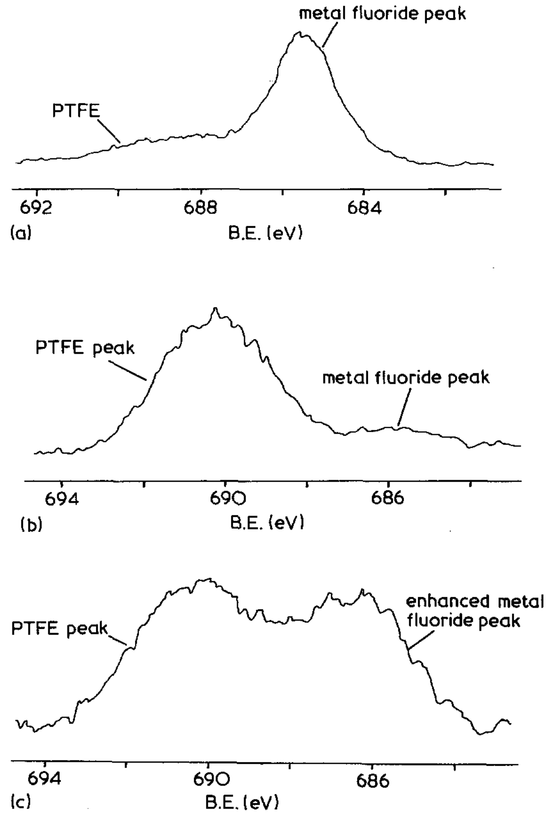

Figure 1 XPS examination of metal–PTFE DSC residues. (a) Cd–PTFE F(1s) spectrum showing presence of fluoride as well as covalent fluorine. (b) In–PTFE F(1s) spectrum showing presence of metallic fluoride as well as covalent fluorine from PTFE. (c) Subsequent argon ion etching of In–PTFE sample showing enhancement of fluoride compared to covalent fluorine.

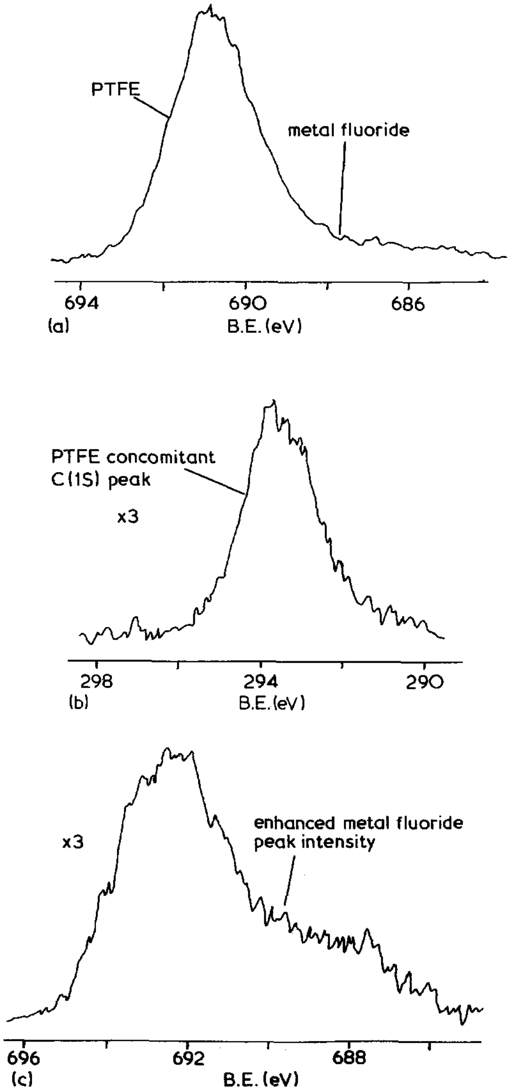

Figure 2 XPS Examination of tin–PTFE DSC residues. (a) F(1s) spectrum. Small amount of fluoride present after allowance for $\alpha_3\alpha_4$ intensity. (b) C(1s) spectrum. PTFE carbon C(1s) peak with contribution from less electropositive carbon satellites. (c) Sample after argon ion etching, F(1s) spectrum. Argon ion etching of residue enhances the production of metal fluoride.

all contain two discrete peaks. These peaks at high binding energy (B.E.) have concomitant C(1s) peaks (Fig. 2b) with a separation of 397 eV and a stoichiometry of $-CF_2-$ indicating that they can be attributed to unreacted PTFE species. The F(1s) peaks at lower B.E. have no concomitant C(1s) peaks and this together with the large chemical shifts involved suggest that they originate from metallic fluorides formed by chemical reaction. No fluorine (F1s) satellites were found for mixtures were reaction could not be detected by other means.

