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NASA Technical Memorandum 106014

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October 1992

(NASA-TM-106014) INTERFACIAL CHEMISTRY OF A PERFLUOROPOLYETHER LUBRICANT STUDIED BY XPS AND TDS (NASA) 39 p

N93-22560

Unclas

G3/27 0150558

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NASA Technical Memorandum 105840

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The report number for the aforesaid Technical Memorandum is corrected to NASA Technical Memorandum 106014.

INTERFACIAL CHEMISTRY OF A PERFLUOROPOLYETHER LUBRICANT

STUDIED BY XPS AND TDS

by

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ABSTRACT

The interfacial chemistry of Fomblin Z25, a commercial perfluoropolyether used as lubricant for space applications, with different metallic surfaces: 440C steel, gold and aluminum was studied. Thin layers of Fomblin Z25 were evaporated onto the oxide-free substrates and the interfacial chemistry studied using XPS and TDS. The reactions were induced by heating the substrate and by rubbing the substrate with a steel ball. Gold was found to be completely unreactive towards Fomblin at any temperature. Reaction at room temperature was observed only in the case of the aluminum substrate, the most reactive towards Fomblin Z25 of the substrates studied. It was necessary to heat the 440C steel substrate to 190 °C to induce decomposition of the fluid. The degradation of the fluid was indicated by the formation of a debris layer at the interface. This debris layer, composed of inorganic and organic reaction products, when completely formed, passivated the surface from further attack to the Fomblin on top. The tribologically induced reactions on 440C steel formed a debris layer of similar chemical characteristics to the thermally induced layer. In all cases, the degradation reaction resulted in preferential consumption of the difluoroformyl carbon ($-OCF_2O-$).

INTRODUCTION

The perfluoropolyethers (PFPE) are a class of fluids presently being investigated for potential applications as high temperature lubricants for advanced gas turbine engines (Refs. 1 to 3). These fluids have also been used extensively as lubricants for space mechanisms (Ref. 4 to 8), generally operating near room temperature.

However, their performance in the presence of ionizing radiation (Ref. 5 and 9), under tribological conditions (Ref. 6 and 10), and in the presence of various catalytic materials (Ref. 11 to 13) has exposed serious deficiencies. In many cases, the PFPE fluids were extensively degraded and caused severe corrosion problems on metal surfaces.

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One explanation for the observed degradation is that the rubbing process removes the protective native oxide from the metal bearing surface and allows the fluid to contact the atomically clean metal (Ref. 6). This clean metal then degrades the fluid by simple contact at room temperature and forms metal fluorides. These fluorides, in turn, attack the PFPE fluid much faster than does the clean metal itself. The attention focused on the interaction with clean metal has led to the study of small model compounds reacting with the oxide-free surface of a pure metal using surface analytical techniques such as X-Ray Photoelectron Spectroscopy (XPS). In fact, the full range of modern surface analytical techniques can be used if the small molecules are accepted as adequate models of the macromolecule that constitutes the lubricant fluid. Several such surface analytical studies have utilized model perfluoroether or partially fluorinated compounds. Techniques used in these studies include transmission infrared spectroscopy (Ref. 9b and 14), thermal desorption spectroscopy (TDS) (Ref. 15 and 16), polarization modulated Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS) (Ref. 17), ultraviolet photoelectron spectroscopy (Ref. 18), mass spectrometry (Ref. 19 to 23), x-ray photoelectron spectroscopy (Ref. 6,9a,10, and 24 to 28) and x-ray reflectivity (Ref. 29). It is, however, more desirable to study the lubricant fluid itself contacting the oxide-free surface of a bearing alloy, instead of a model molecule on a pure metal. Such an effort has not been reported to date, generally because of the technical problem of bringing the fluid into contact with the oxide-free clean metal with a fluid film thin enough to allow a surface analytical technique to study the fluid-solid interface.

This technical problem also arises when considering another explanation offered to understand the observed degradation: direct tribochemical action, in which the shear stress to which the fluid is subjected in the rubbing contact physically damages the macromolecules that constitute the fluid. These activated or damaged molecules can then interact with the substrate bearing surface, clean or oxidized, or with neighboring molecules to continue the chain of chemical events. The study of such tribochemistry has been one of post-mortem analysis of a tribological experiment which is generally run in air, always with the native oxides on the bearing surface and always with an overburden of fluid that must be removed by solvents to allow access to the interface by surface analytical techniques. Such post-mortem analyses, while interesting, face the lack of control and characterization of the bearing surface in the tribo-experiment and thus lack the ability to confidently assign mechanisms to explain the products found by the analysis.

Thus, there is a clear need to devise an experimental approach that establishes a fluid-solid interface that: a) is characterized and controlled with either the native oxide present or absent, b) is accessible to analysis with modern surface techniques, such as XPS, without an intervening exposure to air, and c) is capable of being subjected to high temperature or rubbing without exposure to air and then being analyzed, again without exposure to air.

In this paper these experimental issues are addressed. The metal that is to be in contact with the fluid is first ion bombarded to remove the native oxide and its cleanliness is verified by XPS. Then, without removing this surface from the ultrahigh vacuum environment, it is exposed to the vapor of evaporating fluid and a few monolayers are allowed to condense. Thus a film, thin enough to allow XPS to sense the interface, but thick enough to constitute a true fluid, is established on a clean metal surface. This film-covered surface in an ultrahigh vacuum environment can then be subjected to x-radiation, high temperature and rubbing with a bearing ball and the chemical response of the interface followed by XPS.

The objectives of this paper are first to present the experimental method used for interfacial analysis of a fluid-solid interface that may be subjected to high temperatures and rubbing. XPS and TDS are the principal analytical techniques employed. Second, the interface of a commercial PFPE fluid (Fomblin Z-25) with the oxide-free surface of 440C steel is studied to determine chemical reactivity by room temperature contact. Third, the interfacial thermochemistry of Fomblin Z-25 on gold, 440C steel and aluminum is studied at elevated temperature. Gold was chosen for its lack of chemical activity, aluminum was chosen for its high activity and both could be compared to a standard bearing steel (440C). Finally, the tribochemical response of the fluid-steel interface was studied by rubbing a few monolayers of fluid on steel with a steel ball in an ultrahigh vacuum environment. The thrust is basically phenomenological, seeking an overall characterization of the system and not a detailed study of chemical mechanisms.

EXPERIMENTAL

The experimental system is depicted in Fig. 1. The ultrahigh vacuum system consists of two chambers connected by a gate valve. The analytical chamber, with a base pressure of 1×10^{-10} torr, houses an ion gun used to clean the metal surface, the x-ray photoelectron spectrometer for surface analysis, and a quadrupole residual gas analyzer (RGA) for identifying species released at elevated specimen temperatures. The preparation chamber, with base pressure of 2×10^{-9} torr, houses the fluid evaporator used to deposit the fluid film on the metal surface and the apparatus to rub the fluid-

coated surface with a steel ball. This apparatus is depicted in Fig. 2. The metal surface can be positioned to face the evaporator for film deposition, to face the ball of the rubbing apparatus, or handed off to the XYZΘ manipulator in the analytical chamber for XPS and TDS.

Materials

The fluid used was Fomblin Z-25 (batch P-78), a commercial lubricant. Physical properties for this fluid appear in Table 1. Fomblin Z is a random copolymer of perfluorinated ethylene oxide ($-CF_2-CF_2-O-$) and perfluorinated methylene oxide ($-CF-O-$), made by the UV polymerization of tetrafluoroethylene ($CF_2=CF_2$) in the presence of oxygen (Ref. 30). This polymer contains the difluoroformyl group ($-OCF_2O-$), often referred to as "acetal group." The molecular diameter of the polymer is 6-7 Å (Ref. 31a); in this paper the monolayer thickness will be considered to be 8 Å. This corresponds to the case in which the molecule lies flat on the surface (Ref. 31b). The ratio of the ethylene oxide group to the methylene oxide group is 0.6 to 0.7, i.e., $(-CF_2-CF_2-O-)_x(-CF_2-O-)_y$ with $x/y=0.6$ to 0.7.

Gold and aluminum surfaces were films of about 5000 Å sputter-deposited onto a molybdenum VG heatable stub polished with 1 μm diamond paste. The 440C stainless steel sample was a machined disk (19 mm diam, 4 mm thick) tightly attached to the VG heater stub. Its Vickers hardness was 277 Kg/mm^2. Before loading these surfaces into the preparation chamber, they were rinsed in methanol and subjected to a UV-ozone treatment (Ref. 32) for 10 minutes to eliminate adsorbed carbonaceous impurities difficult to remove by ion bombardment. In the analytical chamber, the samples were then ion bombarded with 2.5 keV Ar$^+$ until no contaminants were detected on the surface by XPS. The clean surfaces were then heated to a temperature, higher than the highest limit of the TDS experiments (~450°C), in order to reduce the amount of oxygen and other contaminants that could diffuse to the surface or desorb during the heating experiments. It is also possible that by heating the samples to ~450 °C the damage induced by sputtering might be reduced or eliminated. The samples were again ion bombarded until the heating did not induce a detectable change in the background pressure.

In order to eliminate any possible reaction Fomblin Z-25 was evaporated from a gold-coated, Mo cup onto the atomically clean substrates at room temperature in the preparation chamber. The fluid was heated to 350-360 °C and about 2-3 monolayers, measured by XPS, condensed in 30 sec on the substrate. Before evaporation, the fluid in the cup was heated to 300 °C and cooled down, in order to eliminate dissolved gases (N_2, O_2, CO_2) thus avoiding the presence of

these active gases that could contaminate the substrate. The film thickness was varied by varying the evaporation time. During the evaporations, the residual gas composition in the preparation chamber ($P < 2 \times 10^{-9}$ torr) was monitored with a quadrupole residual gas analyzer and the fractions commonly observed were: m/e 28, 31, 44, 47, 50, 66, 69 and 119. It was found that the composition of the condensed film (from XPS and high performance liquid chromatography, HPLC, see below) changed after about 20 evaporations, possibly due to thermal decomposition of the residual fluid in the cup. At this point the evaporator cup was cleaned and fresh Fomblin was used.

Analytical Techniques

The XPS spectra were acquired by a Vacuum Generator (VG) Mk II ESCALAB with VGS 5000 enhanced data processing software for peak fit and integration. The x-ray anode used was aluminum with an emission current of 20 mA and an accelerating voltage of 15 keV, which illuminates a < 1 mm x 5mm area on the sample. The window material was aluminum foil. The analyzer operated in the constant analyzer energy mode with 50 eV pass energy. The B.E. of the gold standard was 84.0 eV with a FWHM of 1.4 eV. Monochromatic Al K_α x-rays were used throughout the study to minimize radiation damage to the fluid. The electron optics were set to accept photoelectrons from an area 2 x 5 mm centered on the illuminated area in order to maximize count rate, and minimize exposure time. The acceptance angle (iris) was ±12° and, unless specified, the spectra were taken with the surface plane normal to the analyzer axis.

The photoelectron peaks, including the transition metal peaks, were fitted using combinations of Gaussian and Lorentzian curves with a software package provided by the manufacturer of the spectrometer. The data was first smoothed using a single pass cubic smooth over 1.2 times the full width half maximum (FWHM), then a linear background was subtracted. The peak fit was done over limits ± 1 eV from the end of the photoelectron peaks. Throughout the analysis the FWHM, Gaussian/Lorentzian ratio and binding energy for a given peak were kept constant, allowing only the peak height to vary during the fit. All the peaks in this report are referenced to adventitious carbon (284.7 eV). Literature data, used for comparison with binding energies values assigned in this work were also corrected using this as reference.

The thermal desorption studies (TDS) were performed in the analytical chamber by applying a linear temperature ramp ($\approx$ 2 °C/sec) to the substrate which faced the RGA. The RGA was interfaced to a computer for data acquisition. The RGA collected the intensities of 5 masses versus time. These masses were 31 (CF^+), 47(COF^+), 50 (CF_2^+), 66

(COF_2^+), and 69 (CF_3^+). The RGA has a limited mass range (200 max.) and is not capable of identifying heavy ($\approx$10,000 daltons) molecules. The cracking patterns obtained are used simply as fingerprints to help distinguish Fomblin released intact from the surface from other species. These mass intensities also serve as a convenient supplement to a total pressure measurement to determine the temperature at which reaction/desorption occurs. The sample temperature was determined with an infrared optical microscope (Ref. 33) (reproducibility ±10 °C). This microscope was focussed on a Ta foil flag which had been spot welded to the side of the sample and coated with graphite powder (DAG) for unit emissivity.

