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An XPS Study of the Stability of Fomblin Z25 on the Native Oxide of Aluminum

Pilar Herrera-Fierro, Stephen V. Pepper,
and William R. Jones
*Lewis Research Center
Cleveland, Ohio*

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AN XPS STUDY OF THE STABILITY OF FOMBLIN Z25 ON THE NATIVE OXIDE OF ALUMINUM

Pilar Herrera-Fierro,^{*} Stephen V. Pepper, and William R. Jones
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

Thin films of Fomblin Z25, a perfluoropolyalkylether lubricant, were vapor deposited onto clean, oxidized aluminum and sapphire surfaces, and their behavior at different temperatures was studied using XPS and TDS. It was found that the interfacial fluid molecules decompose on the native oxide at room temperature, and continue to decompose at elevated temperatures, as previous studies had shown to occur on the clean metal. TDS indicated that different degradation mechanisms were operative for clean and oxidized aluminum. On sapphire substrates, no reaction was observed at room temperature. Our conclusion is that the native oxide of aluminum is neither passive nor protective towards Fomblin Z25. At higher temperatures (150 °C) degradation of the polymer on sapphire produced a debris layer at the interface with a chemical composition similar to the one formed on aluminum oxide. Rubbing a Fomblin film on a single crystal sapphire also induced the decomposition of the lubricant in contact with the interface and the formation of a debris layer.

INTRODUCTION

Perfluoropolyalkyl ethers (PFPAE) are promising candidates as lubricants in a wide variety of systems, including magnetic disks, gas turbine engines and space mechanisms, because of their thermal stability and exceptional viscosity-temperature and vapor pressure characteristics. In spite of their stability, PFPAE have been observed to react with active metals such as stainless steel (refs. 1 and 2) and aluminum (ref. 3), causing complete degradation.

The outstanding viscosity-temperature properties of Fomblin Z25, in particular, and the use of aluminum alloys in the aerospace industry is our motivation to study the chemistry of the Fomblin Z25/aluminum alloy interface.

We have previously shown (ref. 4) that Fomblin Z25 on clean aluminum, at room temperature, suffers degradation at the fluid-solid interface to produce a debris layer which is partially passivating. This debris layer, while effective at slowing down the degradation, is not fully protective. At elevated temperatures (≥ 150 °C) the degradation continues until the layer reaches a thickness of about 7 to 8 monolayers. This interfacial layer has a layered structure itself: it comprises an inorganic region composed of fluorides, carbides and oxides; and an organic region constituted mainly of Fomblin and its decomposition products.

We consider herein the question as to whether the native oxide of the aluminum can protect the fluid against chemical attack. The reaction at the interface will be induced by different means: (1) by simple contact between the clean metal oxide surface and the polymer, (2) by heating the substrate, and (3) by sliding at the interface with a sapphire ball to simulate tribological conditions. XPS and TDS will be

^{*}National Research Council—NASA Research Associate at Lewis Research Center.

used to compare the thermally formed debris layer with that which forms in a sliding experiment on a sapphire substrate.

EXPERIMENTAL

Thin films of fluid were vapor deposited onto clean aluminum oxide surfaces in ultra-high vacuum (UHV), where they were studied with x-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). The experimental setup has been described previously (ref. 4). All the techniques are housed in a VG Mark II ESCALAB system (base pressure 1×10^{-10} Torr) equipped with an Al K α monochromatic x-ray source and a Dycor MA200 quadrupole mass spectrometer for residual gas analysis (RGA), interfaced to a computer for data acquisition. The ionizer chamber of the mass spectrometer was shielded to insure that no electrons could escape and reach the polymeric sample. The Fomblin Z25 sample was provided by Ausimont USA, Inc. The polymeric linear chain of Fomblin is composed of (-CF₂-CF₂-O-) and (-CF₂-O-) groups in a ratio of 0.6 to 0.7, respectively. The substrate was a sputter deposited, 4 to 5 μm thick, aluminum film on a VG heater stub. The aluminum oxide surface layer was formed by exposing an UHV cleaned Al surface for 15 min in a UV-ozone box (ref. 5). The oxide layer formed by this method was about 50 \AA thick, with both the Al⁰ and Al³⁺ XPS peaks being clearly visible. The purpose of the UV-ozone box is to eliminate unwanted carbon contamination by oxidizing the surface with O₃. The oxide thus formed is free of carbon contamination. Thinner oxide films (20 \AA) were also used. These films were formed on clean aluminum from a brief exposure to air. The thickness of the films, t , for oxide and polymer, were calculated from the attenuation of the substrate signal intensity at normal exit, using the expression $I_{\text{sub}} = I_{\text{sub}}^0 \exp(-t/\lambda)$. Where I_{sub} and I_{sub}^0 are the substrate photoelectron intensities before and after film deposition, and λ is the inelastic mean free path, IMFP, of the substrate electron in the film. λ was calculated using the expression $\lambda = \kappa E^p$, where $p = 0.5$ for organic overlayers and E is the kinetic energy of the substrate photoelectrons. κ was calculated using the values of $\lambda = 34 \text{\AA}$ reported by Novotny (ref. 6) for the system Fomblin Y on gold ($E = 1200 \text{ eV}$). Core level binding energies are referenced to the Al-2p_{3/2} binding energy, 73.0 eV. For calculating the oxide thickness, the mean free pass used for Al⁰ was $\lambda = 27 \text{\AA}$ (ref. 7).