Argon ion bombardment (30 min, 5×10^{-5} Torr, 1 μA, 700 V) etching of all the samples preferentially removed the fluorine from PTFE (*vide infra*). This released more fluorine atoms/ions capable of bonding to metals as more metallic fluoride (Fig. 2c). Meadows [13] in attempting to catalyse a tin–PTFE reaction with cadmium compounds found that exothermic peaks were detected in the DSC between 623 and 773 K on heating either anhydrous cadmium chloride or oxide with this metal–polymer mixture. XPS analysis of the residues showed no evidence of tin fluoride. However, the cadmium oxide–PTFE–Sn sample showed a fluorine F(1s) peak at 685 eV (Fig. 3b) suggesting that it is due to metal fluoride. The stoichiometry of the cadmium fluoride was about 1:2 obtained from the associated

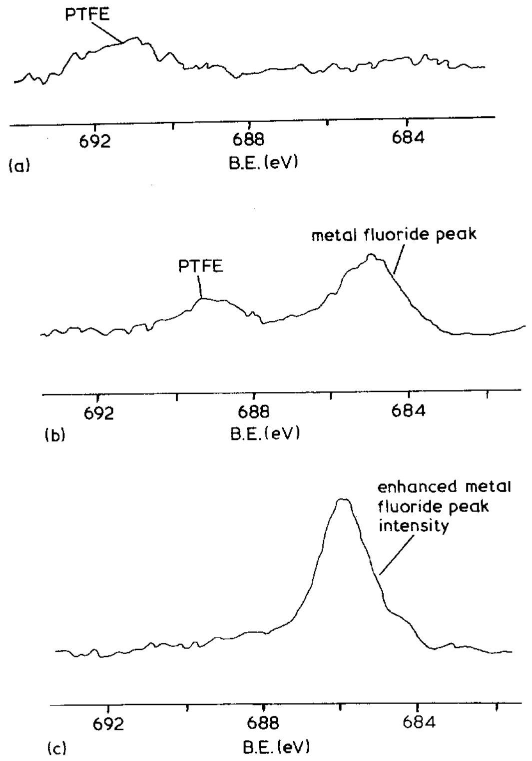

Figure 3 Catalysis of CdO–PTFE by tin metal. (a) CdO–PTFE residue F(1s) spectrum. No metal fluoride detected. (b) CdO–PTFE–Sn residue, F(1s) spectrum. Metal fluoride present; stoichiometry and binding energy suggest cadmium fluoride. (c) CdO–PTFE–Sn residue argon ion etched, F(1s) spectrum. Argon ion etching enhances the production of metal fluoride.

spectra suggesting the reaction product was cadmium fluoride (CdF_2). XPS analysis of a binary mixture of cadmium oxide–PTFE which had been heated to 773 K showed no evidence of fluoride formation (Fig. 3a) only a pair of cadmium 3d peaks attributable to both metal and metal oxide being present.

The cadmium chloride–PTFE–tin residue from heating to 773 K also showed a small fluoride peak in its XPS spectra (Fig. 4) superimposed on the $\alpha_3\alpha_4$* region of the principle F(1s) PTFE peak only when the tin was present (Fig. 4b). This residue was light grey in colour compared to the black of the cadmium oxide ternary mixture sample.