High performance liquid chromatography (HPLC), utilizing size exclusion separatory columns, was used to compare the molecular weight distribution of the condensed Fomblin film to that of a smeared Fomblin layer and that of the bulk Fomblin liquid. All Fomblin samples were dissolved in 2 ml of 1,1,2-trichloro-trifluoroethane, the liquid mobile phase for the HPLC system. 100 μl of the resulting solution was injected into the chromatograph. Separation occurred in a set of three columns connected in series (two μBondagel and one 60 Å μPorasil). The mobile phase flow rate was 0.6 ml/min, and Fomblin was detected by a refractive index detector. This technique is capable of detecting changes in the molecular weight distribution of approximately 5% in a 0.8 μg sample.

Procedure

After ion bombardment and XPS, the clean samples were transferred from the analytical chamber into the preparation chamber and placed on top of the aperture of the collimator of the evaporator. After the surface was exposed to the fluid vapors for a time long enough to obtain the desired thickness of the condensed fluid, the sample was transferred back to the analytical chamber for XPS analysis.

The reactions at the interface were induced by either contact during condensation at room temperature, heating the substrate (thermochemistry) or by rubbing the sample's surface with a steel bearing ball (tribochemistry).

The thermochemistry of the interface was done in three different modes:

A. Linear heating ($\approx$2 °C/sec) to a maximum temperature T_{max} (TDS)

B. Linear heating ($\approx$ 2 °C/sec) to a temperature $<T_{max}$, analyze with XPS (after the sample cools back to room temperature), repeat at successively higher intermediate temperatures until T_{max} is reached.

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C. Heating at constant temperature for long periods of time at a temperature at which the interface reaction, if

there is one, has already begun. In this way the Fomblin layer is in lengthy contact with a reacted substrate

at elevated temperature.

After each heating cycle was completed, the interface was analyzed using XPS.

The film-covered surface was subjected to rubbing by the tribometer depicted in Fig. 2. A 440C steel bearing ball,

6 mm diameter, was loaded onto the surface with a normal force of 0.98 N (100 gmf) leading to an average Hertz

pressure of 0.43 GPa (Hertzian diameter = 54 μm). A reciprocating sliding motion with a velocity 0.3 mm/sec was used.

A lateral translation of 50 μm at the end of each stroke produced a rectangular patch 5 mm x 8 mm. The pressure in the

preparation chamber during sliding was $1-2 \times 10^{-9}$ torr.

RESULTS

Characterization of the Condensed Films

It is first necessary to establish that the condensed monolayers used in this study of the liquid-solid interface are in

fact representative molecules of the starting fluid and neither a light distillate or chemically degraded fragments. HPLC

determined the molecular weight distribution and XPS determined the relative C:O:F concentration and bond type. An

effort is made to demonstrate that the condensed material is in fact a continuous film and not agglomerated droplets with

exposed substrate between them. Finally, an assessment is made of the damage to the films and the resulting artifacts on

the different metals induced by the monochromatized x-ray bombardment during XPS analysis.

HPLC

HPLC in the size exclusion mode (Ref. 34) was used to analyze thick (≈500 Å) films condensed on gold and 440C

steel. The molecular weight distributions of these films were compared to that of bulk liquid and with films that had

been smeared (in air) onto the substrate surface. There were no differences in molecular weight distribution between

these films, indicating that the evaporation did not produce decomposition or chain scission of the polymer, and thus the

condensed film is a good representation of the starting liquid.

XPS

XPS is used here to determine the thickness of the condensed films by the attenuation of the substrate signal

intensity at normal photoelectron exit using $I_{sub}=I^{\circ}_{sub} \exp (-t/\lambda)$ where t is the film thickness and λ is the inelastic mean

free path of the substrate photoelectron in the film. $I°_{sub}$ and I_{sub} are the substrate photoelectron intensities before and after film deposition, respectively. The values of λ used here are tabulated in Table 2 for the different substrate photoelectrons. The conversion into monolayer (ML) thickness, assuming a uniform condensed film (discussed below) is made by taking 8 Å as the thickness of one monolayer. Using this method, the spectra due to a 27 Å thick ($\approx$3 ML) film on clean 440C steel is shown in Fig. 3, spectrum a. The C, O, and F spectra were processed with the semiquantitative routines for elemental sensitivities supplied with the spectrometer to obtain the elemental concentrations and binding energies in Table 3. Similar results were obtained for the relative elemental concentrations from thicker condensed films (thick enough to be analyzed by HPLC after removal from the stub by a solvent) and smeared-on films. There is good agreement of the relative elemental concentrations with those specified by the manufacturer. Also, the binding energies and spectral line shapes agree with those found in the literature for this fluid (Refs. 9a,24,37, and 38) It is thus concluded that, based on the analytical techniques used, these condensed films are chemically indistinguishable from the starting fluid.

Although uniformity and continuity of the film is assumed in the above thickness determination, the film may actually be agglomerated into small droplets. This may be tested by varying the photoelectron take-off angle from normal to grazing exit in our angle-resolved electron spectrometer. If the droplet's height is much greater than the photoelectron escape depth, then the spectral intensities from the film relative to the substrate will not change when the take-off angle is changed from normal to grazing exit. On the other hand, the intensities from a uniform, continuous, thin film will increase relative to those from the substrate with this change in take-off angle. In Table 4, the 17 Å film-substrate intensity ratio is seen to increase as the take-off angle is changed from normal to grazing exit, thus ruling out agglomeration into thick droplets. Further exploration of the film's morphology by the angular dependence of the spectral intensities is possible (Refs. 39 and 40). However, the finite surface roughness of our polished substrates introduces its own angular dependence, and thus complicates and limits the usefulness of this approach, which is not pursued further here. Although the assumptions of film uniformity (or at least non-agglomeration) is based on this limited evidence, it is in accordance with other work with fluids that also show uniform spreading of PFPE films on surfaces (Refs. 38,41,42, and 43). Since the film is considered uniform and continuous and substrate signals are observed in the spectra, then, in

addition to the substrate and the bulk of the film, there is information on their interface in the spectra. Thus, one of the main objectives of this paper--a method to study the fluid-solid interface chemistry--has been achieved.

Radiation Damage

Although XPS may be effectively used as indicated above, the destructive effect of x-rays on PFPE fluids introduces an artifact. The bulk fluid's decomposition under x-irradiation has already been reported (Refs. 9a,44,45, and 46) and observed mainly by the evolution of C 1s spectrum. However, here the interface is studied, and we have observed reactions between the fluid and the substrate due to radiation damage. Such irradiation-induced interfacial artifacts must be carefully distinguished from the interfacial thermochemistry and tribochemistry sought here. These artifacts, whose intensity increases with irradiation time, are specific to the substrate material. The inert gold substrate exhibits no interfacial artifacts. The spectra of a ≈80 Å Fomblin film on 440C steel irradiated 16 hours is shown in Fig. 3, spectrum b. New features have appeared for fluorine, F^a (684.0 eV), oxygen, O^a(530.2 eV), and iron, Fe^b and Fe^c (709.8 eV and 711.9 eV respectively) corresponding to the formation of iron oxide and iron fluoride. In the carbon spectrum b an extra feature, C^f, at 291.5 eV can be detected, this peak has previously been attributed to the basic structure of the fluid (Ref. 47). Probably other carbon containing species also exist on the surface but the low intensity of the carbon signal makes their identification difficult.

On the aluminum surface, new features were observed in the fluorine, F^a(684.0 eV), and aluminum, Al^c(76.6 eV), spectra due to the formation of aluminum fluoride. We note that the fluorine feature at 684.0 eV has not been reported before as a radiation-induced feature, and appears to be a unique and clear signature of radiation-induced reaction with the substrate. In particular, it is not the spectral feature usually associated with a metal fluoride. These XPS spectral features and others found in this study have been labeled and collected in Table 5 where assignments and supporting references are provided.

Under irradiation, a thinning and a relative fluorine enrichment of the remaining film were generally observed, together with the appearance in the gas phase of Fomblin fragments COF^+ and COF_2^+ as major constituents. The x-ray damage was highly localized, being limited only to the area of the sample illuminated by the monochromatic x-ray source. Translation of the sample to illuminate a new area resulted in a spectrum of undamaged Fomblin, even after the adjacent area had been subjected to several hours of exposure to x-rays. After approximately four hours of exposure to

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the monochromatic x-ray beam, signs of Fomblin degradation and interfacial reaction on gold, 440C or aluminum were evident. This is enough time for a few XPS analyses after different thermal or tribological treatments.

The Interface at Room Temperature

The films were deposited onto the clean metals nominally at room temperature. Evidence for interfacial chemical activity was sought by inspecting the spectra of both film and substrate for deviations from the spectra of thick, smeared-on film and clean metals. It was found that there were no such deviations for thin films on both gold and 440C steel for any take-off angle. This result may be expected for the inert gold substrate, but was somewhat unexpected for the more active steel surface. An example for steel is provided by Fig. 3, spectrum a. No change from the Fe or Cr (not shown) spectra in the clean state was discerned and the spectra from the film's elements were the same as for the thick film. It is concluded that no observable chemical reactions occur by contact of Fomblin with either clean gold or 440C steel at room temperature.

Deposition onto clean aluminum yields quite different results: after an exposure for which spectral features of Fomblin are clearly evident on gold and steel, no such features are found in spectra from the aluminum surface. Instead, spectral features due to reaction of aluminum with the C, O and F constituents of Fomblin are found. This is illustrated in Fig. 4, which presents spectra at progressively higher coverages. For spectra b, none of the features for C, O and F appear with binding energies associated with Fomblin, but instead C^a, F^b, F^d, O^d and O^e due to carbide, fluoride and oxide compounds with aluminum are present, the assignments are indicated in Table 5. There are also satellite features in the aluminum spectrum (Al^b, Al^c) corresponding to aluminum oxide and fluoride which are too small to be seen in the figure, but are evident after curve fitting the Al peak, and also at higher Fomblin coverage. Thus the Fomblin molecules in contact with the clean aluminum completely decompose at room temperature, with the constituent elements reacting with the surface to form aluminum compounds. We will also refer to the interfacial layer of compounds formed from the products of the decomposition reaction of Fomblin on these surfaces as a "debris" layer.

At higher coverages ($\approx$4 ML), spectra c, the features due to aluminum compounds increase in intensity, but are complemented by features due to unreacted Fomblin molecules: C^g, C^h, O^f and F^e. Thus, the debris or reaction layer is protective at room temperature and allows Fomblin molecules to condense intact and evolve into a Fomblin fluid film.

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Finally, for long exposures, very thick films (spectra d, 26 ML) result with only the features due to the intact Fomblin molecules evident. The debris layer is buried but some substrate features can still be observed. Since Fomblin can eventually be condensed, the reactions that produced the debris layer at low coverages are confined to the vicinity of the interface and do not propagate through the thick film at room temperature.

Elevated Temperature

The film-covered substrate was subjected to two or more of the heating modes described in the Procedures section. The species desorbed from the surface were analyzed by the RGA during heating and the surfaces were examined by XPS at room temperature after the heating.

Gold: A clean gold surface with a ~50 Å film of Fomblin was subjected to mode A heating (TDS), and the desorption spectrum for the intensities of two of the five fragments monitored is shown in Fig. 5. The intensity of all of the monitored fragments exhibit maxima at the same temperature, 290 °C, and their relative intensities are shown inset in Fig. 5. The single desorption feature is dominated by m/e = 47(COF^+). The XPS of this surface after TDS to 400 °C showed the complete absence of spectral features due to C, O or F. The gold surface was clean and devoid of fragments that might result from the thermal decomposition of the Fomblin molecules. Since the film condensed from the vapors released from the gold-plated evaporation cup had all the characteristics of bulk Fomblin, the species released from the gold film during the TDS are considered to be Fomblin molecules as well. The fragment intensity distribution in Fig. 5 is therefore considered to be that of the intact Fomblin molecule as it enters the ionization chamber of the RGA. This distribution, or cracking pattern, will be compared with the composition of vapors released from chemically active surfaces at elevated temperatures.

Gold, covered with a ~40 Å film, was also subjected to mode C heating: 160 °C for 240 min. XPS then showed only an increase in the intensity of the substrate features. The intensity of the Fomblin-related C, O and F features decreased, but their relative intensity (including the C 1s structure) remained the same. Thus, the Fomblin film did not itself degrade or react with the substrate at these temperatures, but only thinned due to evaporation.