To perform the TDS experiments, the sample was positioned facing the mass spectrometer, to allow only the desorbing molecules to enter the mass spectrometer's ionization chamber. The substrate temperature was then increased at 2 $^\circ\text{C}/\text{sec}$. To read the substrate's temperature an IR pyrometer-microscope was focussed on a dark spot (emissivity ≈ 1) painted on the side of the VG stub (ref. 8).

Sliding experiments were also done in UHV. A sapphire bearing ball was slid against a sapphire substrate which had been previously covered by a thin film of Fomblin ($\approx 90 \text{\AA}$). For these experiments, the oxide layer formed by the UV-ozone exposure on the aluminum samples was not thick enough to sustain the load during sliding. It was therefore necessary to use a harder substrate, namely, a single crystal of sapphire, which has similar surface-chemical composition, albeit different morphology and crystallographic structure. Prior to their introduction into the UHV system the sapphire flats were cleaned by ultrasonically washing them in research grade methanol, followed by a 30-min exposure in the UV-ozone box. No ion bombardment, UHV cleaning, was performed because of the surface damage it induces. The sapphire ball used in the sliding experiments was cleaned following the same procedure as the substrates. The treatment described was not completely successful in eliminating the adventitious carbon on the sapphire surface. Contamination in the order of a few atomic percent was still present.

Samples covered with thin films of PFPPE were subjected to two heating schedules. Fast heating ($\approx 2 \text{ }^\circ\text{C}/\text{s}$) was done from room temperature up to 400 $^\circ\text{C}$, while five ions from the desorbing molecules were monitored as a function of time: CF⁺, COF⁺, CF₂⁺, COF₂⁺, and CF₃⁺. The relative intensities of

the monitored masses, and the temperature of the maximum of the desorption peak was used here only as a crude fingerprint to help distinguish Fomblin desorption from reaction-product desorption. The system studied is so complex that no attempt were made to extract kinetic or thermodynamic information from the TDS data.

In the second type of heating, the sample was kept at constant temperature (150 °C) for long periods of time (4 to 6 hr), in order to study the behavior of the interface before desorption occurred. The very low vapor pressure of Fomblin Z allowed this type of experiment without significant loss of material by evaporation. Previous heating experiments indicated that the rate of evaporation of the Fomblin overlayer at 150 °C was about 1 monolayer (1 ML) per hour. The polymer-metal oxide interface was characterized by XPS before and after every heating experiment.

The exposure of the PFPPE film to the x-ray beam was minimized to avoid radiation damage, although the use of the monochromatized x-ray source allowed us at least three hours of exposure before any sign of degradation was detected.

RESULTS AND DISCUSSION

Room Temperature Experiments

XPS analysis of a thin ($\approx 8 \text{ \AA}$) Fomblin Z25 film, vapor deposited onto either thin and thick oxide surfaces at room temperature, showed a number of peaks in the C-1s, O-1s and F-1s region none of which are associated with molecular Fomblin. They can be assigned to oxides, carbides, and fluorides that form on the clean oxide surface upon arrival of the Fomblin molecules. Table I lists the possible binding energies assignments, in the Al, C, F, and O region, found in this work. Upon longer exposure to the PFPPE vapor, the XPS peaks corresponding to molecular-bulk Fomblin were detected: C-1s (293.0 and 294.7 eV), O-1s (535.5 eV) and F-1s (688.7 eV). A plausible explanation for this behavior is that the polymer decomposes into its elemental constituents upon contact with the active surface, and secondary reactions among the fragments and the (active) oxide sites on the surface creates a layer of the species mentioned above (carbides, oxides, and fluorides). Build up of that layer covered the active sites allowing a molecular Fomblin layer to build up on top. This behavior has been observed previously for the adsorption of small perfluoroalkylether molecules on gold (ref. 9).