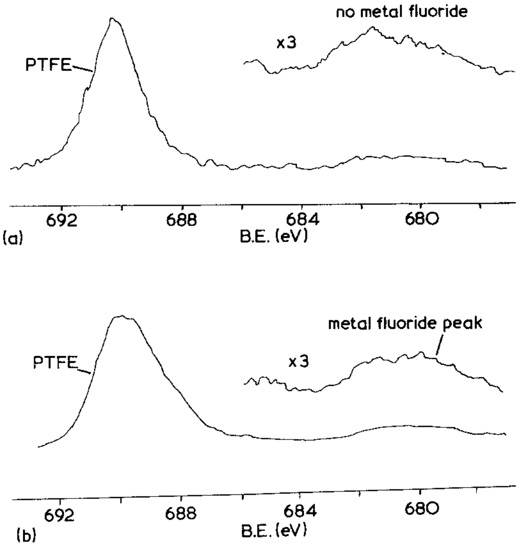

Figure 4 Catalysis of anhydrous $CdCl_2$–PTFE reaction by tin metal. (a) $CdCl_2$–PTFE residue F(1s) spectrum. Intensity of 682 eV region can be accounted for by $\alpha_3\alpha_4$ radiation. (b) $CdCl_2$–PTFE–Sn residue F(1s) spectrum. Small metal fluoride peak left after subtraction of $\alpha_3\alpha_4$ intensity.

3.2. Evaporation of metals on to clean PTFE surfaces

Tin, indium, lead and gold were evaporated on to a clean PTFE surface under UHV conditions at less than 10^{-8} Torr pressure. All the samples except gold were found to display two peaks in the F(1s) spectrum upon XPS examination (Fig. 5). The higher binding energy peak can be attributed to PTFE origin but the low B.E. one can be assigned to fluoride (metal–fluoride) formed by the initial condensation of metal atoms. In the tin case, this B.E. was 685.2 eV (Fig. 5a) compared to 684.7 eV when tin was evaporated on to graphite fluoride [12]. The indium fluoride (F1s) peak at 684.8 eV B.E. (Fig. 5b) is identical to that found in the metal–graphite fluoride case. The Sn(3d) and In(3d) doublet peaks also exhibited shifted satellites attributable to these metallic fluorides. Stoichiometries were approximately SnF_2 and InF, respectively. The 3 eV shift of the Sn(3d) compares favourably with the 2.8 eV found in the tin/$(CF)_n$ case and also with a value of 1.7 eV measured for bulk tin oxide. Argon etching of

---

*The X-ray source used for this work was the Mg$K\alpha_{1,2}$ unresolved doublet emission line resulting from 2 $P_{\frac{3}{2}} \rightarrow$ 1s and 2 $P_{\frac{1}{2}} \rightarrow$ 1s transitions. Similar transitions within multiply ionized atoms (e.g. $K\alpha_3$, $K\alpha_4$) result in additional satellite peaks ($\alpha_3\alpha_4$) with separation (and intensities in brackets) relative to the principal peak of 8.4 eV (9.2%) and 10.0 eV (5.1%), respectively [18].

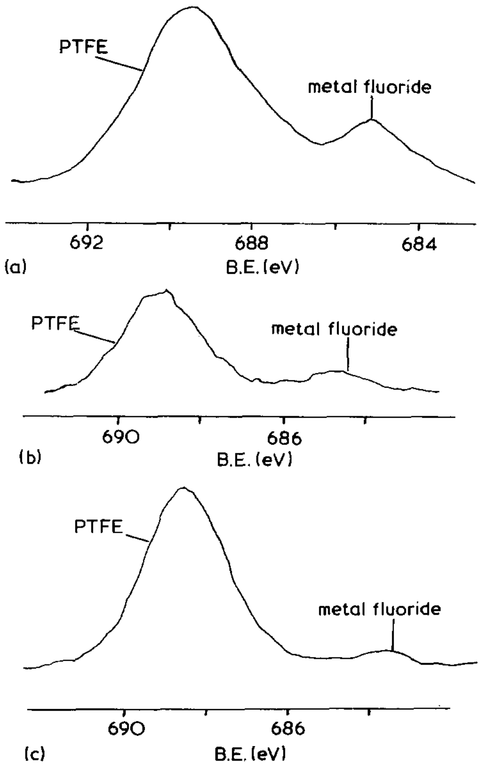

Figure 5 Metals evaporated on to PTFE. (a) Tin evaporation F(1s) spectrum. Prominent fluoride peak apparent. (b) Indium evaporation, F(1s) spectrum. Fluoride from metal fluoride detected. (c) Lead evaporation, F(1s) spectrum. Metal fluoride formed.

these metal-coated polymer surfaces enhanced the metal fluoride F(1s) peaks and after 2h the stoichiometries approached SnF_4 and InF_3 while the B.E. increased by only 0.2 eV. This was a similar result to that found in the indium-coated graphite fluoride.