To summarize the observation on gold: No reaction was observed for Fomblin deposited at room temperature and no reaction was found at elevated temperatures. The fluid simply evaporated as intact Fomblin molecules.

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440C Steel: The TDS, for which the maximum temperature is 400 °C, of a 36 Å film on clean 440C steel is shown in Fig. 6. There is a single maximum at 270 °C, close to that observed for Fomblin on gold, Fig. 5. However, the feature is not as symmetric as that for gold, exhibiting shoulders both at lower and higher temperatures for the different masses. The intensity distributions of the monitored fragments are inset in the figure and it is seen that the composition below and at the peak is the same. Since this distribution is the same as that found for desorption from gold, which was attributed to release of intact Fomblin molecules, it is concluded that Fomblin itself is desorbing from 440C at these temperatures. The low temperature asymmetry is attributed to desorption from a locally hotter spot on the specimen--recall that it is mechanically joined to the heater stub, and thus may have less uniform temperature distribution than the sputter-deposited aluminum and gold films on the heater stub. The composition above the peak is different from those at lower temperature, being dominated by $m/e=31$ and not $m/e=47$. This shoulder is due to release of species other than Fomblin and is the initial indication that chemical reaction is taking place on 440C steel.

The XPS of the surface after completion of the TDS is presented in Fig. 7. There are no spectral features due to Fomblin. However, unlike the desorption from gold, the 440C surface has not been restored to its original clean state after the TDS. Instead, features are found that are attributed to iron fluoride (Fe^c and F^c), chromium fluoride (Cr^c and F^c), iron oxide (Fe^b and O^a), chromium oxide (Cr^b and O^b) and a metal carbide (C^b). There is a feature at 284.7 eV (C^c) that is the usual value for adventitious carbon and is here attributed to a saturated carbon. Finally, there is a feature at 533.4 eV (O^e) which has been identified by others (Ref. 48) as an oxyfluoride species formed at the polymer-metal interface. Thus we conclude that, although most of the polymer molecules desorb intact, some have reacted with the 440C surface at elevated temperatures to produce a reaction layer of the above metal compounds. It is the desorption or the decomposition of some of these reaction compounds that is associated with the high temperature shoulder of the TDS that is dominated by $m/e=31$. It is estimated from the attenuation of the metallic substrate features that this reaction layer is 10 Å thick.

At the conclusion of this TDS, the polymer molecules had already undergone reaction and their products partially desorbed. It is of interest to stop the TDS before the desorption peak is reached to observe the reaction in progress. The spectra due to the mode B heating of a film >100 Å to 250 °C are presented in Fig. 8. The Fe and Cr spectral intensities after film deposition, although not zero, are very weak and therefore not shown in the figure. After heating to 250 °C,

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spectra c for Fe and Cr (i) are now intense because some of the overlying Fomblin has desorbed and (ii) have acquired additional features ($Fe^{b,c,d}$, $Cr^{b,c,d}$) due to their oxides and fluorides. Spectra c (for the elements C, O and F) indicate that (i) some Fomblin ($C^{g,h}$, O^f, F^e) remains, having been neither reacted nor desorbed (ii) reaction products of oxides ($O^{a,b}$), a fluoride (F^c) and a carbide (C^b) have formed that are partners to the compounds found in spectra c for Fe and Cr and (iii) there is a C 1s spectral region, 284 eV - 292 eV, where new intensity is found and an attempt is made here to resolve the features in this region. The feature at 284.7 eV (C^c) is clearly identified and has been assigned to a saturated carbon network. The remaining intensity in this region was resolved into features C^{d-f} which possible assignments are provided in Table 5. The curve fitting also shows an increase in the C^g/C^h ratio compared to that of bulk Fomblin (1.2). This indicates a preferential consumption of C^h over C^g. Matching assignments in the oxygen spectrum $O^{e,f}$ are also provided in Table 5. In spite of the uncertainty of the specific deconvolutions and assignments, it seems clear from elementary arguments of electronegativity, that the intensity in this region is due to carbon bonded in a variety of ways to oxygen, fluorine and other carbon, but not in the highly organized way found in Fomblin ($C^{g,h}$). It is concluded that these carbon and oxygen spectral intensities (underlined in spectra c) are due to a layer of Fomblin degraded by chemical attack from the active 440C steel substrate. We note that the Fomblin alone does not suffer simple thermal degradation since degradation has not been observed here on the inert gold substrate under these conditions of elevated temperatures.

Thus, there is evidence in spectra c for a number of phases: unreacted 440C, reacted 440C, degraded Fomblin and intact Fomblin. A comparison of such spectra at both normal and grazing photoelectron exit angle indicated that the unreacted Fomblin was atop the reaction layer of metal compounds and degraded Fomblin, which in turn were supported by the metal.

The fate of these phases after a final excursion to 400 °C is presented in Figure 8, spectra d. No features due to Fomblin remain. Most of the features due to degraded Fomblin are also gone except for the saturated carbon debris (C^c). The surface consists mostly of this carbon debris, chromium oxides and fluorides and unreacted iron. It appears that the conversion of iron fluoride to chromium fluoride has occurred, which has also been seen by Miki et al. (Ref. 49). A comparison of Fig. 7 and Fig. 8 indicates that this conversion has not occurred at the end of the TDS at a lower temperature of 365 °C. Therefore, this final high temperature treatment has desorbed all the remaining Fomblin and its degradation products, leaving behind a carbonaceous residue and chromium compounds.

It is seen that interfacial reaction at elevated temperature generates metal compounds, especially fluorides. The idea (Refs 7 and 13) that these fluorides are catalysts or accelerators for decomposition of Fomblin can be evaluated by raising the temperature to a value at which the fluorides are generated and then holding at constant temperature (mode C). If these metal compounds are more aggressive than the metal itself, then the overlying Fomblin should rapidly decompose. Accordingly, a 90 Å film was held at 190 °C for approximately 5 hours. Reaction was observed, with the interfacial reaction product quickly reaching a thickness of ≈24 Å, on top of which was observed (by grazing exit) <u>unreacted Fomblin</u>. The spectra are quite similar to those in Fig. 8c, which also shows unreacted Fomblin. It thus appears that the debris or reaction products do not preferentially attack the Fomblin, but instead act as a passivation layer, protecting the Fomblin against further decomposition for many hours at this temperature. We note that the coexistence of reaction products and fluid at 190 °C on 440C steel is similar to that observed (above) on aluminum at room temperature.

To summarize the observations on 440C: No reaction was observed for Fomblin deposited at room temperature, but there is definite evidence for reaction at elevated temperatures. Some of the fluid adjacent to the metal is consumed by this reaction, but much survives to evaporate as intact Fomblin molecules. It is also evident from the XPS results that the difluoroformyl carbon atom is preferentially consumed during the decomposition reaction.

<u>Aluminum</u>: The TDS for a 20 Å Fomblin film on aluminum is shown in Fig. 9. There is one asymmetric feature with an intensity maximum at 180 °C. This temperature is well below the temperature of the intensity maximum found for desorption from gold (290 °C) or steel (270 °C). The relative intensity of the mass fragments at 180 °C, inset in Figure 9, is dominated by m/e=31. This distribution is not due to desorption of Fomblin (from gold for example) but instead is similar to the distribution from the products of reaction of Fomblin and 440C steel - the high temperature shoulder in Fig. 6. These results indicate that Fomblin is not desorbing during the TDS, but is completely reacting and some of the reaction products are instead desorbing at a temperature much lower than that for Fomblin itself.

The XPS of the surface after TDS showed that the surface was virtually clean metallic aluminum, with submonolayer concentrations of C, O and F. The degree of cleanliness is indicated by a comparison of the Al 2p spectra, both clean and after the TDS, shown in the inset in Fig. 9. The small feature at higher binding energy is attributed to a small amount of Al_2O_3. Since the Fomblin itself is not desorbing to leave behind a clean surface, the relative cleanliness

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of the surface implies that the reaction products themselves are desorbing rather completely within the TDS feature centered at 180 °C.

The TDS and XPS imply that there is vigorous reaction between Fomblin and aluminum. In order to observe this reaction more directly, a 220Å film was heated for 3 hours at 145 °C (mode C), a temperature below the TDS peak. The spectra of this surface are shown in Figure 10. The Al 2p spectrum has acquired additional features, compared to the spectrum shown in Figure 4a, easily identified as the oxide (Al^b) and fluoride (Al^c) from the thermally induced reaction with Fomblin. Another intense feature, Al^d, is less easily assigned. Since it is shifted by the large value of 5 eV from Al^o, it must be due to aluminum coordinated with more than three fluorine atoms, which produced a shift of only 3 eV (Al^c). Aluminum coordinated to more than three fluorine atoms can be formed in the presence of excess fluorine.[50] The Al^d feature is thus identified with such a compound from the thermally induced reaction with Fomblin.

Spectra for C, O and F indicated that (i) some Fomblin remains, having been neither reacted nor desorbed, supported by the presence of $C^{g,h}$, O^f, F^e. The lower relative intensity of C^h, the difluoroformyl group, compared with that corresponding to bulk Fomblin is an indication of the preferential consumption of this part of the molecule during the decomposition reaction, as in the case for 440C (ii) features are present in the oxygen (O^d) and fluorine (F^d) spectra that are partners to the compounds identified in the aluminum spectra: Al^b and Al^c respectively (iii) the presence of in the F 1s spectrum a feature (F^b) previously suggested to be a type of oxyfluoride by other authors (Ref. 48) (iv) a feature in the carbon spectrum, C^a, is identified as an aluminum carbide, although the corresponding feature in the aluminum spectrum can't be resolved from the Al^o feature (v) the carbon spectrum exhibits a distribution of intensities 282 eV - 292 eV that has previously been identified with Fomblin degraded by chemical attack by the 440C steel and is assigned to this material for reaction on aluminum as well. The O^e feature is also assigned to this material.

Thus, the spectra of Figure 10 are consistent with the presence of: aluminum metal, aluminum compounds, degraded Fomblin and intact Fomblin. Variable take-off angle XPS indicates that the structure of the material is the same as that found after mode C heating on 440C steel: unreacted Fomblin resides on top of a debris layer, which is on the aluminum metal substrate.

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It is interesting to note that the aluminum fluorides and carbide compounds formed in mode C heating do not appear at the conclusion of the TDS at 400 °C. Although aluminum fluoride has high vapor pressure and may be expected to sublime, the oxide has very low vapor pressure and is not expected to sublime.

The observations made here on aluminum may be summarized as follows: Fomblin deposited at room temperature reacts to form a passivating film that allows an intact Fomblin film to condense with continued deposition. Other passivating film have been reported on iron with model perfluorinated compounds (Ref. 45). This passivating film is also observed at moderately elevated temperatures (145 °C). This film has similar chemical characteristics to that found on 440C steel, after heating to 190 °C. However, at higher temperatures, the fluid reacts completely, consuming all the Fomblin molecules before they can evaporate, demonstrating that aluminum is much more aggressive than 440C steel in its attack on Fomblin. The degradation of Fomblin on aluminum, as in the case of 440C steel, causes a preferential chemical attack on the C^h site of the molecule.

Tribology

The response of Fomblin on 440C steel to a tribological stress was studied by sliding a 440C steel bearing ball on the 440C steel disk covered with a 50 Å film. This disk's Vickers hardness was 277 Kg/mm^2 (2.7 GPa). Since the film was unreacted as deposited, a comparison of spectra before and after sliding could reveal reactions induced by sliding.

After sliding, during which the coefficient of friction was 0.17, the surface was examined by XPS without exposing it to air. This spectra is shown in Fig. 11. The Fomblin film was still present, but with a reduced thickness, attributed here to transfer of fluid to the sliding ball and to its physical displacement from the analyzed region. The major finding was the appearance of spectral features F^c and Fe^c that indicates the formation of metal fluorides. Additional, but less intense, new features were also formed in the carbon and oxygen spectra. In particular, additional intensity appeared in the carbon spectral region 282 eV - 292 eV that has been identified above as due to Fomblin that had undergone thermochemical attack by 440C steel. There is also a decrease in the relative C^h/C^g intensity, similar to that induced by thermochemical attack in mode C heating. There is clear evidence for chemical changes induced by rubbing and this is usually denoted as tribochemistry.