For a thin film of Fomblin (a few monolayers thick) on aluminum oxide, the experimental ratio of the two C-1s peaks characteristic of the molecule was different from the stoichiometric value or the ratio measured for a similar film on an unreactive gold surface. A decrease in the intensity of the high energy C-1s peak, also called acetal carbon, ($-\text{O}-\text{C}(\text{F}_2)-\text{O}-$), was observed. This suggested a preferential consumption of this portion of the molecule, as a result of the decomposition reaction which occurred when the Fomblin molecules contacted the clean surface.

Contrary to the results found for the native oxide layer of aluminum or clean aluminum surfaces, Fomblin condenses on a sapphire surface without degradation. XPS analysis of the clean sapphire surface covered with a thin layer of Fomblin a few angstrom thick, showed no peaks other than those corresponding to molecular Fomblin, with no preferential consumption of the acetal carbon.

Heating Experiments

The desorption temperature of molecular Fomblin from an unreactive metal like gold, is 270 °C, and $m/e = 47$ is the most abundant desorbing species (ref. 4). TDS of thin layers of PFP AE evaporated onto a clean native oxide layer of aluminum, both thin and thick, showed only a single desorption peak, at 160 °C. The major constituent of this peak was CF_3^+ ($m/e = 69$) with a lesser amount of COF^+ ($m/e = 47$). This mass distribution is not due to the desorption of Fomblin itself, as it has been assigned for the case of gold, but to the desorption of other species which originated from the Fomblin Z25 decomposition products on the surface. The composition at the desorption peak was also different from that obtained in the TDS from a clean Al surface, where the major species was $m/e = 31$, and where decomposition was also observed, although the temperature of the peak maximum was the same for both surfaces. XPS analysis after TDS, on both oxidized and clean metal surface, revealed the presence of AlF_3 , Al_2O_3 , Al carbide and adventitious carbon. All the Fomblin related peaks were absent. These results imply that there is a reaction between the Fomblin and the aluminum oxide surface, and that the oxide is not passive towards Fomblin. The composition of the desorption peak indicates that this reaction path is different from that which takes place on a clean aluminum surface. TDS experiments with the sapphire substrate were not possible because the poor thermal contact between the heater and sapphire prohibited comparable heating rates.

In order to study this reaction in more detail, the temperature was held constant just below the desorption peak for a long period of time, after which the interface was analyzed. This second type of heating experiment was conducted on all the substrates studied including sapphire. The substrates were held at 150 °C for 4 to 6 hr while the evolved gases were monitored with a mass spectrometer. In all cases, the composition of the residual gas was similar to that obtained at the desorption peak during fast heating (TDS). The RGA showed that CF_3^+ ($m/e 69$) was the most abundant Fomblin-related fraction, except for the clean Al surface where the most abundant species was CF^+ ($m/e 31$) (ref. 4).

The XPS spectra of figure 1 show the $Al-2p_{3/2}$ spectrum, after prolonged heating in the presence of Fomblin, for the four different substrates used: **A** clean aluminum, **B** thin aluminum oxide (20 Å) on aluminum, **C** thick oxide (50 Å), and **D** sapphire single crystal. Fomblin Z films, at least 100 Å (± 20 Å) thick, were used in these experiments. The $Al-2p_{3/2}$ region in spectrum **A** shows the following peaks (see table I): Al^0 (73.0 eV), Al_2O_3 (75.1 eV), AlF_3 (76.6 eV) Al carbide (73.7 eV) and a peak at 78 eV assigned to a high coordination aluminum fluoride species (AlF_6^{-3}). This AlF_6^{-3} species has been previously studied using XPS (ref. 10) and x-ray diffraction (ref. 11) and is known to form when Al is exposed to an excess of fluorine for long periods of time (ref. 12).