The fluoride F(1s) spectrum (Fig. 5c) found after lead evaporation on to PTFE had a B.E. of 682.7 eV but was too small to be able to detect any shift in the metal 4(f) spectrum. The separation of this fluoride F(1s) from the one due to polymer was 4.5 eV compared to 4.3 eV found for bulk lead difluoride. No indication for any reaction was found in the gold case.

Cadmium, nickel and silver atoms were condensed on to a PTFE surface in an Edwards evaporator external to the spectrometer for practical reasons. XPS analysis showed two discrete F(1s) peaks in the cadmium and nickel cases: the higher binding energy peaks being attributed to a PTFE origin. No fluoride peaks were found after the silver evaporation.

The B.E. in the cadmium fluoride sample was 683.7 eV which agrees with the shift found between PTFE F(1s) and that of cadmium (II) fluoride of 4.2 eV. The B.E. of this fluoride peak

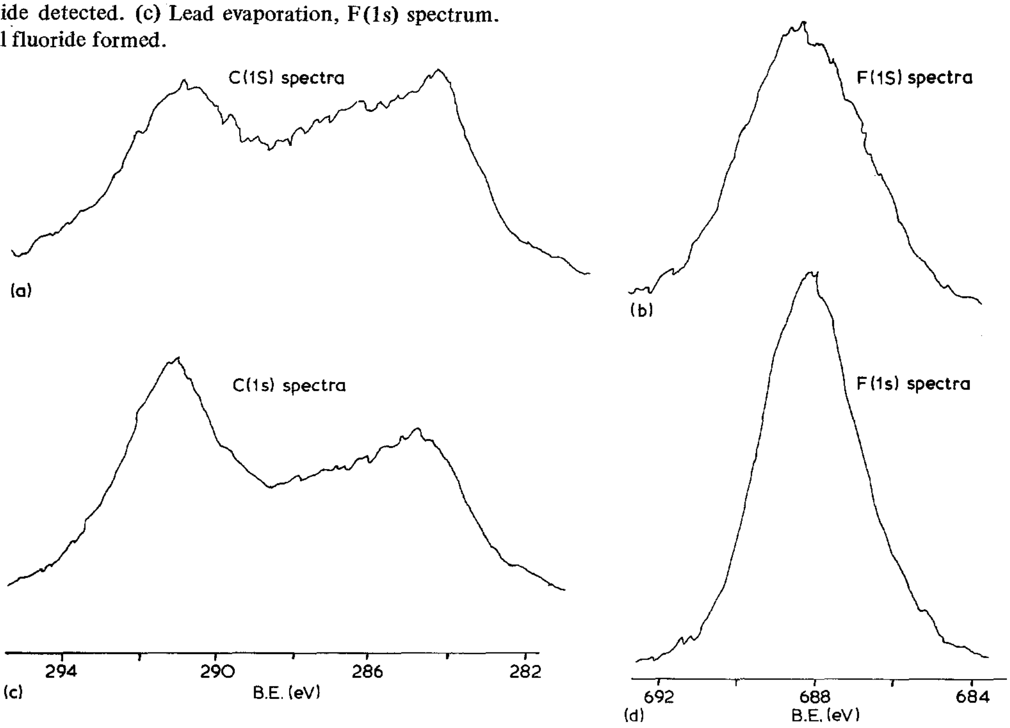

Figure 6 PTFE; argon ion etched (30 min, 5 × 10^{-5} Torr). (a) Immediate examination. (b) Examination after 12 h. After etching 700 V, 1 μA for 30 min F(1s) is very broad and shifted to lower B.E. Carbon C(1s) satellites appear due to less electronegative carbon. On standing for 12 h, PTFE peaks enlarge in intensity relative to those at lower B.E.

in the nickel case was 683.9 eV. In these latter examples the presence of oxide contamination on the metal impedes any interpretation of metal spectra.