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The physical as well as the chemical state of the disk was changed by rubbing. Optical microscopy, (see Fig. 11) scanning electron microscopy and stylus profilometry of the surface showed uniform scratches about 600 Å deep and 75 μm wide. Thus plastic deformation of the surface took place during rubbing.

The above experiment was repeated with a harder 440C steel disk (Hv=700 Kg/mm^2). The coefficient of friction was 0.08. The scratches due to rubbing were shallower (100 Å) and narrower (50 μm) than on the softer steel. Microscopy also indicated a less disrupted surface.

XPS analysis of this rubbed surface indicated, by the appearance of F^c, that a metal fluoride was also formed, but with less intensity than was the case from the soft steel. Since fluorine provides the strongest XPS signal in this system, the low F^c intensity implies that the corresponding O, C and metal compound indicators of Fomblin degradation should be even smaller and in fact were not observed on this rubbed surface. It is concluded that some tribochemistry occurred on the hard steel, but less than on the soft steel. We assume that this is simply due to the reduced real area of contact on the hard steel relative to the soft steel.

DISCUSSION

A method has been presented here to place a polymeric fluid film in contact with a controlled, atomically clean substrate. The fluid film is thin enough to allow analysis of the fluid/substrate interface by XPS. Although motivated by tribological considerations, the method developed here is appropriate for an *in-situ* approach to the study of the liquid/solid interface. In the present system configuration, the interface can be stressed by radiation, elevated temperature or rubbing and then analyzed by XPS without exposure to air. It is, however, restricted to fluids that evaporate without decomposition and have a vapor pressure low enough at room temperature so there is negligible evaporation loss of film material in the hour or so required for the experiment.

Interfacial chemical reactions were observed with both XPS and TDS. The most obvious evidence in XPS was the appearance of metal compounds--oxides, fluorides, and carbides--that were not initially present. New distinct features in both the metal spectra and the fluorine and oxygen spectra were easy to observe. Important, but less obvious, were two changes in the carbon spectra. The first was the decrease in the intensity of the O$\underline{C}$F$_2$O (C^h) feature relative to the intensity of the C$\underline{C}$F$_2$O (C^g) feature, indicating a preferential chemical attack on the difluoroformyl group (C^h) (Ref. 10). The second was the appearance of intensity in 284 eV - 292 eV spectral region that has been attributed to carbon bonded

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in a disorganized way, possibly crosslinked or branched, to fluorine, oxygen and other carbon. Both these aspects of the carbon spectra are attributed here to degraded fluid and not to direct interaction with the metal and/or metal compounds.

The other evidence of reaction was through TDS. The simplest use of TDS was to observe a difference in the peak desorption temperature from the peak temperature from unreactive gold. The second was to use the cracking pattern of the desorbing gas as a fingerprint to distinguish the desorption of Fomblin molecules from the desorption of reaction products.

A general ranking of chemical reactivity toward Fomblin was found for the three metals studied here. Gold appears to be totally inert at all temperatures, allowing the arriving Fomblin molecules to condense at room temperature without reaction and to desorb at elevated temperatures without reaction. 440C steel allows the arriving Fomblin molecules to condense at room temperature without reaction, but reacts with them at elevated temperatures to leave a metal compound residue after most of the molecules have desorbed intact. Aluminum is the most aggressive metal, decomposing the arriving Fomblin molecules upon contact at room temperature and consuming all of the condensed layer at elevated temperature before the molecules can desorb intact.

Variable take-off angle XPS after mode C heating revealed the vertical structure of the surface region. It was found that the metal compounds on the base metal lay under a degraded layer of Fomblin and that intact Fomblin could exist on top of this degraded layer. The layer of metal compounds and degraded Fomblin appear to play a role in determining reaction kinetics of the system: they are formed immediately upon reaching a given temperature (mode B), but then grow no thicker upon heating for an extended period of time (mode C), during which intact Fomblin resides on top. They thus appear to act as a barrier to continued reaction and consumption of Fomblin. The diffusion of species through either its degraded layer to reach the metal compounds or through both the degraded layer and the metal compounds to reach the nascent metal is probably the rate-determining step in the reaction kinetics. We note that this reaction barrier has no direct counterpart in those studies (Refs. 15,16, and 45) which use small molecules to represent the polymeric lubricant. The coverages in those studies are one monolayer or less and thus the kinetic limitations provided by the above reaction layers are not present. Of course, such studies may provide a more detailed understanding of mechanisms leading to bond cleavage and reaction.

There have been two approaches to study the detailed chemistry of fluorinated ether molecules with surfaces. The first type uses surface analytical techniques to study the interaction of small molecules with flat metal surfaces (Refs. 15,16,45, and 48). Unfortunately, these studies are of limited relevance to the present work since the molecules used lacked the difluoroformyl group which we have found here to be vulnerable to attack. The second type studies the thermochemistry of Fomblin fluids themselves with powders such as Fe_2O_3, Al_2O_3 and FeF_3. These compounds are formed on steel bearing surfaces and are considered to be specific catalysts or accelerators for fluid degradation[6,11,51]. Because of the very large surface area and uncertain surface chemical constitution of these powders, these studies do not lend themselves to direct comparison with the present study on flat clean metal surfaces. In particular, these studies (Refs. 6,11, and 51) have not led to an understanding at the molecular level of the aggressiveness of the aluminum attack relative to that of 440C steel. Since this relative aggressiveness is one of our principal unequivocal observations, it is considered an important result to understand.

There are three implications of these results for tribology to be discussed: reaction on contact at room temperature, acceleration of the reaction by reaction products at elevated temperature, and reactions initiated by rubbing (tribochemistry). Recall that this study was motivated by tribological experiments with 440C steel that found metal fluorides on the rubbed surfaces. We have found that fluorides are not formed by simple contact of Fomblin with clean 440C steel. Thus, the idea of fluoride formation simply by contact of Fomblin with clean 440C steel exposed by rubbing off the native oxide at room temperature is not supported in this work. Note that even though removal of the native oxide by rubbing does not provide a degradation mechanism at room temperature, it does provide one at elevated temperature by allowing Fomblin to react with clean metal. On the other hand, such contact reaction at room temperature has been found here for the case of clean aluminum metal. This may be part of the explanation for the field experience that Fomblin-based lubricants are not appropriate for use with aluminum based alloys (Refs. 12 and 52).

The second implication for tribology is that reaction products, specifically metal fluorides, formed by contact with the clean metal, have been proposed to accelerate or catalyze further degradation of the lubricant. This idea has been pursued by experiments with fluoride and oxide powders in contact with Fomblin and vigorous reaction has indeed been observed (Refs. 11,13, and 51). However, a comparison of reaction rates on clean metal, with those on the metal compounds was not possible since only the metal compounds were used. We have sought evidence for the acceleration

by comparing the film subjected to mode **B** heating (where a reaction product is formed in a few seconds) to mode **C** heating (where the temperature is held constant for several hours). It is expected that if the initial reaction product catalyzed or accelerated further degradation, then the Fomblin would be consumed rapidly by further heating at constant temperature. We found just the opposite: instead of being consumed once the initial reaction product is formed, the Fomblin appears to persist indefinitely, as discussed above. Thus the "catalysis" mechanism of tribo-degradation of Fomblin on bearing steel is not supported by our results.

Our final implication for tribology is our tribological experiment of rubbing a film-covered 440C steel surface and observing reaction products of Fomblin on the surface. This appears to be a clear demonstration of tribochemistry—the initiation of chemical reaction by rubbing. The similarity of the products to those found by heating implies that high temperatures may be generated during rubbing. One is thus lead to consider whether "flash temperatures" (Refs. 53 and 54) at the sliding contact could be as high as the 200-300 °C found necessary for the initiation of reaction on 440C steel. Ashby et al. (Ref. 54) have recently presented calculations of flash temperatures for a steel pin on steel disk. For our experimental conditions of Hertz pressure $\leq$ .43 GPa and velocity = .3 mm/sec, their Fig. 3 shows flash temperatures much less than their lower temperature contour of 100 °C. Thus a classical approach does not yield the temperature required for reaction. The inadequacy of this macroscopic approach opens the issue of whether inelastic events on the atomic level associated with rubbing may in some sense constitute "temperatures" that degrade the fluid. We call attention to recent work by Hirano and Shinjo (Ref. 55) on the atomic origin of friction, wherein inelastic vibrations of atoms mechanically excited during sliding serve as the energy sinks for the loss of mechanical energy that is called friction. Perhaps such an "atomistic flash temperature" can account for the degradation observed here.

Aside from these considerations of the origin of tribochemistry, the rubbing process provides two mechanisms for fluid degradation in practical tribology. One is the direct degradation observed above, whereby the rubbing removes surface oxides, allowing clean metal/fluid tribochemistry in the sliding contact. Millions of cycles of reciprocating motion in vacuum, as in a bearing of a satellite mechanism (Ref. 8), may lead to macroscopic degradation of the fluid by tribochemical action. Another is that rubbing removes the layers serving as thermochemical barriers, allowing the fluid to contact clean metal at elevated temperatures in a high temperature bearing. Degradation would then proceed along the thermochemical path in which the reaction on clean metal is much faster than on the reaction layers.

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CONCLUSIONS

One of the objectives of this work, to develop a new experimental method for the study of the liquid/solid interface has been proven feasible. Layers of Fomblin Z25, thin enough to allow spectroscopic access to the interface, have been reproducibly deposited onto atomically clean metal substrates under ultra high vacuum. The interface was then stressed, thermally or mechanically, and then analyzed *in-situ* with XPS and TDS.

From these studies, it is concluded that gold is non reactive towards Fomblin Z25 at any temperature. 440C steel, on the other hand, showed no reactivity at room temperature, but heating to 190 °C initiated some decomposition of the fluid, forming a debris layer at the interface. This debris layer is composed of both inorganic fluorides, oxides and carbides, and organic decomposition products. This layer, when fully formed, acts as a protective layer preventing further decomposition of the fluid remaining on top. The major feature in the TDS from 440C steel appeared at 270 °C and the desorption products were mostly molecular Fomblin Z25. The clean aluminum surface reacts with Fomblin Z25 at room temperature, producing a debris layer , also at the interface, of similar chemical characteristics to that formed on 440C steel. Heating the aluminum continues the decomposition reaction, with a complete breakdown of the polymer, so that the major feature in the TDS from Al appeared at 180 °C and consisted primarily of reaction products of Fomblin Z25. Therefore, we can conclude that the presence of the metals 440C steel and aluminum do accelerate the degradation of the fluid and that the thermal reactivity of the substrates studied towards Fomblin decreases in the following order: Al>440C steel>Au.

The tribological experiments showed that the decomposition of the polymer also occurs, at room temperature, when the interface is stressed mechanically. The polymer reacts with the surface creating a debris layer, similar to the one induced thermally. In all cases, thermally and tribologically induced, the degradation of Fomblin resulted in a preferential consumption of the difluoroformyl or "acetal" carbon.

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TABLE 1.—PHYSICAL PROPERTIES OF

FOMBLIN Z-25

Average molecular weight	9500
Kinematic viscosity at 20 °C, Cs	255
Viscosity index	355
Pour point, °C	-66
Density at 20 °C, g/ml	1.851
Surface tension at 20 °C, dyne/cm	25
Vapor pressure, torr at 20 °C	3×10^{-12}
Vapor pressure, torr at 100 °C	1×10^{-8}

TABLE 2.—INELASTIC MEAN FREE PATHS λ OF SUBSTRATE PHOTOELECTRONS IN FOMBLIN Z-25

[The value of 34 Å for 1200-eV electron kinetic energy (Ref. 35) is used with the kinetic energy dependence $\lambda \approx (E_K)^{1/2}$ to obtain these values (Ref. 36).]

Substrate	Core level (B.E.)	λ, Å
Gold	Au $4f_{7/2}$ (84.1 eV)	37
440C	Fe $2p_{3/2}$ (706.7 eV)	27
Aluminum	Al $2p_{3/2}$ (73.0 eV)	37

TABLE 3.—ELEMENTAL CONCENTRATIONS AND CORE LEVEL BINDING ENERGIES OF THE ELEMENTS IN FOMBLIN Z-25 OBTAINED FROM OUR CONDENSED FILMS

Nominal atomic conc. based on manufacturers specifications[a]		Experimental atomic concentrations	B.E., eV
$^b C^g$	14.6 to 15.7	15.6	293.0
$^b C^h$	12.2 to 11.2	12.7	294.7
O	19.5 to 19.1	17.5	535.5
F	53.7 to 53.9	54.2	688.7

[a]Based on an x/y = 0.6 - 0.7.
[b]Refer to Table 5 $(C^g/C^h)_{exp} = 1.22$.