In the case of the thin oxide layer, spectrum **B**, the amount of high-coordination species (AlF_6^{-3}) is smaller than in the case of the clean Al surface. This means that the thin oxide layer is not protective enough and species can transport through it and the reaction with the underlying metal can still occur. In fact, exposure of this thin oxide (≈ 20 Å) to air, for longer time, will continue the oxidation reaction until a thicker layer (≈ 50 Å) is formed. The AlF_6^{-3} species was not formed on the surface when the oxide layer was thick (50 Å), spectrum **C**, or in the case of sapphire, spectrum **D**. This indicates that the oxide layer is indeed inhibiting the formation of this species. Aluminum compounds formed as a result of the decomposition of Fomblin were observed on all four surfaces, suggesting that the Al atoms in the oxide are still available to react with the PFP AE and decompose it. The F-1s spectrum, shown in the insert of figures **1C** and **1D** for thick oxide and sapphire shows the Fomblin peak at 688.7 eV, and two fluoride peaks at 687.2 and 685.1 eV, assigned to AlF_3 and Al-oxyfluoride, respectively. In these two spectra, **C** and **D**, the $Al-2p_{3/2}$ signal corresponding to the fluorides is small compared with that of the oxide peak and the small binding energy difference between them, ≈ 1.5 eV, complicates its identification. However, the presence of the fluoride is unambiguously confirmed by the F-1s spectrum.

Grazing angle XPS indicated that in all cases, a layer of molecular PFPAE survived on top of the reacted layer, after heating was stopped. The thickness and continuity of the surviving molecular PFPAE film depended on the original amount; in cases where the film was thinner only patches of molecular Fomblin were found after the heating as determined by angle resolved XPS, while with the originally thicker films, a continuous layer of Fomblin remained after heating. The C-1s spectra of these four surfaces showed still the presence of the two the high binding energy carbon peaks corresponding to Fomblin, although the ratio between them indicated that there was a preferential consumption of the acetal carbon. Thus the organic overlayer contained both molecular and decomposed Fomblin. Decomposed Fomblin is the source of all the C-1s peaks with binding energies between 292 and 286 eV.

Grazing exit XPS indicated that the AlF_3 species was formed at the PFPAE/oxide interface. If AlF_3 is the catalyst for Fomblin degradation as it has been reported (refs. 13 and 14) the co-existence at higher temperatures of the PFPAE with the metallic fluoride would not be possible. Probably, because of the presence, also at the interface, of the debris layer, which acts as a passivating film.

Tribo-experiments

Tribo-experiments in which a sapphire surface coated with a thin film, $\approx 90 \text{ \AA}$, of PFPAE was contacted with a sapphire ball (0.5 mm diam.) that moved in a single pass, reciprocating pattern over an 8- by 5-mm area, were also performed in UHV. The interface was analyzed with XPS before and after the tribo-experiments. The friction coefficient, μ , was ≈ 0.16 for a load of 100 gmf (0.98 N) and a speed of 0.3 mm/sec. XPS of the mechanically damaged surface shows Fomblin degradation at the interface, evidenced by the appearance, after sliding, of a F-1s peak at 687.2 eV, corresponding to aluminum fluoride and again, the peak at 685.1 assigned to Al-oxyfluorides species. The C-1s and O-1s peaks also show signs of the Fomblin degradation (fig. 2). Besides the Fomblin peaks there are other peaks corresponding to the organic debris layer formed by Fomblin degradation products. In the C-1s region this degradation is also evidenced by the preferential consumption of the acetal carbon (the high energy Fomblin peak).

The $\text{Al-}2p_{3/2}$ peak, in figure 2A, shows mainly the Al^{3+} signature from the oxide. It can be seen that there is a tailing on the high energy side of the peak, corresponding to the presence of aluminum fluorides produced during the tribo-experiments.

Comparison of these XPS spectra with previous ones obtained after heating, revealed the formation of the same type of compounds at the interface. Therefore, it can be concluded that thermally and tribologically induced decompositions of Fomblin Z produce similar reaction products. This same effect was previously observed when sliding a 440C ball against a 440C surface with a Fomblin Z overlayer (ref. 4). It has been suggested previously (refs. 1, 2, and 15) that the tribological decomposition of Fomblin Z is actually thermally induced by asperity interactions. The similarity between the debris layer formed by thermal reaction and by a tribologically induced reaction could, also, lead us to conclude that the tribological reaction is indeed a thermal effect. Flash temperature calculations (refs. 16 and 17) do not agree with this suggestion since the temperature values obtained, considering the friction coefficient, load, and physical properties of the surface, are much lower than the ones expected based on the thermal reaction onset ($150 \text{ }^\circ\text{C}$). Another important aspect to consider is that in a tribological environment new, fresh surface is constantly being created by the interaction of the two surfaces. This fresh surface, as it has been demonstrated in this work, is active towards Fomblin Z, even at room temperature. It might be a combination of both this constant generation of active surface and the rise of temperature at the interface that is responsible for the decomposition observed.

It seems contradictory that sapphire does show reactivity at room temperature when in a tribological environment but lacks reactivity when the clean surface is exposed to the Fomblin vapors at room temperature. This might be due to the small amount of carbon contamination still present after the UV-ozone treatment of the sapphire substrate. This carbon contamination might act as a poison of the active sites on the surface that can react with Fomblin.

CONCLUSIONS

The conclusions can be summarized as follows:

1. We have shown that Fomblin Z decomposes on the native oxide even at room temperature. Decomposition on sapphire is not observed at room temperature.
2. TDS indicates a desorption peak from the oxide surface at about the same temperature as on clean metal, although the desorption products are different, indicating different mechanisms for the oxide and the clean metal.
3. Heating Fomblin Z to 150 °C on aluminum oxide (native oxide or sapphire) induces the decomposition of Fomblin Z until a thick passivating debris layer is generated on which unreacted Fomblin can reside.
4. Sliding sapphire on Fomblin-lubricated sapphire also induces the decomposition of Fomblin Z, yielding surface species similar to those found by thermal decomposition, as evidenced by XPS measurements.
5. The acetal group of Fomblin is preferentially attacked by both heating and rubbing.

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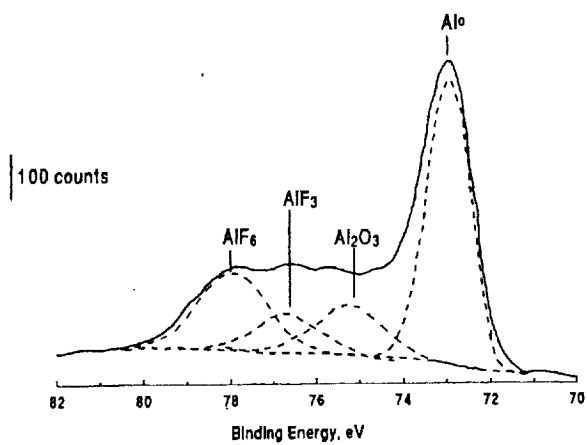
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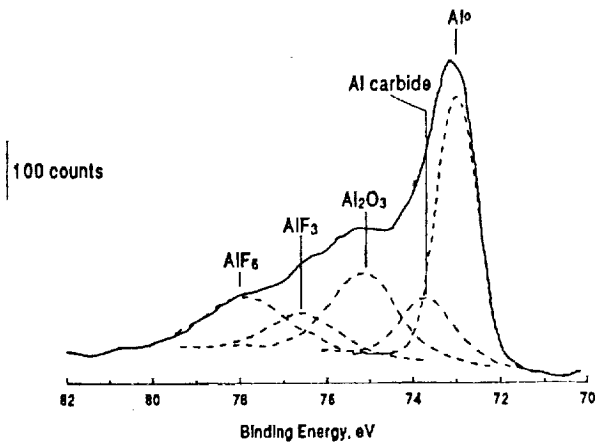
TABLE I.—XPS SPECTRAL FEATURES
AND THEIR ASSIGNMENTS

[The values presented in this table are values found in this work.
The values in the references have been corrected using
 $C_{1s} = 284.7$ eV.]

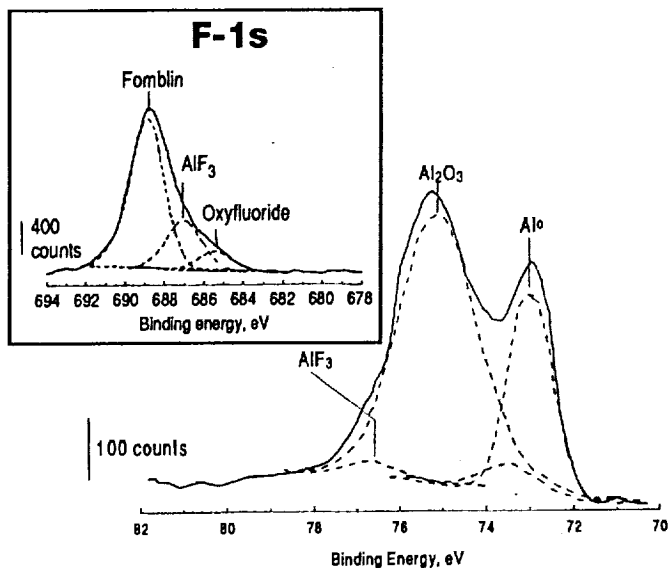
Element	B.E. (± 0.2 eV)	Assignment
C_{1s}	293.0	O- $\overline{C}F_2$ - CF_2 -O (Fomblin)
	294.7	CF_3 or O- $\overline{C}F_2$ O (Fomblin)
	284.7	C-C, aliphatic or adventitious carbon
	282.2	Aluminum carbide (ref. 18)
O_{1s}	535.5	Fomblin
	532.0	Al_2O_3
F_{1s}	688.7	Fomblin
	687.2	AlF_3 (ref. 7)
	685.1	Al-oxyfluoride (ref. 19)
Al_{2p}	73.0	Al^0
	73.7	Al-carbide
	75.1	Al Oxide
	76.6	Al Fluoride
	78.0	AlF_6^{3-}



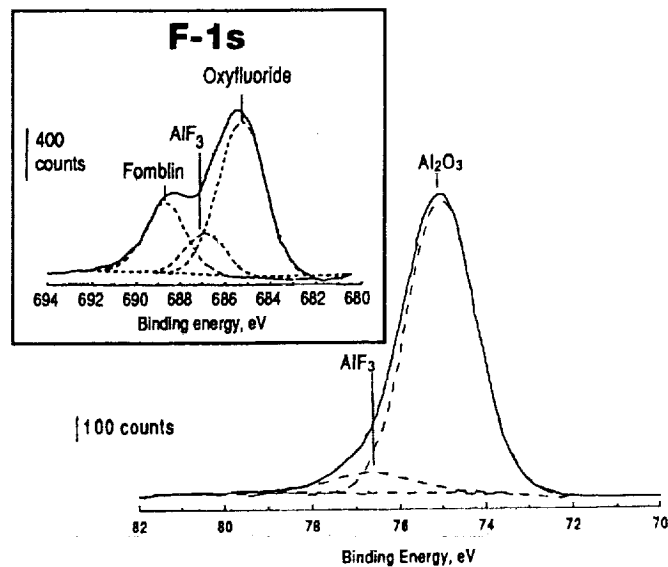
(a) Clean aluminum surface.



(b) Thin aluminum oxide (20 Å).

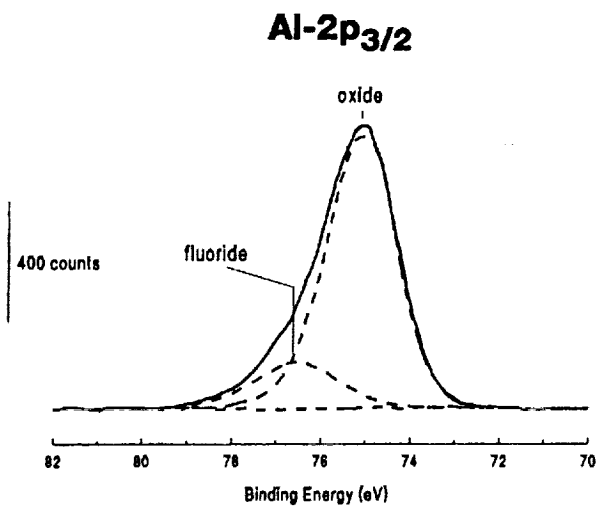


(c) Thick aluminum oxide (50 Å).

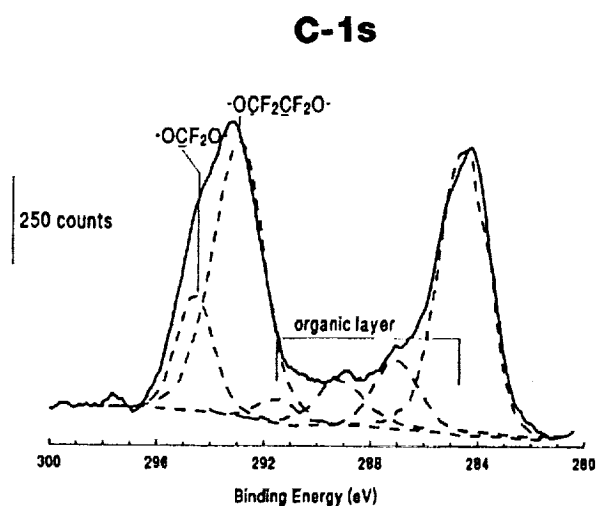


(d) Sapphire.

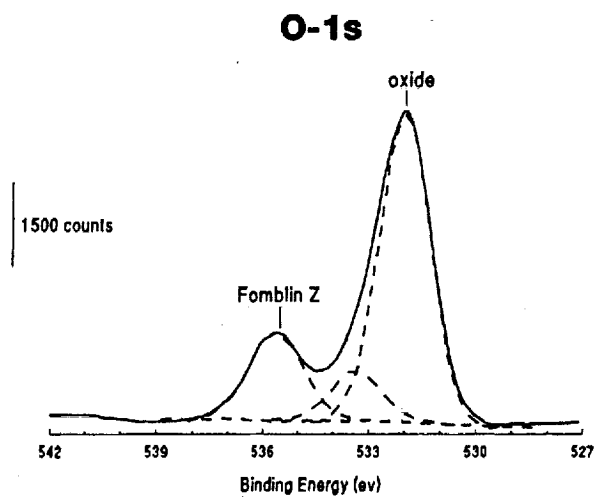
Figure 1.—Al-2p_{3/2} XPS spectra after heating the Fomblin coated substrate at constant temperature (150 °C) for 4-6 hr. The curve fitting was done using the VG software which uses a mixture of Gaussian and Lorentzian curves. The FWHM, B. E. and Gaussian to Lorentzian ratio for a given peak was kept constant throughout the analysis.



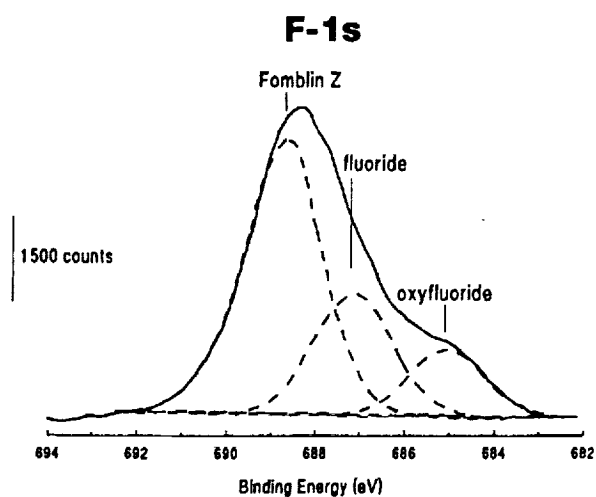
(a) Al-2p_{3/2} region.



(b) C-1s.



(c) O-1s.



(d) F-1s.

Figure 2.—XPS of the wear area after sliding the Fomblin on Sapphire sample with a sapphire ball.

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13. ABSTRACT (Maximum 200 words) Thin films of Fomblin Z25, a perfluoropolyalkylether lubricant, were vapor deposited onto clean, oxidized aluminum and sapphire surfaces, and their behavior at different temperatures was studied using XPS and TDS. It was found that the interfacial fluid molecules decompose on the native oxide at room temperature, and continue to decompose at elevated temperatures, as previous studies had shown to occur on the clean metal. TDS indicated that different degradation mechanisms were operative for clean and oxidized aluminum. On sapphire substrates, no reaction was observed at room temperature. Our conclusion is that the native oxide of aluminum is neither passive nor protective towards Fomblin Z25. At higher temperatures (150 °C) degradation of the polymer on sapphire produced a debris layer at the interface with a chemical composition similar to the one formed on aluminum oxide. Rubbing a Fomblin film on a single crystal sapphire also induced the decomposition of the lubricant in contact with the interface and the formation of a debris layer.			
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