3.3. Argon etching of PTFE

The XPS spectra of clean PTFE showed one single F(1s) peak and one carbon (1s) peak (separation 397 eV and stochiometry CF_2). After etching for 30 min (5×10^{-5} Torr) the fluorine F(1s) peak (Fig. 6a) diminished in intensity and broadened considerably (FWHM* increased from 2.2 eV to 3.6 eV). The C(1s) spectrum showed the presence of several superimposed peaks attributable to carbon atoms bonded to two, one and no fluorine following the preferential removal of fluorine. After standing in the vacuum for various periods of time up to several hours the sample was re-examined. The carbon C(1s) intensity corresponding to $-CF_2-$ was found to increase with time and the fluorine F(1s) FWHM decreased to 2.8 eV after about 12 h (Fig. 6b). In the latter time, the PTFE content had increased by about 30%. After further etching a similar increase in the PTFE signal was also found.

3.4. PTFE rubbed against aluminium

XPS examination of aluminium after rubbing with PTFE showed the presence of two distinct F(1s) peaks (Fig. 7) with their concomitant carbon C(1s) signal: both sets of peaks could be attributed to PTFE origin. When the sample was scraped with a stainless steel razor blade at first the higher B.E. peaks diminished in intensity and then both sets were affected. Concurrent with this diminution there was the emergence and growth of a small F(1s) peak at lower B.E. (686 eV) which could be ascribed to fluoride form a metal fluoride formed at the substrate–polymer interface during the initial stages of the rubbing process. Argon ion bombardment (5×10^{-5} Torr pressure, 30 min) of the above sample diminished the PTFE peaks but not the metallic fluoride F(1s).

4. Discussion

Chemical reactions between several metals and PTFE have been found to occur under various conditions. PTFE reacts with tin, cadmium and indium, respectively, at temperatures below 773 K to form metal fluorides. Although the temperatures of these reactions may not always be reached under normal tribological conditions, other effects such as pressure or catalysis could provide other pathways at lower temperatures. Under 10 tons in.$^{-3}$ pressure tin and graphite fluoride [12] react at only 523 K. Copper is thought to catalyse a reaction between tin and PTFE at 700 K [8].

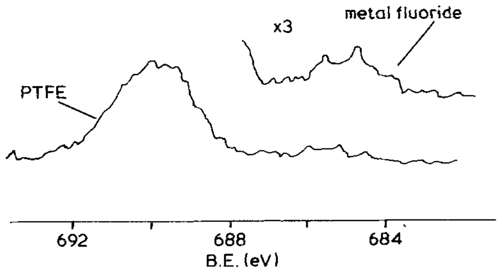

Figure 7 Al rubbed against PTFE and scraped with a razor blade. F(1s) Spectrum. Metal fluoride formed by rubbing. Shift shows this is due to aluminium fluoride not iron fluoride.

In this work it seems as though tin catalyses a reaction between PTFE and anhydrous cadmium oxide forming cadmium fluoride with metallic cadmium as a possible intermediate. Tin may also catalyse a chemical reaction between anhydrous cadmium chloride and PTFE. To obviate the effect of surface contamination, metals were evaporated on to a clean PTFE surface. The results showed that for a number of metals there was considerable chemical reactivity at the metal–polymer interface resulting in the formation of metallic fluorides.

Argon ion bombardment can initiate further chemical reaction in these systems by releasing more fluorine species from the PTFE. This etching process preferentially removes the fluorine from the PTFE leaving a surface which is carbon-rich and probably highly cross-linked. On standing, the PTFE molecules gradually re-appeared in the surface region over a time period of several hours. There must be polymer molecules labile enough to diffuse to the surface at a significant rate at room temperature. These molecules are probably ones of lower molecular weight which were either present in the original polymer or were formed by the etching process itself. This self-regeneration of a PTFE surface may be of importance in the use of this material where its unique surface properties

---

*FWHM is the full width of the peak at half the maximum height.

are required such as in bearings. The cross-linked carbon-rich surface region initially produced by etching is probably similar to that made by Benderly [14] and found to be ideal for forming strong adhesive joints. These chemical reactions of PTFE with metals may also be suitably advantageous for preparing PTFE surfaces for bonding to substrates. Cadmium, in particular, reacts vigorously with PTFE and may be an alternative to the standard sodium/lithium chemical etching process used to promote adherence of PTFE to other surfaces [15, 16].

Previously, metallic fluorides have been found at the polymer–metal interface for stainless steel and nickel [11]. The aluminium work described above supports the conclusion that the fluoride is formed at the substrate–polymer interface and not by the stainless steel razor blade because the chemical shifts of the two metal fluorides (aluminium and iron) are so different.

A partial explanation for the fluoride production under these conditions is probably that the wear process itself regenerates fresh, highly reactive metal atoms from beneath any surface layer contamination. Mild steel has been previously found to react with microwave-discharged hexafluoroethane [19] giving (in the manufacture of PTFE films) iron fluoride formation, thus showing the chemically reactive nature of such systems. Toy [17] found that initial formation of metal fluoride at the interface from the reaction of fluorine with steel improves the wear properties of fluoropolymer films by possibly strengthening the adhesion of the polymer-to-metal interface. Such adhesion could be important in an aqueous environment where the adhesion of PTFE is small.

Comparison of the results obtained with PTFE with those found for graphite fluoride [12] show that these two materials have similar properties with some metals.

In conclusion, the occurrence of chemical reactions of PTFE with metals has been demonstrated. Similar reactions have been found to occur when PTFE is rubbed against a metal surface. Such reactions may be of importance in determining the wear rate in bearings containing PTFE.

Acknowledgement

We wish to thank ICI Ltd for the donation of the Fluon L 169B powder.

References

1. K. V. SHOOTER and P. H. THOMAS, *Research* 2 (1949) 533.
2. K. V. SHOOTER and D. TABOR, *Proc. Phys. Soc.* **B65** (1952) 661.
3. C. M. POOLEY and D. TABOR, *Proc. Roy. Soc. London Ser. A* 329 (1972) 251; *Nature Phys. Sci.* 237 (1972) 88.
4. K. TANAKA, Y. UCHIGAMA and S. TOYOOKA, *Wear* 23 (1973) 153.
5. P. CADMAN and G. M. GOSSEDGE, *Wear* 51 (1978) 57.
6. G. C. PRATT, *Plastic. Inst. Trans. J.* 30 (1964) 755; 32 (1966) 58.
7. *Idem,* Plastics Institute Conference, Solihull (1973).
8. G. POCOCK and P. CADMAN, *Wear* 37 (1976) 129.
9. W. A. BRAINARD and D. H. BUCKLEY, *ibid* 26 (1973) 75.
10. *Idem, Carbon* 13 (1975) 501.
11. P. CADMAN and G. M. GOSSEDGE, *Wear* 54 (1979) 211.
12. *Idem, J. Mater. Sci.* 14 (1979) 1465.
13. B. MEADOWS, M.Sc. University of Wales (1978).
14. A. A. BENDERLY, *J. Appl. Polymer Sci.* 6 (1962). 221.
15. J. JANSTA and T. P. DOUSEK, *Electrochem. Acta* 20 (1975) 1.
16. R. J. PURVIS and W. R. BECK, US Patent, 2 789 063, April (1957).
17. M. S. TOY, *J. Polymer Sci. C* 34 (1971) 273.
18. D. BRIGGS (editor), "Handbook of Photoelectron Spectroscopy" (Heyden, London, 1977) Ch. 4, using data of M. O. Krause and J. G. Ferreira, T. A. Carlson, "Photoelectron and Auger Spectroscopy" (Plenum, New York, 1976).
19. G. M. GOSSEDGE, PhD, University of Wales (1979).

Received 27 February and accepted 24 May 1979.