TABLE 4.—RATIO OF
SPECTRAL INTENSITIES
OF C, O, AND F IN A
17 Å FOMBLIN FILM
TO THE Fe INTENSITY
IN 440C STEEL

[Photoelectron take-off angles,
90° and 30° from the surface
plane.]

Ratio	Take-off angle	
	$90°$	$30°$
C/Fe	0.16	0.36
F/Fe	1.78	4.04
O/Fe	.35	.80

TABLE 5.—SPECTRAL FEATURE BINDING ENERGIES (eV±0.2 eV) AND

THEIR ASSIGNMENTS

[The references are listed at the end of this table. Only small charging was observed in the polymeric films (0.7 eV max). The binding energies are referenced to C^c.]

C 1s	BE., eV±0.2 eV	
a	282.2	Al-$\underline{C}$[12]
b	283.3	Fe-$\underline{C}$ (metallic carbide)
c	284.7	$\underline{C}$-$\underline{C}$ aliphatic, adventitious[3,4]
d	286.8	$\underline{C}$-O[2,3,4]
e	289.0	O$\underline{C}$O$^-$ bent[3,4] or >$\underline{C}$=O[10]
f	291.5	$\underline{C}$F$_2$[3]
g	293.0	O-$\underline{C}$F$_2$-$\underline{C}$F$_2$-O (Fomblin)[4,8]
h	294.7	$\underline{C}$F$_3$ or O-$\underline{C}$F$_2$-O (Fomblin)[3,4,8]
O 1s		
a	530.2	Iron oxide in mixed chromium-iron oxide[1]
b	531.5	Chromium oxide in mixed Cr-Fe oxide[6]
c	532.0	O$\underline{C}$O$^-$ bent[4] or >C=$\underline{O}$[10]
d	532.0	Al oxide[7,14]
e	533.4	Metal-C-$\underline{O}$ in fluorine matrix[4,5,9]
f	535.5	$\underline{O}$-CF$_2$-CF$_2$-$\underline{O}$, $\underline{O}$-CF$_2$-$\underline{O}$ (Fomblin)[4]
F 1s		
a	684.0	Metal fluoride (x-ray degradation of Fomblin)
b	685.1	Al-oxyfluoride[15]
c	685.5	Cr or Fe-$\underline{F}_x$ from thermal reaction
d	687.2	Al$\underline{F}_3$ reaction with Al surface[15]
e	688.7	Fomblin
Fe 2p$_{3/2}$		
a	706.7	$\underline{Fe}^\circ$ metallic[1]
b	709.8	$\underline{Fe}$-O from oxide
c	711.9	$\underline{FeF}_2$[7,11]
d	714.0	$\underline{FeF}_3$[7,11] from reaction with Fomblin
Cr 2p$_{3/2}$		
a	574.3	$\underline{Cr}^\circ$ metallic
b	576.6	$\underline{Cr}$ oxide[11,16]
c	577.8	$\underline{Cr}$-F_x[11] from reaction with Fomblin
d	580.0	$\underline{Cr}F_3$[7] from reaction with Fomblin
Al 2p		
a	73.0	$\underline{Al}^\circ$ metallic
b	75.1	$\underline{Al}$ oxide
c	76.6	$\underline{Al}F_3$[14] x-ray degradation, and Fomblin reaction
d	78.0	High coordination $\underline{Al}$ fluoride[13], $\underline{Al}F_6^{3-}$
Au 4f$_{7/2}$		
a	84.0	$\underline{Au}^\circ$ metallic

[1]C.R. Brundle, T.J. Chuang, and K. Wandelt, Surf. Sci., 68 (1977) 459.

[2]E. Desimon, et al., Surf. Int. Anal., 15 (1990) 627.

[3]Gerenser, et al., Langmuir, 1 (1985) 305.

[4]See Ref. 24 in text.

[5]P. Stoyanov, S. Akhter, and J.M. White, Surf. Int. Anal., 15 (1990) 509.

[6]This value coincides with that of FeOOH.

[7]"Physical Electronics Handbook of Photoelectron Spectroscopy," Perkin-Elmer, Eden Prairie, MN, 1979.

[8]See Ref. 37 in text.

[9]See Ref. 38 in text.

[10]M.A. Golub, and R.D. Cormia, Polymer, 30, (1989) 1576.

[11]A.L. Cabrera, E.J. Karwacki, and J.F. Kimen, J. Vac. Sci. Technol., A8 (1990) 3988.

[12]B. Maruyama, F.S. Ohuchi, L. Rabenberg, J. Mat. Sci. Lett., 9 (1990) 864-866.

[13]See Ref. 50 in text.

[14]B. Strohmeir, Applied Surf. Sci., 40 (1989) 249.

[15]See Ref. 48 in text.
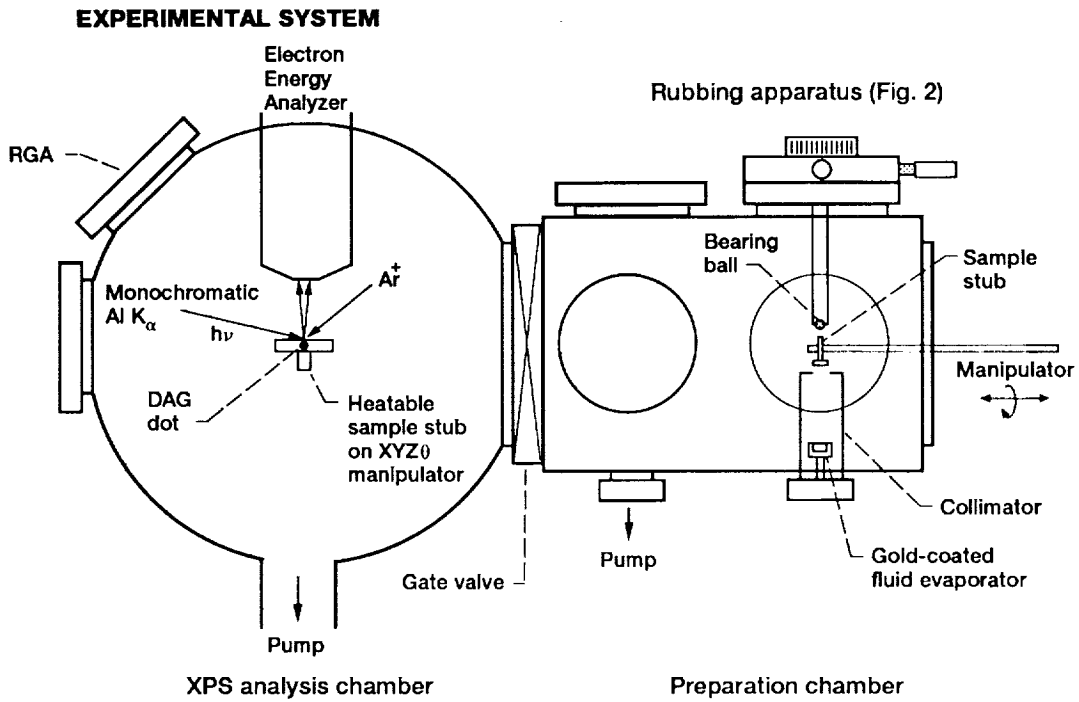
[16]C. Xu, et al., Surf. Sci., 258 (1991) 23-24.

EXPERIMENTAL SYSTEM

Figure 1.—The experimental system.

Motorized
Y-axis
micrometer

Bellows

Z-axis

Contact
indicator

Load

Flex
pivot

Strain
gauge

X-axis
micrometer

Electrical
feed-through

CD-91- 52065

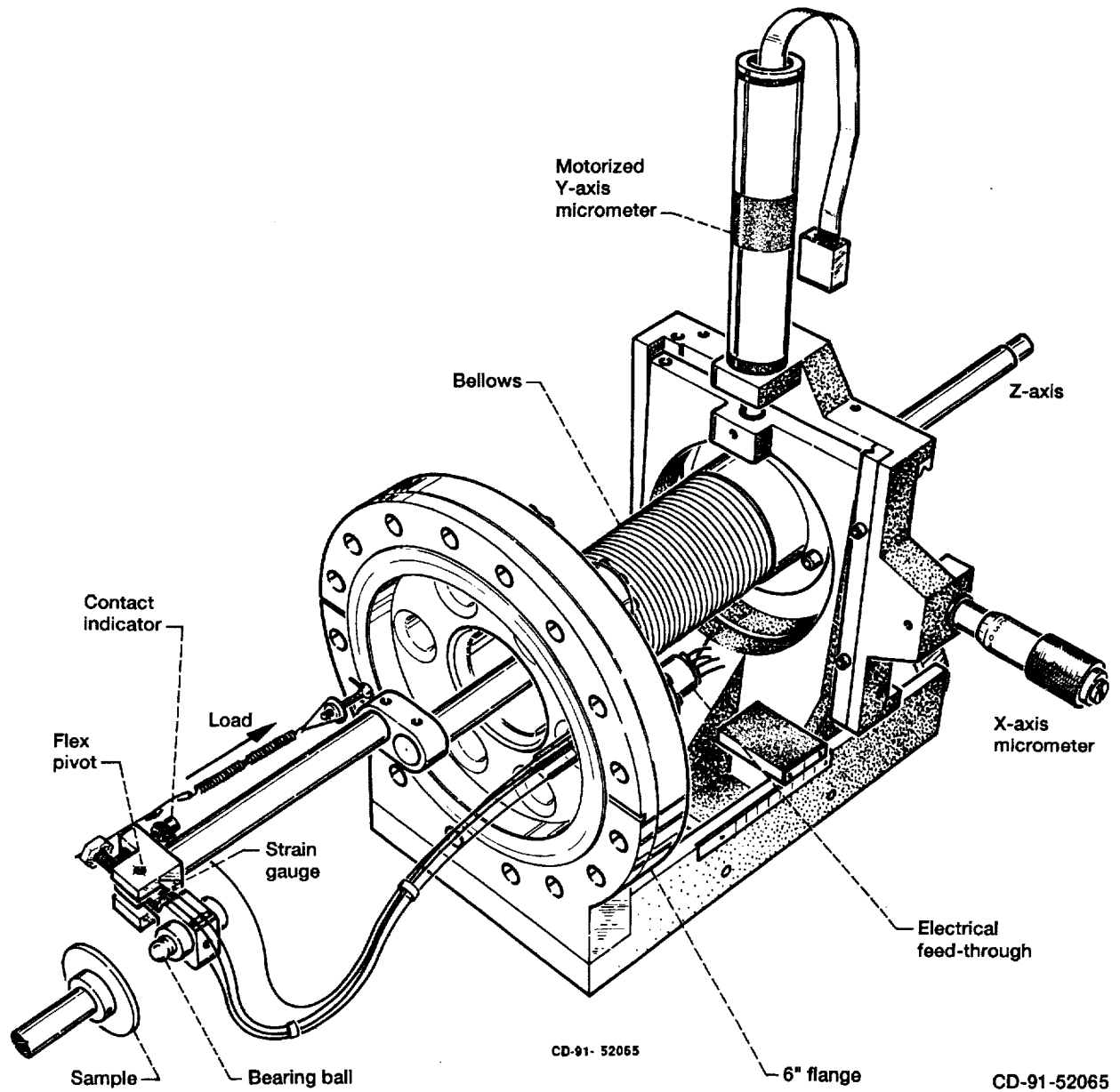Sample

Bearing ball

6" flange

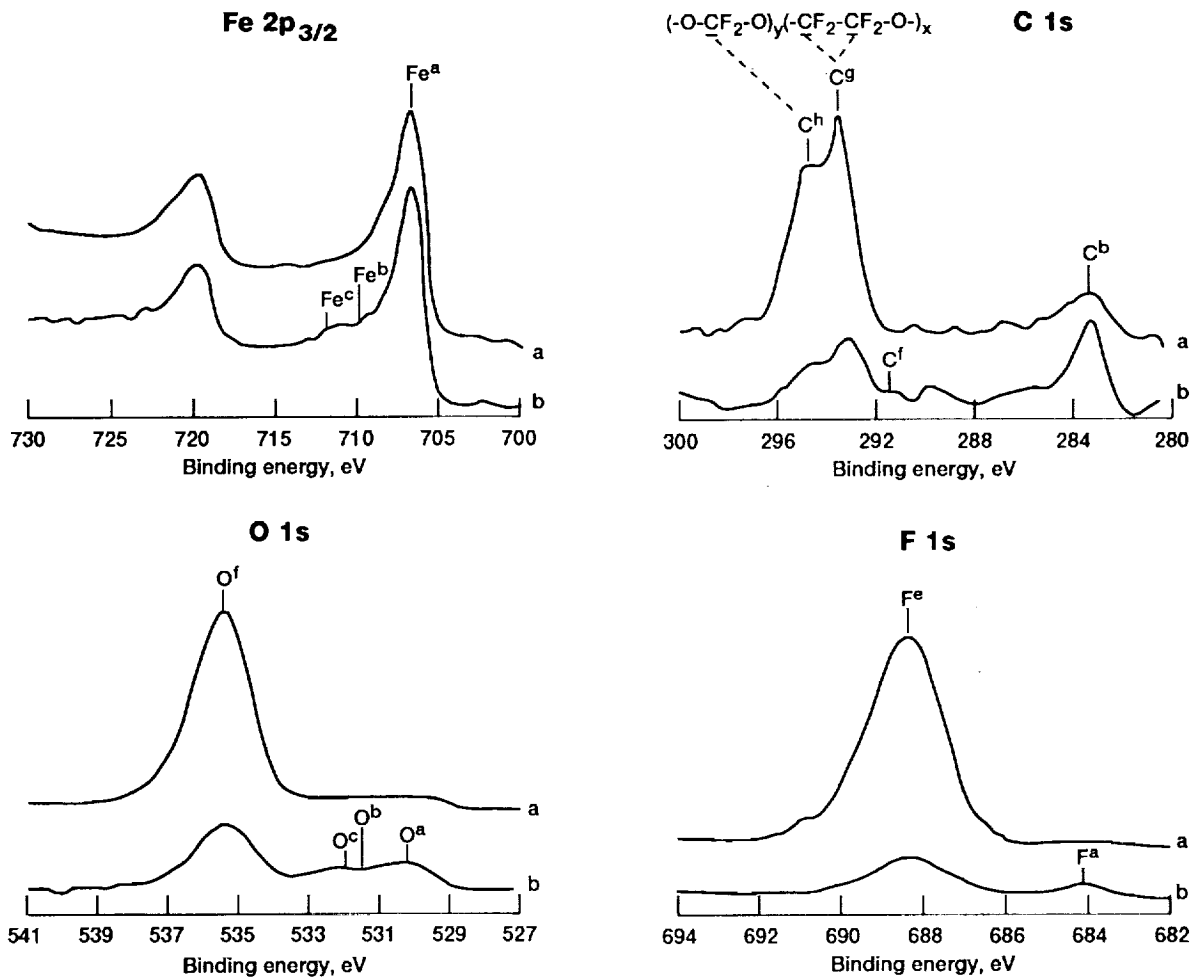CD-91-52065

Figure 2.—The rubbing apparatus (tribometer).

28

Figure 3.—Spectral regions for Fe $2p_{3/2}$, C 1s, O 1s and F 1s for (a): Fomblin film (27 Å thick) immediately after condensation on 440C steel. C^b in C 1s is due to carbide in 440C; (b): Fomblin film (≈80 Å thick) on 440C steel after 16 hours of exposure to the monochromatized x-ray beam.
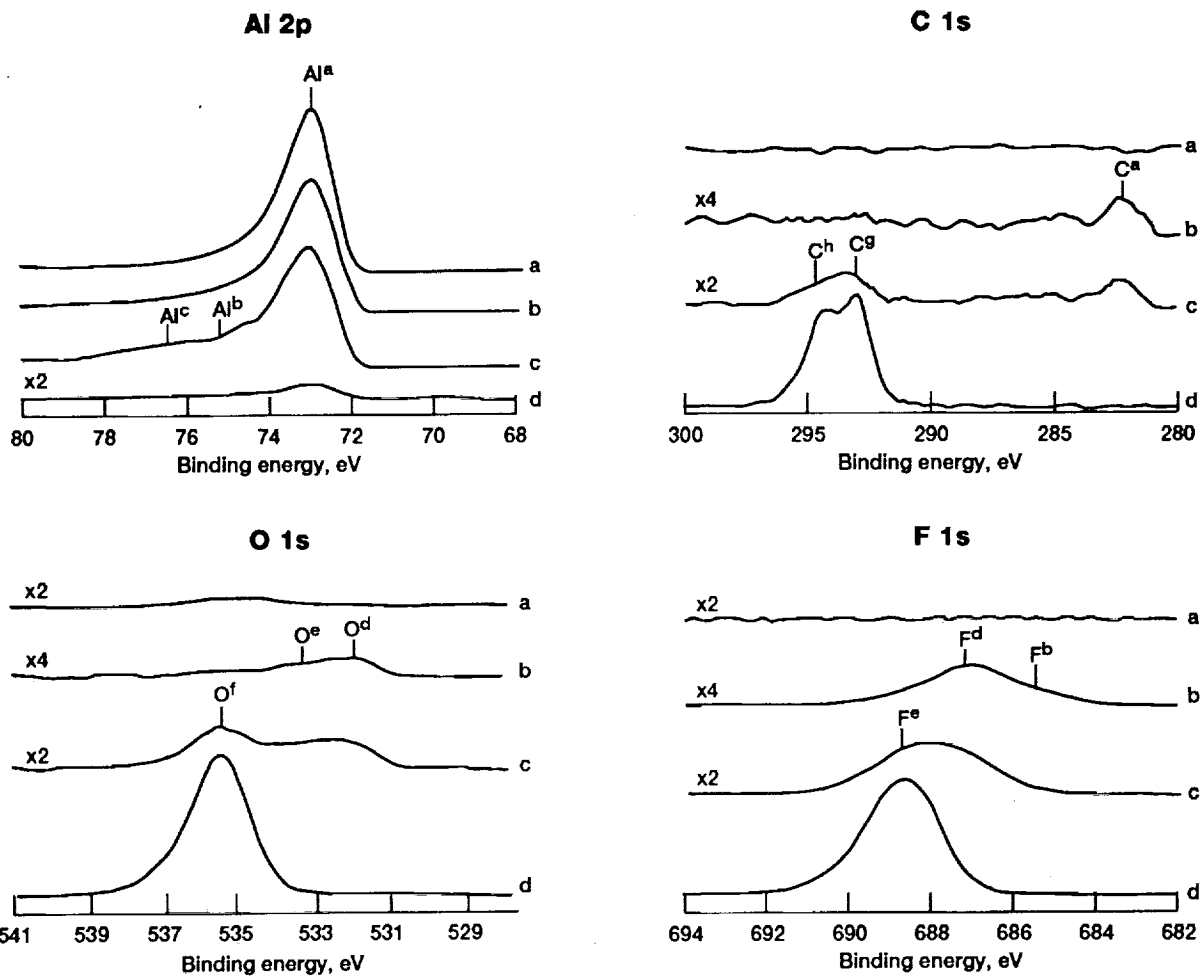
29

Al 2p

C 1s

O 1s

F 1s

Figure 4.—Spectral regions for Al 2p, C 1s, O 1s and F 1s for Fomblin films of progressively higher coverages on clean aluminum.   (a) clean, (b) ≈1 ML, (c) ≈4 ML, (d) ≈26 ML.
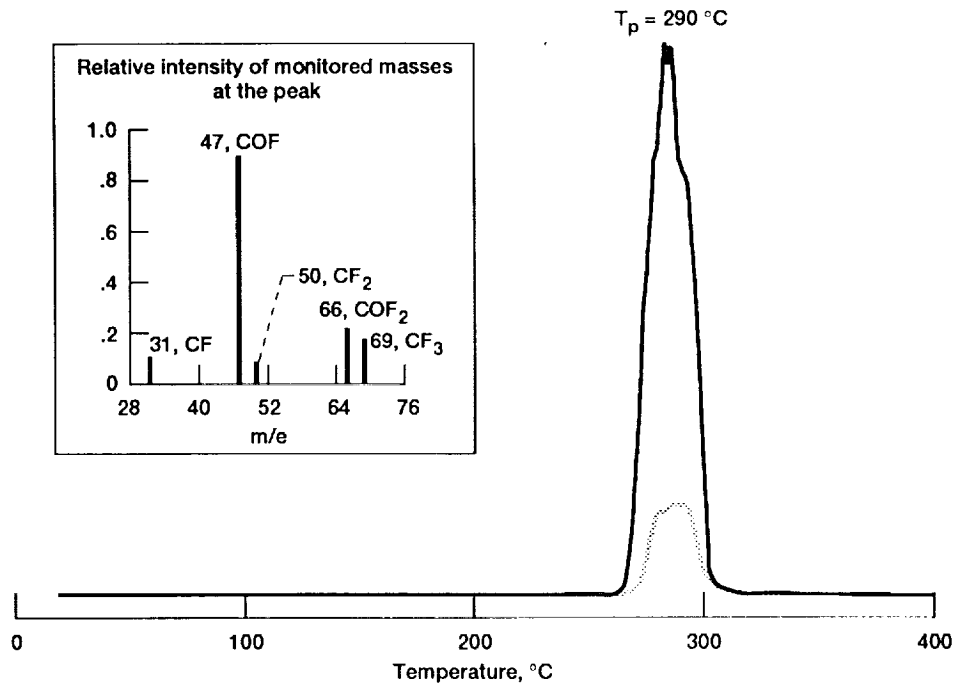
Figure 5.—Thermal desorption spectrum of a Fomblin film 7 ML thick on gold. Solid line m/e = 47, dotted line m/e = 31. The insert shows the relative composition at 290 °C of the monitored masses.
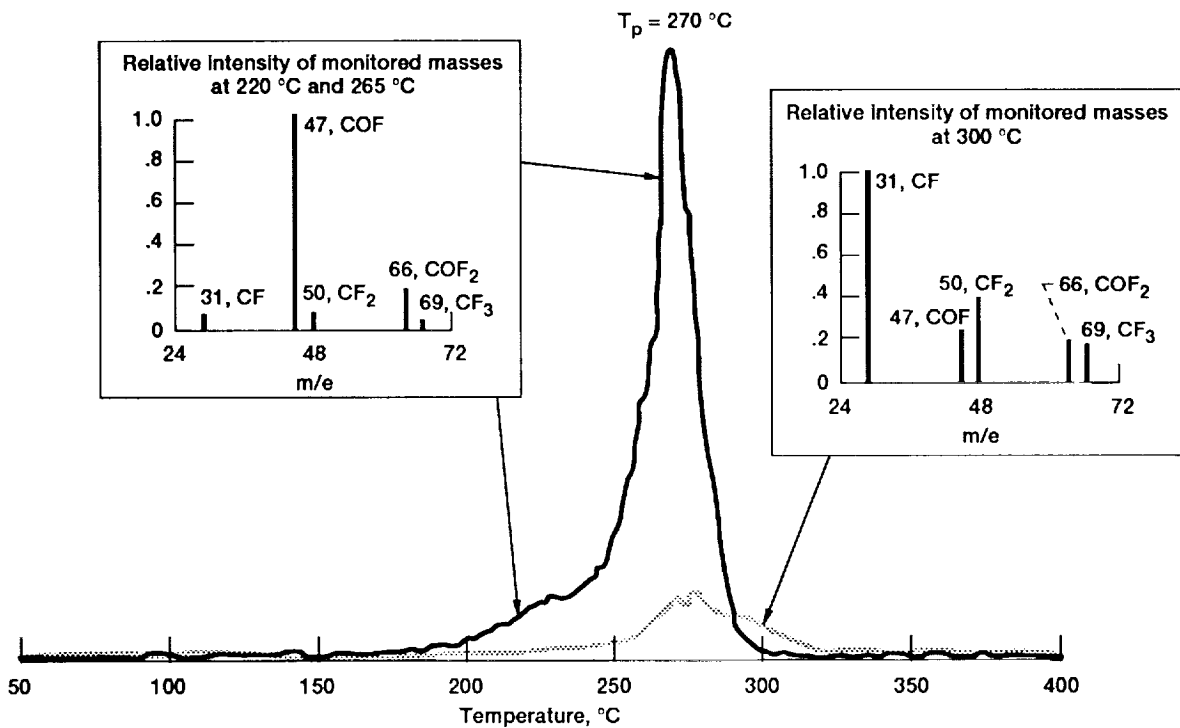

Figure 6.—Thermal desorption spectrum of a Fomblin film 5 ML thick on 440C steel. Solid line is m/e = 47 (COF$^+$) and dotted line is m/e = 31 (CF$^+$). The insert on the left shows the relative intensity of the fragments monitored at 190 °C and 265 °C. The insert on the right shows the relative intensity on the fragments monitored at 300 °C.

31

Fe 2p$_{3/2}$

Fe^a

Fe^b

Fe^c

730   725   720   715   710   705   700
Binding energy, eV

Cr 2p$_{3/2}$

Cr^a

Cr^b

Cr^c

590   585   580   575   570
Binding energy, eV

F 1s

F^c

695   693   691   689   687   685   683   681
Binding energy, eV

C 1s

C^b

C^c

300   296   292   288   284   280
Binding energy, eV

O 1s

O^a

O^b

O^e

540   538   536   534   532   530   528   526
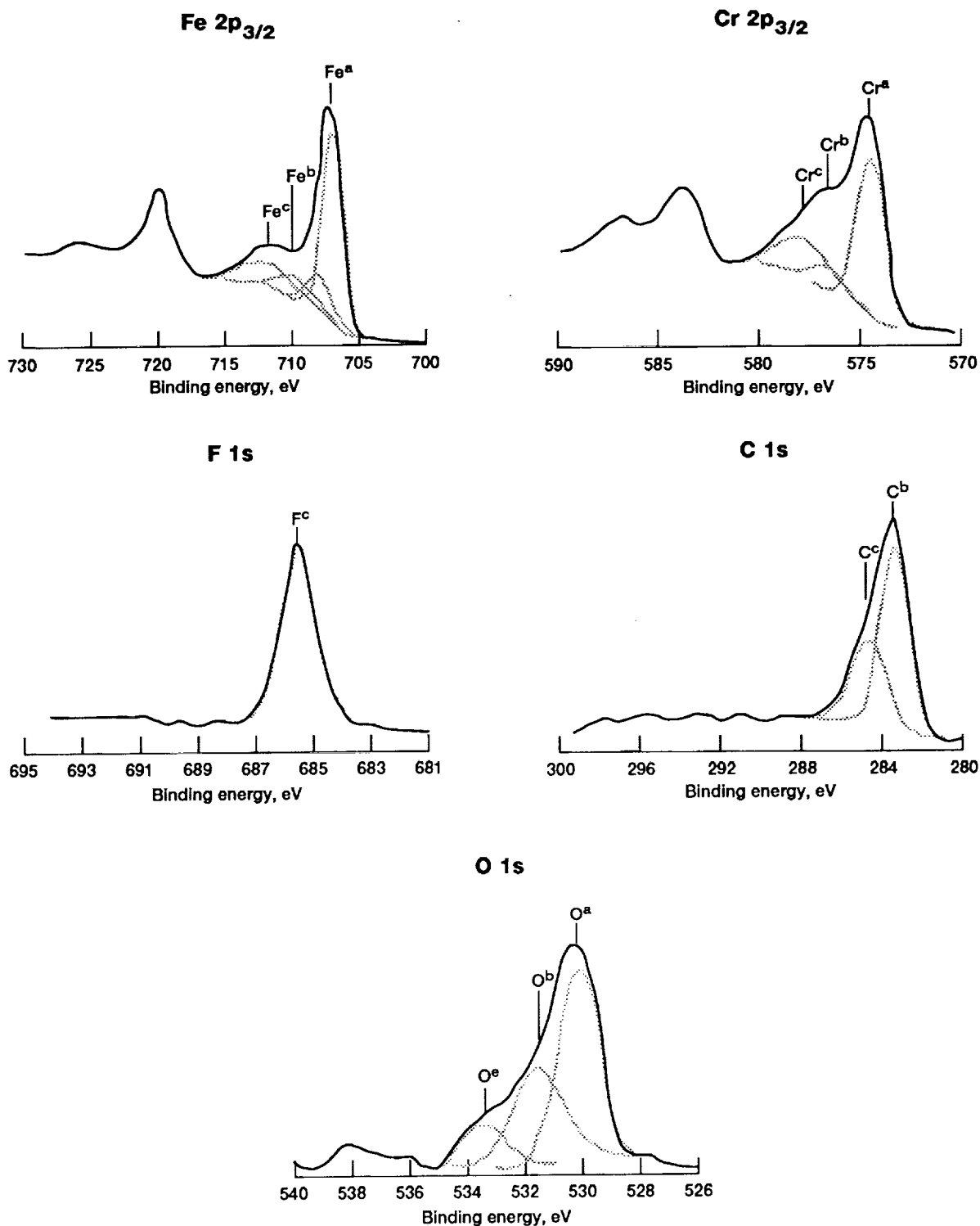Binding energy, eV

Figure 7.—High resolution XPS of the 440C surface after stopping a thermal desorption similar to that depicted in Fig. 6 at a lower temperature (365 °C). The dotted lines represent the peak fitting for the different species found on the surface. The labeling of the peaks was done according to Table 5.
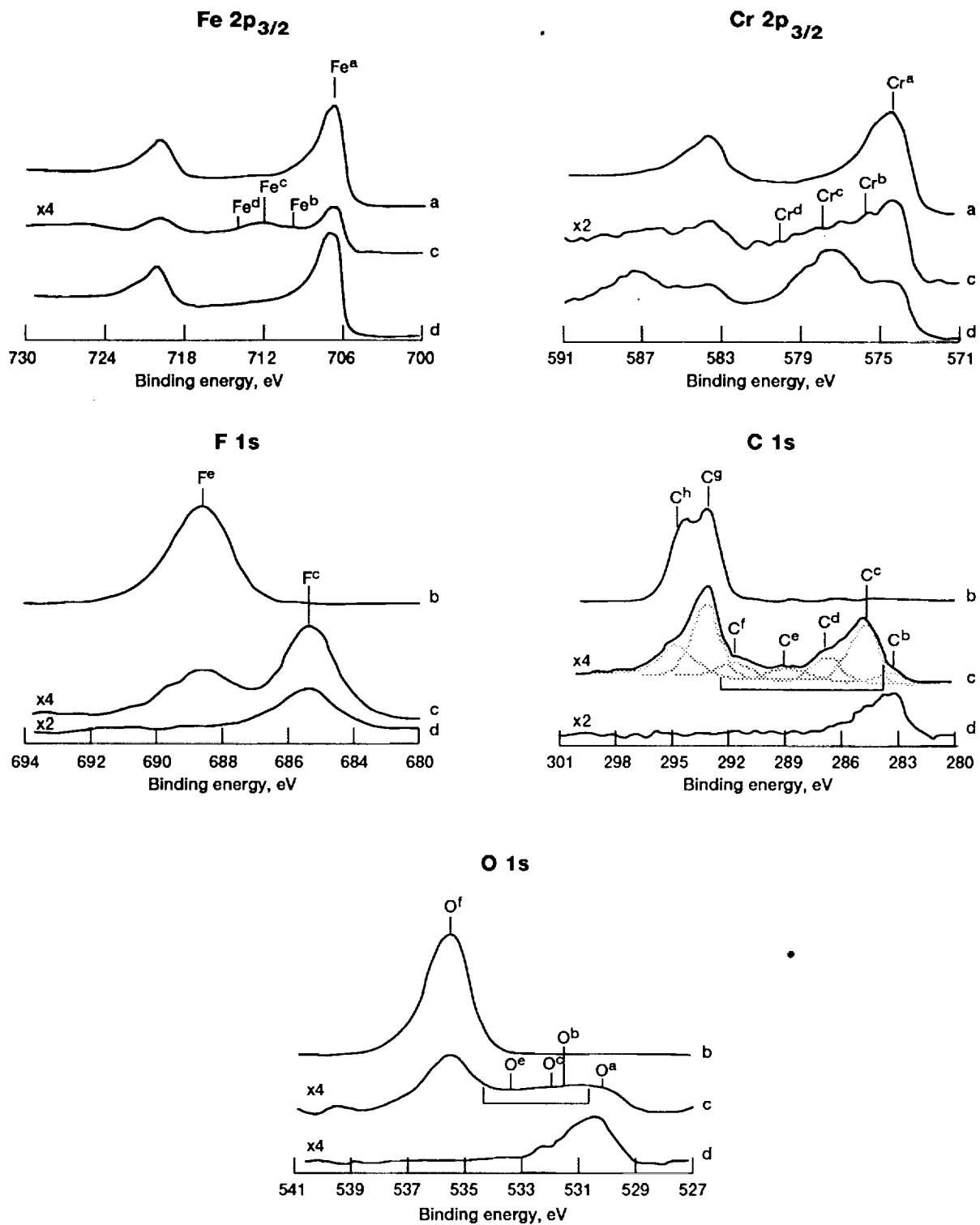
32

Fe 2p$_{3/2}$

Fe^a

Fe^c

Fe^d Fe^b

x4

a

c

d

730   724   718   712   706   700

Binding energy, eV

Cr 2p$_{3/2}$

Cr^a

Cr^d Cr^c Cr^b

x2

a

c

d

591   587   583   579   575   571

Binding energy, eV

F 1s

F^e

F^c

b

x4

x2

c

d

694   692   690   688   686   684   680

Binding energy, eV

C 1s

C^h C^g

C^c

C^f C^e C^d C^b

x4

b

c

x2

d

301   298   295   292   289   286   283   280

Binding energy, eV

O 1s

O^f

O^e O^c O^a

O^b

b

x4

c

x4

d

541   539   537   535   533   531   529   527

Binding energy, eV

Figure 8.—High resolution XPS spectra of a 100 Å film of Fomblin on clean 440C steel subjected to mode B heating.
(a) Clean 440C, (b) Fomblin film as condensed at room temperature, (c) after heating to 250 °C, (d) after heating to 400 °C.
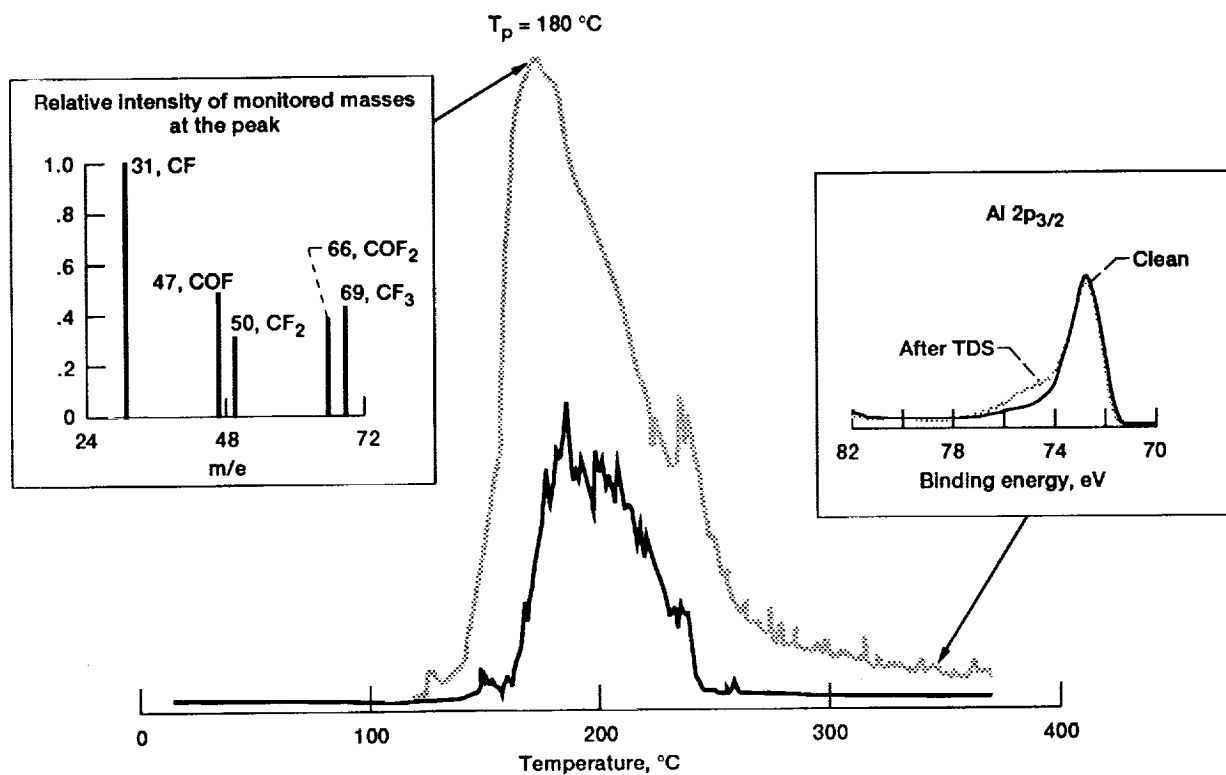
33

Figure 9.—TDS of of 20 Å Fomblin film on clean aluminum metal. The relative composition in the monitored masses at the desorption peak (180 °C) is shown in the insert at the left. The solid line represents m/e = 47 (COF^+). The dotted line represents m/e = 31 (CF^+). The Al 2p high resolution XPS before Fomblin evaporation and after TDS (360 °C) is shown in the insert on the right.
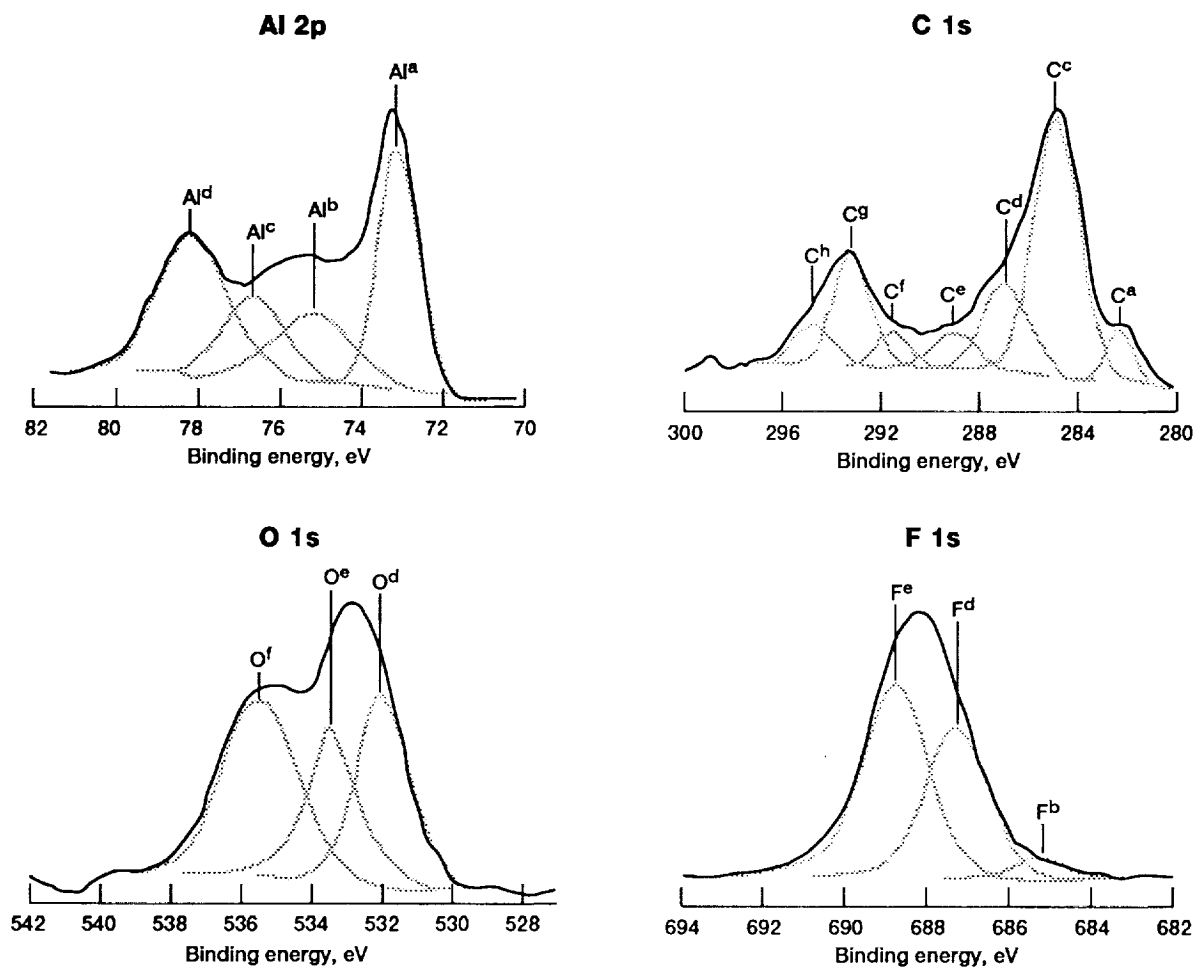
Al 2p

C 1s

O 1s

F 1s

Figure 10.—High resolution XPS of a (220 Å thick) Fomblin film on clean aluminum subjected to mode C heating for 3 hours at 145 °C. The solid line shows the actual data while the dotted line shows the peak fitting for the different species found on the surface.
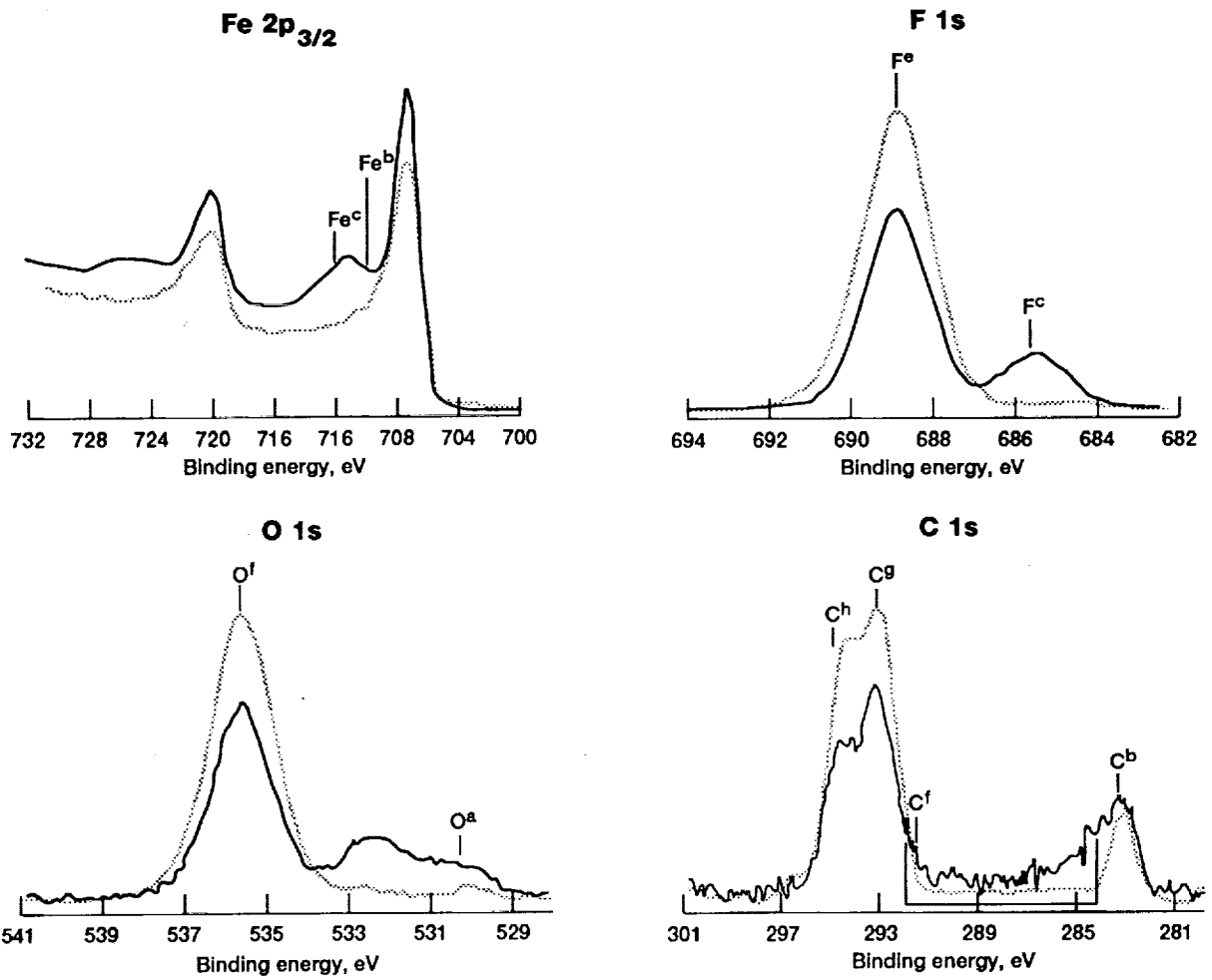
35

Figure 11.—High resolution XPS of the worn area after sliding a Fomblin Z25 film 50 Å thick on 440C steel disk with a 440C ball. The dotted line represents the surface before the triboexperiment.
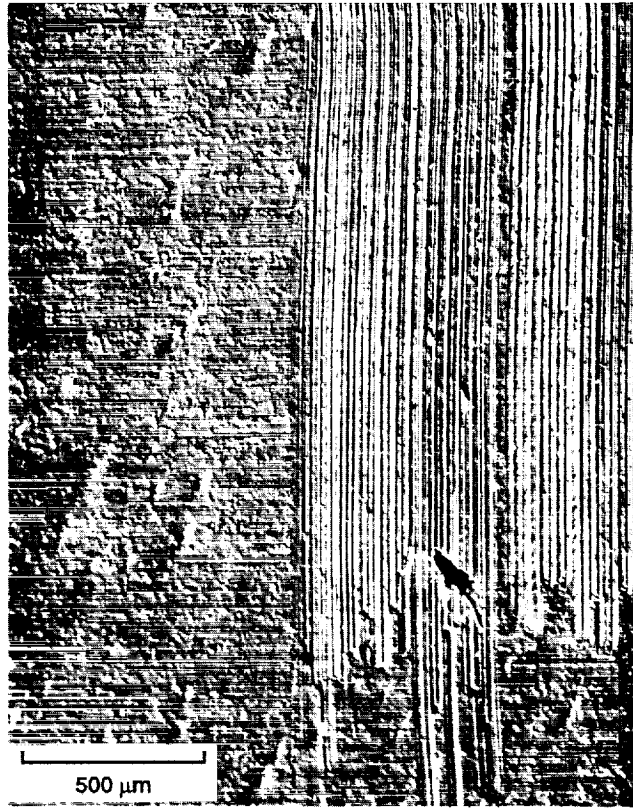
500 μm

Figure 12.—Optical micrograph of soft 440C steel surface
after rubbing with a 440C bearing ball. Grooves are 75 μm
wide and about 600 Å deep.

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REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE April 1992	3. REPORT TYPE AND DATES COVERED Technical Memorandum

4. TITLE AND SUBTITLE

Interfacial Chemistry of a Perfluoropolyether Lubricant Studied by XPS and TDS

5. FUNDING NUMBERS

WU–505–63–5A

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–6889-1

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM– 106014

11. SUPPLEMENTARY NOTES

Pilar C. Herrera-Fierro, National Research Council – NASA Research Associate at Lewis Research Center. William R. Jones, Jr. and Stephen V. Pepper, NASA Lewis Research Center. Responsible person, Pilar C. Herrera-Fierro, (216) 433–6053.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 27

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The interfacial chemistry of Fomblin Z25, a commercial perfluoropolyether used as lubricant for space applications, with different metallic surfaces: 440C steel, gold and aluminum was studied. Thin layers of Fomblin Z25 were evaporated onto the oxide-free substrates and the interfacial chemistry studied using XPS and TDS. The reactions were induced by heating the substrate and by rubbing the substrate with a steel ball. Gold was found to be completely unreactive towards Fomblin at any temperature. Reaction at room temperature was observed only in the case of the aluminum substrate, the most reactive towards Fomblin Z25 of the substrates studied. It was necessary to heat the 440C steel substrate to 190 °C to induce decomposition of the fluid. The degradation of the fluid was indicated by the formation of a debris layer at the interface. This debris layer, composed of inorganic and organic reaction products, when completely formed, passivated the surface from further attack to the Fomblin on top. The tribologically induced reactions on 440C steel formed a debris layer of similar chemical characteristics to the thermally induced layer. In all cases, the degradation reaction resulted in preferential consumption of the difluoroformyl carbon ($-OCF_2O-$).

14. SUBJECT TERMS

Interfacial chemistry; Lubricant; Perfluoropolyether; XPS; TDS

15. NUMBER OF PAGES
38

16. PRICE CODE
A03

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT