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Tribological Applications of Surface Analysis

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TRIBOLOGICAL APPLICATIONS OF SURFACE ANALYSIS

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Abstract

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For some years, surface analysis has been used in fundamental studies of solid-solid contacts as they exist in tribological systems. Analysis was used to detect material transfer in sliding contacts. It has also been used to monitor surface films in studies of the effects of such films on the adhesion of contacts. Finally electron spectroscopic analysis of interfaces has shed some light on the fundamental electronic nature of the interfacial bond.

More recently, surface analysis has been applied to many tribological engineering problems. In particular, identification of chemical films formed during the sliding contact of lubricated systems and study of the surface chemistry of lubricant additives have been active areas of research.

In all of these studies one or more of four properties of the analytical technique will be important in determining its utility. The four are: lateral resolution, specimen damage, depth resolution and the availability of chemical information. In each of the applications discussed here, the important factors are brought out.

Introduction

Tribology is the study of friction, wear, and lubrication. At its most fundamental level it is a study of the basic physics and chemistry of the solid-solid interface. At its most applied it is the specification of lubricants for actual machinery. Surface analysis is finding many applications in this broad field. This review will attempt to cover these applications. However, tribology is an eclectic subject which

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draws on many disciplines in which surface analysis is important: metallurgy, thin-films, surface chemistry, and surface physics, to name a few. It would be impossible to review these fields, but it should be kept in mind that many such applications of surface analysis are, more or less directly, applications to tribology.

Although applied tribology is an ancient field (Dowson, 1979), modern tribology can be dated to the work of Bowden and Tabor. Their two books (Bowden, 1950 and 1964) are still the best source for the fundamentals of the subject, and two recent reviews by Tabor (1977 and 1981) are excellent accounts of the current state of understanding of the fundamentals. The adhesion theory of friction proposed by Bowden and Tabor is the core idea in much current work in tribology.

When two surfaces are brought into contact they touch first at the tips of microscopic irregularities. As a load is applied to this contact, these "asperities" yield plastically until the actual total area of asperity contact is large enough to support the applied load. For engineering surfaces, this real area of contact will be only a fraction of the apparent area of contact, and the individual asperity contacts may be as small as microns in diameter. Wear is presumed to occur when such a junction shears in the bulk of one or the other contacting body rather than at the interface.

The simple adhesion theory is certainly not the only mechanism responsible for friction and wear. Even in the absence of adhesion, surface damage and friction may be produced by micro-abrasion, micro cutting, deformation losses and by surface fatigue arising from repeated loading of surface asperities. Nevertheless, the adhesion process is often an important element in the friction of solids. Furthermore, it focuses attention on the interfacial regions and draws attention to the fundamental nature of the bond across the interface. For practical purposes, it is also important to know how that bond may be modified: by surface films, for example. Surface effects in tribology are the subject of a recent monograph (Buckley, 1981). It is just in these areas where surface analysis has made the greatest contribution.

For the purposes of this review, tribology will be divided into applied and fundamental parts. Applied tribology will be taken to be the study of real machine parts, such as bearings, and the study of lubricated systems. By contrast, fundamental tribology consists of studies of solid-solid contacts in which the condition of the surfaces is strictly controlled. Normally, control is achieved with ultra-high vacuum. A large subfield of tribology is concerned with antiwear and antifriction coatings. Surface analysis is so widely employed in this field, that it would require a review in itself. Moreover, it is as closely allied with film deposition studies as with tribology. It is, therefore, excluded from this review.

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are, by a wide margin, the surface analytical techniques most used in tribology. Figure 1 is a brief reminder of the principles of the techniques. Both begin with the creation of a core hole. The exciting radiation is X-rays in XPS and electrons in conventional AES although X-ray excited AES is common. For XPS the energy of the ejected core electron is analyzed. The binding energy of the vacant core level is then easily obtained. In the case of AES the excited atom relaxes by emitting an outer shell electron. The energy of that electron is related to both the core level and outer shell binding energies. The spectrum, is, therefore, not as simply interpreted as the XPS spectrum but is nonetheless characteristic of the excited atom.

Four crucial characteristics of these spectroscopies for the purposes of tribology are listed in Table 1. The comments in Table 1 are brief and will be expanded upon below. Because the true contact area in real solid contacts is of the order of microns, it is essential to have good lateral resolution for applied studies. It will be seen that fundamental studies can often be designed to avoid this requirement. In applied studies, depth profiling is an important technique. Ion beam etching is the usual technique, but angular dependence can also be used. In the latter technique the intensity of electron emission normal to the surface and at nearly grazing angle is measured. Emission from atoms near the surface is less affected by the change in angle than that from atoms deeper in the bulk, and a rough depth distribution can be calculated. Depth resolution is, of course, not as good for this technique as for ion etching, but there is less specimen damage. Specimen damage is also produced by the excitation radiation: electrons in AES or X-rays in XPS. This is most severe in AES and makes XPS the simpler technique for work with polymers, lubricants, and organic surface films. Both AES and XPS are sensitive to the chemical state of the analyzed element as well as its abundance. This chemical information is somewhat more accessible in the photoelectron spectrum, however examples using both spectroscopies will be shown.

Low energy electron diffraction (LEED) was available before AES or XPS. It was used in the pioneering applications of surface analysis to fundamental tribology. Its application will be

reviewed, first. Applications involving field ion microscopy (FIM), ion scattering spectroscopy (ISS), and secondary ion mass spectroscopy (SIMS) will also be mentioned. The references that follow are not exhaustive, but those given are believed to be representative of the work of the authors on particular subjects. They should serve as entry points to the literature. Historically, surface analysis was used first in fundamental studies, and those applications will be reviewed first. Quite recently, the number of uses in applied studies has been growing rapidly. These will constitute the second part of the review.

Fundamental Studies of Solid Contacts

Ferrante et. al. (1973) and Buckley (1978) have previously reviewed applications of surface analysis in fundamental tribology. The earliest studies attempted to deduce criteria for the transfer of material from one member to the other in a sliding couple. As the use of these tools become more routine they were used for the monitoring of the surface condition in a wide variety of tribological experiments. Finally, as the physical basis of the techniques becomes better understood, they are being used to examine the nature of the interfacial bond. This review of fundamental work will touch on all three ways of using surface analysis.

Material Transfer

As early as 1967, Buckley (1967) used LEED to detect the transfer of gold to copper in adhesion tests. He also used it to study the effect of chemisorbed films on the transfer and friction of tungsten (Buckley, 1968). However, LEED is sensitive to the crystal structure of the surface and is only useful when the structure is well defined. It is not commonly used in tribology because of the surface damage normally accompanying tribological experiments. For the same reason, field ion microscopy (FIM) which employs an atomically regular field emission tip is not a common tribological tool. However it was used by Brainard and Buckley (1971 a, b) to study transfer of metals to metals and polymers to metals in static contacts.

By far the most widely used surface analytical tools in tribology (and probably in other fields, as well) are AES and XPS. In 1971, Pepper and Buckley (1971) incorporated an Auger electron spectrometer in a friction test apparatus (figure 2). Using this, the transfer of material from the rider to the rotating disk in various metal on metal sliding couples was detected (Pepper and Buckley, 1972). Some of the results are shown in Table 2. The significance of these results is that from the cohesive energies of the metals involved, one would have predicted that transfer would occur in every case. Apparently the situation is a good deal more complex. Strain hardening in the fcc and bcc metals was invoked to explain their lack of transfer, while texturing and easy shear in the hcp Co was thought to be the reason it transferred so easily.

Pepper (1974) has also used AES to study the nature of the transfer film formed when polymers slide on metal surfaces. By measuring the attenuation of the substrate signal, he showed that the transfer films of polytetrafluoroethylene (PTFE), polyvinylchloride (PVC) and polychlorotrifluoroethylene (PCTFE) are only a few atomic layers thick. The fact that macroscopic phenomena like the friction or wear of sliding materials can be influenced by microscopic entities such as few atomic layers of polymeric material is one of the important results of the use of surface analysis in tribology and one that will arise again.

The effect of the electron beam used in AES on the specimen cannot be ignored. This is especially true in the study of polymers as Pepper found in his work, but it is also true for other organic materials (Bahr, et al. 1965). The problem can be surmounted by moving the sample so that fresh material is continually fed into the beam (Pepper, 1973). This is a simple, but effective technique that might be of use in SEM experiments, as well.

XPS is a technique which produces much less beam damage than AES. It also has the advantage of providing a certain amount of easily accessible chemical information, and it is relatively easy to quantify. However, until very recently, commercial XPS instruments had poor lateral resolution. The analyzed area ranged from a few square millimeters to a square centimeter.

In order to study the transfer of PTFE to Ni using XPS, a multiple track technique was used (Wheeler, 1981) to produce specimens of large area. To determine the amount of Ni left uncovered by PTFE, oxygen was adsorbed onto the specimen. Since oxygen does not adsorb on PTFE, the ratio of detected oxygen on the transfer specimen to that on a clean Ni specimen gave the proportion of Ni surface not covered by PTFE. Ironically, it was found in these studies (Wheeler and Pepper, 1982) that PTFE is susceptible to radiation damage even from the low energy X-rays used in XPS. It was possible, however, to confirm that the PTFE transfer film was on the order of a monolayer thick on the average.

Surface Films

Surface films have a profound effect on the friction and adhesion of solid contacts. Surface analytical instruments have provided an ideal monitor of these films in tribological experiments. In this role, the poor lateral resolution of XPS is often no handicap, and both XPS and AES are used routinely. As in the studies of transfer, the analytical instrument is usually in the same ultra-high vacuum chamber as the test apparatus so that there will be no doubt about the condition of the surfaces.

The effect of adsorbates on metal adhesion was one of the earliest questions of interest. Buckley (1970), using AES, found that the adhesion of polycrystalline specimens was drastically reduced by even submonolayers of adsorbates. Measurement of the static coefficient of friction for several metal couples as a function of adsorbate coverage (Wheeler, 1976) confirmed the reduction in interfacial strength. The

reduction was independent of the adsorbate, and seemed to be due to attenuation of the metallic bond at the interface. Later direct measurements of the adhesion of metal contacts confirmed that contamination reduced the adhesive strength (Pollock, et al, 1977, Pethica and Tabor, 1979 and Pashley and Tabor, 1981). In very recent studies, however, Hartweck and Grabke (1981) claim to have seen an increase in the strength of iron contacts covered with submonolayers of C, N, S, and P.

In the case of metal-ceramic couples, there is ample evidence (Pepper, 1979) that adsorbates in amounts up to a monolayer can either increase or decrease the strength of the contact. Table 3 shows the effect of adsorbed oxygen and chlorine on the shear strength of the contact between sapphire and a variety of metals. Note that the Fe-sapphire contact is weakened by chlorine and strengthened by oxygen. Note further that the effects are detectable for exposures that produce much less than a monolayer of adsorbate. Figure 3 shows the sliding friction of the iron-sapphire couple when exposed to 10^{-6} Torr of oxygen or chlorine (Pepper, 1976). Once again, adsorption in the submonolayer regime is seen to produce gross changes in friction behavior.

Both AES and XPS have frequently been used to check the cleanliness of surfaces placed into contact. A limitation of both techniques is illustrated by a study of the strength of the copper-diamond interface in which AES was used to monitor the condition of the diamond surface (Pepper, 1982). It was found that the static coefficient of friction more than doubled after the diamond was annealed at 900° C although AES showed no change in the surface. Ionization loss spectroscopy did reveal a change in the electronic structure of the surface, and it was later found that diamond, as polished, has a hydrogen layer on its surface which is removed by annealing at 900° C. The contact strength is greatly affected by this layer, but neither AES nor XPS is sensitive to hydrogen.

Nature of the Interfacial Bond

There is ample evidence that, at least in the carefully controlled contacts used in fundamental tribological work, adhesion is of fundamental importance. It is natural, then, to proceed to the study of the interfacial bond, itself. The adhesive bond across a material interface, like any chemical bond, is electronic in nature. Since most surface analytic spectroscopies are electronic spectroscopies, they have been used to help elucidate the nature of the bond.

The metallic bond is thought to be much the same at metal interfaces as in the grain boundaries between metals (Harweck and Grabke, 1981). That is not to say that it is well understood. Much of the work on the effects of surface films discussed above is directly applicable. However, tribologists have left this area largely to the metallurgists. There is more tribological work on the nature of the bond between metals and non-metals. A great deal of this work is not strictly tribological in the sense of involving a sliding interface. Rather it

often involves the study of static interfaces formed by some method of film deposition. This review will try not to stray too far into the realm of film deposition.

A fundamental question in the adhesion of polymers is whether the bond is chemical in nature or due only to dispersive forces - i.e., physical. Burkstrand (1981) has shown clear evidence of chemical bonds at several polymer-metal interfaces. Tribological studies of these systems would be of interest, but are lacking. Fluoropolymers - PTFE in particular - are of special interest to tribologists because of their remarkably low friction. Cadman and Gosledge (1978) studied the transfer film of PTFE formed by sliding on nickel. They attribute its adhesion to a chemical interaction, citing XPS evidence of metal fluoride at the interface. Other work (Wheeler, 1981) confirms the presence of fluoride during XPS analysis, but attributes it to the damaging effect of X-rays on the polymer. X-ray damaged PTFE shows clear evidence of chemical bonding to metals, in XPS studies (Wheeler, 1983). Figure 4 shows the C(1s), F(1s), and Ni(2p) XPS spectra from a thin film of Ni evaporated onto X-ray damaged PTFE. Besides evidence of fluoride in both the Ni and F spectra, there is a peak in the C spectrum that may be associated with a carbide-like interaction. Adhesion tests in the author's laboratory on evaporated Ni films show that X-ray damage is correlated with greater interfacial adhesion. This is presumably the result of chemical bonds.

In these investigations, access to the interface was available from both sides. The transfer layer of PTFE developed in sliding is thin enough that the interfacial region can be analyzed through it. Also, metal films thin enough to allow analysis of the interface are easily deposited on the bulk polymer. In fact, the metal films were deposited less than one monolayer at a time, while analysis was performed between depositions. Thus, the interface could be analyzed at stages in its development.

Rather than attempt analysis of the interface directly, one may measure the electronic properties of the surfaces before contact is made. Then the contact strength between bulk materials can be correlated with the state of the surface. The strength of the diamond-metal interface has been correlated with the electronic structure of the diamond surface (Pepper, 1982), in just this way. Electron energy loss spectroscopy (EELS) showed the presence of unoccupied states in the band gap of annealed diamond (figure 5). There were no such states in unannealed diamond. As noted above the static friction between metals and diamond was higher after annealing. It was proposed that the gap states may be partially filled by electrons from the Fermi level of the metal thus forming a chemical bond between the diamond and the metal.

To date, direct analysis of the electronic structure of surfaces and interfaces has not been applied widely in tribological work. This is probably because few experimental situations

give access to the interface, and those that do are likely to be far from typical of real world problems which concern many tribologists. In the next section the growing number of applications of surface analysis to these real-world problems will be reviewed.

Applied Tribology

The distinction between applied and fundamental tribology is vague. In this review, applied work will generally be work on actual machine elements or studies of lubricants. However, the author's intent will also be considered in classifying a study as applied. There is currently rapid growth in the use of surface analysis in tribology as evidenced by the number of articles in journals such as the Transactions of the American Society of Lubrication Engineers. However there was also much work in the 1970's. Reviews by Singer and Murday (1980) and by Ferrante (1982) are a good introduction to the earlier work.

Applied studies fall into three rather well defined categories. First there are analyses of coatings applied for tribological purposes. As noted in the Introduction, this area will not be covered in this review. There is a related area of surface modification by procedures such as ion-implantation, nitriding, etc. This too, is beyond the scope of this review. A second large category of studies is investigation of the chemistry of tribological surfaces. The absorption and decomposition properties of solid lubricants and the surface chemistry of liquid lubricants would fall into this category. No actual wear testing is involved. Finally, there is the category of analysis of worn surfaces. This is of the greatest practical interest and presents the greatest experimental problems for the analyst. This review will begin with applications of XPS to the analysis of worn surfaces followed by XPS analysis of the chemistry of lubricated surfaces. Applications of AES to these fields will then be discussed. The discussion is separated by technique, because the emphasis throughout will be on the analytical problems rather than the importance of the results for tribology.

XPS Analysis of Worn Surfaces

Most effort has been devoted to the surface films formed by three types of lubricant additives: the organo disulfides, the metal dialkyl dithiophosphates, and additives of the tricresyl phosphate type. All of these can be classed as antiwear additives of some sort, and all are thought to act by forming a protective chemical film on the rubbing surfaces. The identity of this film and the conditions under which it forms have been the objects of most surface analyses of lubricated specimens.

Because of the availability of chemical information, XPS is an obvious choice for analysis of reaction films. However, Singer and Murday (1980) point out that because of the lack of reliable binding energy values for the various chemical states of some systems such as iron-sulfur, results must be interpreted with caution. Furthermore, because of the poor

lateral resolution of XPS, wear scars must be produced that are large, but still representative of the concentrated contacts found in real wear situations. The preparation of suitable wear scars is the major problem in the application of XPS to the analysis of worn surfaces, and its various solutions will be emphasized in the discussion to follow.

Bird and Galvin (1976), in perhaps the first work of this sort, used an oscillating flat on cylinder device. By moving the line contact continually over the flat surface they could produce large area wear scars from a highly concentrated contact geometry. They were able to conclude that metal sulfide was a major constituent of the wear film formed by the organic disulfide additives.

This work was also notable in the variety of solvents and reagents used to treat the worn surfaces before and between surface analyses. A certain amount of "wet chemistry" could be done to clarify the nature of the films. Since that time, this aspect of sample preparation has been neglected. In the work referred to below, sample preparation consists of rinsing the specimen in an inert solvent such as Freon before exposing it to the spectrometer vacuum.

In a very thorough investigation Baldwin (1976 a) has shown that sulfur additives do, indeed, form sulfide films on worn surfaces. Moreover, he demonstrated a correlation between the sulfide concentration and the degree of wear, even when other sulfur species (e.g., sulfates) predominated in the wear scar. The test device in this case was a Falex tester which wears the cylindrical face of a pin rather uniformly. The cylindrical geometry was ideal for the spectrometer used. The technique was also used to study the effect of boron containing additives (Baldwin, 1976 b).

The present author (Wheeler, 1978) has used a device to raster the point contact between a sphere and a flat over the flat surface, thus producing large area wear scars from concentrated contacts. Studies of sulfur additives with this device confirmed Baldwin's observation. It was also shown that the sulfide film formed above a critical load. Using a flat on flat wear test device at heavy loads to produce large worn areas a profound effect of oxygen on the effectiveness of the antiwear film was demonstrated (Wheeler, 1979).

In another case (Faut and Wheeler, 1982) iron was substituted for steel, when friction results showed the same behavior in both materials. The softer iron produced a wear scar large enough to analyze. Those results showed that a phosphate film formed on specimens worn in tricresyl-phosphate (TCP) but only above a critical temperature.

XPS was used in a study of the transfer of material from PTFE bearing liners to bearing balls (Bramham, et al, 1981). Both the liners and balls are suitable subjects for XPS analysis since they are large in area and worn rather uniformly. This would seem to be an ideal test system since it is a real machine element and yet produces specimens large enough for XPS analysis. The difficulty is that bearing tests

are normally very long term tests, because the bearings are so effective in preventing wear. Furthermore, failure of a bearing ball, which is an extremely interesting event for the tribologist, occurs in a very small area. It is, thus, a difficult problem for the surface analyst. Nonetheless, it is to be hoped that this method of testing will be pursued.

XPS Studies of The Chemistry of Lubricated Surfaces

XPS has also been widely used in the analysis of surfaces that have been prepared for tribological purposes but not actually worn. In this role lateral resolution is of no concern, and the chemical sensitivity and quantitative nature of XPS make it a most powerful tool. The effectiveness of bearing cleaning procedures was evaluated by both XPS and AES (Bernett, et al, 1981 and 1982). It was found that hydrocarbon contamination remained after standard solvent bath cleaning. Fluorocarbon vapor extraction produced the least contaminated surfaces.

The changes in surface chemistry of silicon-carbide at temperatures up to 1500° C have been correlated with friction properties (Miyoshi and Buckley, 1983). At about 800° C the carbon detectable on the surface was found to transform from carbide to graphite. The transformation is accompanied by a dramatic reduction in coefficient of friction from 0.7 to 0.3. Once more, the surface sensitivity of tribological effects is evident.

Finally, the surface chemistry of TCP on iron and gold has been used to explain the differences in friction of those materials lubricated with TCP (Wheeler and Faut, 1983). It was found that decomposition of TCP on iron at about 200° C was accompanied by a reduction in the coefficient of friction. When it was found that TCP did not decompose on gold but desorbed, it was predicted that gold would not exhibit a decrease in friction but an increase as the protective surface was lost. This has been confirmed in recent work in the author's laboratory.

AES Analyses

AES was available commercially earlier than XPS, it is cheaper, and its good lateral resolution makes it ideal for the analysis of concentrated contacts. It is also particularly suited to depth profiling by ion etching. For all these reasons, it was applied early to the study of lubricated systems (Phillips, et al, 1976). As with XPS, most of the interest has been in the nature of the film formed by lubricant additives. Notable work has been done by Gauthier et al (1982) on the additive TCP. Using quantitative AES assisted by XPS they identified two types of films formed in their wear tests. One is a ferrous oxide and phosphate mixture. The other is an organic phosphate, possibly polymeric. Standards were used to quantify the AES data, and peak shapes to identify the phosphate species.

Mathieu, et al have studied wear scars formed in lubricants containing phosphorus and sulfur additives (Mathieu, et al, 1981 and Schumacher, et al, 1983). They found that, at

fixed load, an inverse correlation exists between wear and the concentration of both sulfur and phosphorus in the wear scar. A notable feature of their work was the ability to follow the development of the surface reaction film as the wear test progressed. For the phosphorus additives, a detailed chemical mechanism was proposed.

The important effect of oxygen on the activity of lubricant additives was noted above (Wheeler, 1979). It has been the subject of several recent studies (Willermet, et al., 1983 and Brainard and Ferrante, 1979 and 1983) of the surface chemistry of zinc-dialkyl-dithiophosphate (ZDP). All find that, generally, wear is much less in the presence of air than in a nitrogen atmosphere. However, Brainard and Ferrante (1983) find that the effect depends upon the carrier lubricant and that, in air, wear is usually no less with ZDP than without it. This last observation raises an important issue in all tribology; results from a wear test are only applicable to the conditions of that test. Under different conditions, the wear mechanism may be different. Thus, the chemistry of formation of a particular surface film may change, and the effect of that film on the wear may also be different. Since all the pertinent test conditions may not be specified or even known, the application of test results to real practice is fraught with uncertainty.

One test parameter is the load on a contact. The influence of load on chemistry was studied by McCarrroll et al (1977) and Debies and Johnston (1980). Both studies used sulfur containing additives. In both it was found that sulfur concentration increased as the severity of the wear conditions increased. That is in general agreement with the XPS result mentioned above (Wheeler, 1978).

AES Studies of The Chemistry of Lubricated Surfaces

The adsorption of water and organic vapors on molybdenum disulfide has been studied (Matsunaga, et al, 1982). It was suggested that differences in adsorption between the basal and prismatic planes might account for the well known difference in lubricating properties of those two planes.

The difficulty of extracting chemical information from AES has undoubtedly contributed to a lack of work of this sort, to date. It is, therefore, notable that Shafrin and Murday (1977) have, recently, demonstrated the chemical sensitivity of AES by distinguishing a variety of phosphorus compounds formed during the pre-soak treatment of bearing steel in TCP. The distinction between phosphide and phosphate AES lines is shown in figure 6. Both the iron and phosphorus lines show clear differences.

ISS/SIMS Applications to Applied Tribology

Although not widely used, ISS and SIMS have been applied to tribology. The reaction film formed during sliding in a ZDP containing lubricant was studied (Oppelt et al, 1981). The small ion beam permitted good lateral resolution. However it appeared that element interferences in ISS limited its usefulness, while the difficulty of interpreting the SIMS data made it most useful for detecting very low

concentration constituents. In another investigation (Montes et al, 1977) SIMS was used to detect iron phosphate in steel specimens worn in phosphorus additives.

Conclusions

Attention will now be focused on current problems in the application of each surface analytical technique to tribology, as they have been illustrated in the work already discussed. Possible approaches to these problems will be assessed, and the importance of new developments in instruments and techniques will be commented on. Finally, some goals for further work will be suggested.

Auger Electron Spectroscopy

Recent growth in the use of AES by tribologists shows that it is becoming a standard technique in the field. However, to exploit it fully, its experimental difficulties must be confronted. To date, they have been largely ignored.

There is no lack of chemical information in the AES spectrum, but because of the breadth of the peaks and their differentiated form, the information is not easily extracted. The best technique appears to be "fingerprinting" of standard compounds as was done for the phosphorus-iron system (Shafrin and Murday, 1977). That is a practical proposition, because the number of systems of interest in tribology is not extensive. In this regard the "factor analysis" method of resolving multi-component spectra may be useful (Garenstroom, 1981). An alternative approach is the calculation of Auger line shapes from molecular orbital theory (Turner et al, 1980). If generally possible and reliable, this would be preferred to "fingerprinting".

In many cases the application of AES is complicated by changes in the surface produced by the electron beam. These can take the form of chemical reduction of species or electron stimulated adsorption or desorption. The problem is especially acute for organic materials which are of great interest in applied tribology. The simple expedient of moving the sample (Pepper, 1973) rapidly enough to avoid the problem sacrifices the good lateral resolution of AES. While beam damage may be negligible in any particular case, it must be considered in every case. Performing typical analyses over a range of beam current densities and extrapolating to zero current density may be the only course presently open.

A similar problem arises in depth profiling by ion etching. The energetic ions are known (Kim, et al, 1974) to reduce a wide range of compounds. This can cause errors of both quantitative and chemical interpretation. There is little the analyst can do but be aware of this problem. Other difficulties in the depth profiling of worn surfaces are more tractable. Shadowing of parts of the surface by irregularities can be minimized by using multiple ion beams (Brainard and Ferrante, 1983). However worn surfaces are not only rough, they are patchy. Areas of true contact are on the order

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of microns and are surrounded by low areas that accumulate wear debris and degraded lubricant. One must know which sort of area is being analyzed. This makes a Scanning Auger Microprobe (SAM) a remarkably useful analytical instrument for tribological surfaces.

Finally, quantitative AES measurements must be made with great caution. Chemical changes in an element can alter the shape of its AES peak. A change in shape can change the size of the differentiated peak in the spectrum, even when the amount of the element is unchanged. This is avoided in newer instruments that make integral as well as derivative spectra available. There are also potentially serious matrix effects to be taken into account. Standards that are as near as possible to the specimens to be analyzed are a solution to this problem that is well known to the electron microscopist. However the surface sensitivity of AES must be kept in mind. If the sampled volume of the specimen is vertically inhomogeneous, homogeneous standards cannot be used.

X-ray Photoelectron Spectroscopy

From the review of previous work, it is obvious that an important experimental problem in the use of XPS has been the production of worn surfaces large enough for analysis. The solution, until now, has been to use simulated wear tests, rather than real specimens. Recently, instruments using focusing X-ray monochromators, multichannel detectors and improved electron optics have opened new possibilities (Kelley, 1984). These instruments have analyzed spot sizes of 300 micrometers or less in diameter. That makes possible the analysis of some real-world samples, although it is still not possible to analyze the inhomogeneities within a wear scar with XPS in the way one can with a SAM system. These new instruments also permit more reliable and convenient depth profiling, because ion beam etching is more rapid and uniform over the smaller area. The new machines also offer lower X-ray exposure. That should reduce beam damage to some delicate materials such as polymers.

A limiting factor in quantitative analysis using XPS is the accuracy of values of the inelastic mean free path of electrons in various materials. The problem is most severe for organic and polymeric materials where empirical data are scarce (Seah and Dench, 1979). Since this is not a fundamental problem, there is reason to hope for improvement.

Other Techniques

Ion beams with focal spots less than 0.2 micrometers in diameter are available for SIMS. This lateral resolution is very satisfactory for tribological work. With its extraordinary sensitivity and its wealth of chemical information, SIMS has great potential in tribology. However, interpretation of the data is not yet routine or reliable. In the discussion of the review by Ferrante (1982) it is pointed out that this may be due to the great quantity of information produced in a SIMS analysis. At any rate, progress is being made.

In the author's laboratory, low energy electron loss spectroscopy (EELS) will soon be

available for tribological research. EELS gives data on molecular energy levels similar to that obtained from infra-red spectroscopy, but it is surface sensitive. It will be used to study the adsorption and reaction of organic molecules of tribological interest. It is hoped that, when combined with LEED, this technique will give definitive information on the reaction mechanisms of important lubricant additives.

Goals

The applications of surface analysis to tribology discussed here, especially in applied tribology, should be viewed as pioneering work. The problems that can be found in this work are the best guide to goals for future work. These problems and goals are where this review will conclude.

The preparation of lubricated samples must be carefully examined. The work of Bird and Galvin (1976) on the effect of solvents on the surface species should be followed-up, and the significance of this surface chemistry for tribology must be clarified. Friction and wear testing also needs critical examination. At the very least, some agreement on standard tests and test conditions for the simulation of real wear situations would be welcome. However, this problem cuts across all tribology, not just that part involved with surface analysis.

Past work on lubricated systems has produced a reasonable idea of the composition of worn surfaces in a number of cases. Future work needs to address two important questions. First, what are the chemical mechanisms that produce the observed compositions. This question has only recently been considered (Wheeler and Faut, 1983 and Schumacher et al., 1983) and it is of crucial importance. Conversely, the influence of the rubbing process on surface chemistry has long been neglected. This "tribo-chemistry" is an open area for fundamental studies.

Physical as well as chemical mechanisms are important in tribology. While it is well established that sulfur additives produce a sulfide film on worn surfaces, it is not at all clear how that film acts to prevent wear or lower friction. Since the solid contact is very much like a grain boundary, ideas such as embrittlement may well apply, but there is as yet no coherent model for the mechanical strength of the contact.

It should be emphasized that no single technique is adequate in every study. Tribology is too diverse a field and the specimens usually too complex for a single technique to tell all. Furthermore, surface analytical techniques are themselves complex, and their interpretation is fraught with ambiguity. The wider the variety of analytical methods employed, the greater the probability that the analyst will produce data of real significance to the tribologist.

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TABLE 1. - TRIBOLOGICALLY IMPORTANT PROPERTIES OF AUGER ELECTRON AND X-RAY PHOTOELECTRON SPECTROSCOPIES

Property	AES	XPS
Lateral resolution	0.1 - 1 μ	Millimeters
Depth profiling	Routine	Difficult
Specimen damage	Common	Rare
Chemical information	Difficult	Routine

TABLE 2. - METALLIC TRANSFER FOR DISSIMILAR METALS IN SLIDING CONTACT (Pepper and Buckley, 1972)

Counterface	Slider	Transfer
Tungsten	Iron Nickel Cobalt	Yes Yes Yes
Tantalum	Iron Nickel Cobalt	No No Yes
Molybdenum	Iron Nickel Cobalt	No No Yes
Niobium	Iron Nickel Cobalt	No No Yes

TABLE 3. - FRACTIONAL CHANGE IN THE SHEAR COEFFICIENT OF METALS ON SAPPHIRE IN THE PRESENCE OF AN ADSORBATE (Pepper, 1976)

	Ag	Cu	Ni	Fe
Oxygen	+0.23	+0.43	+0.48	+0.54
Chlorine	0	-0.07	-0.52	-0.97

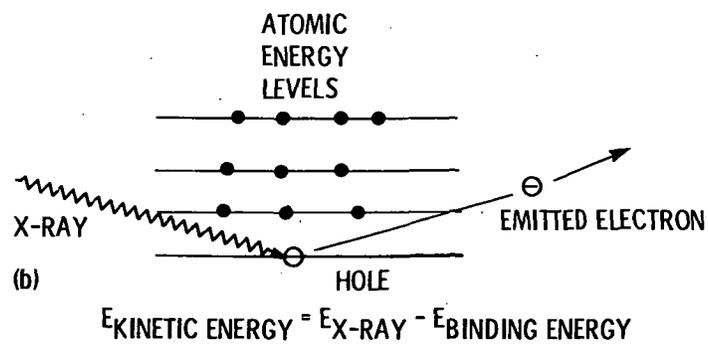
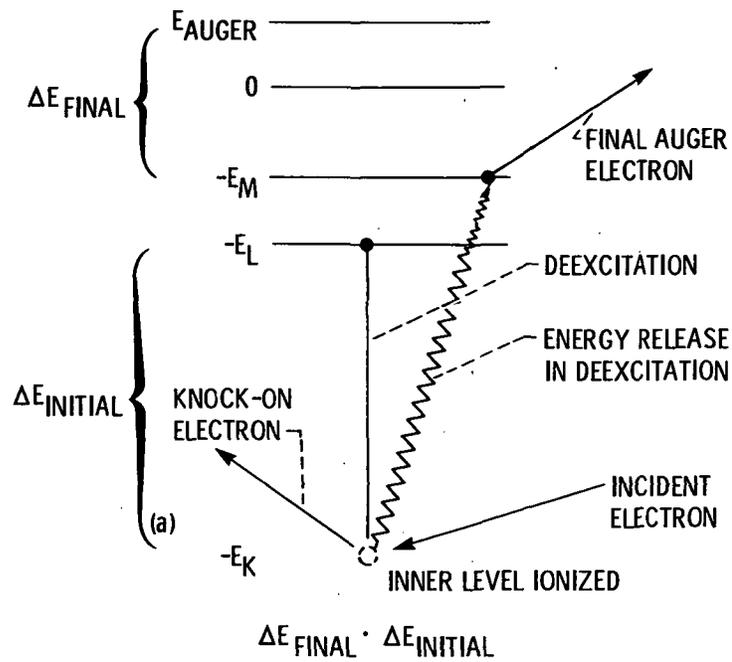


Figure 1. - Principles of (a) Auger electron spectroscopy and (b) x-ray photoelectron spectroscopy.

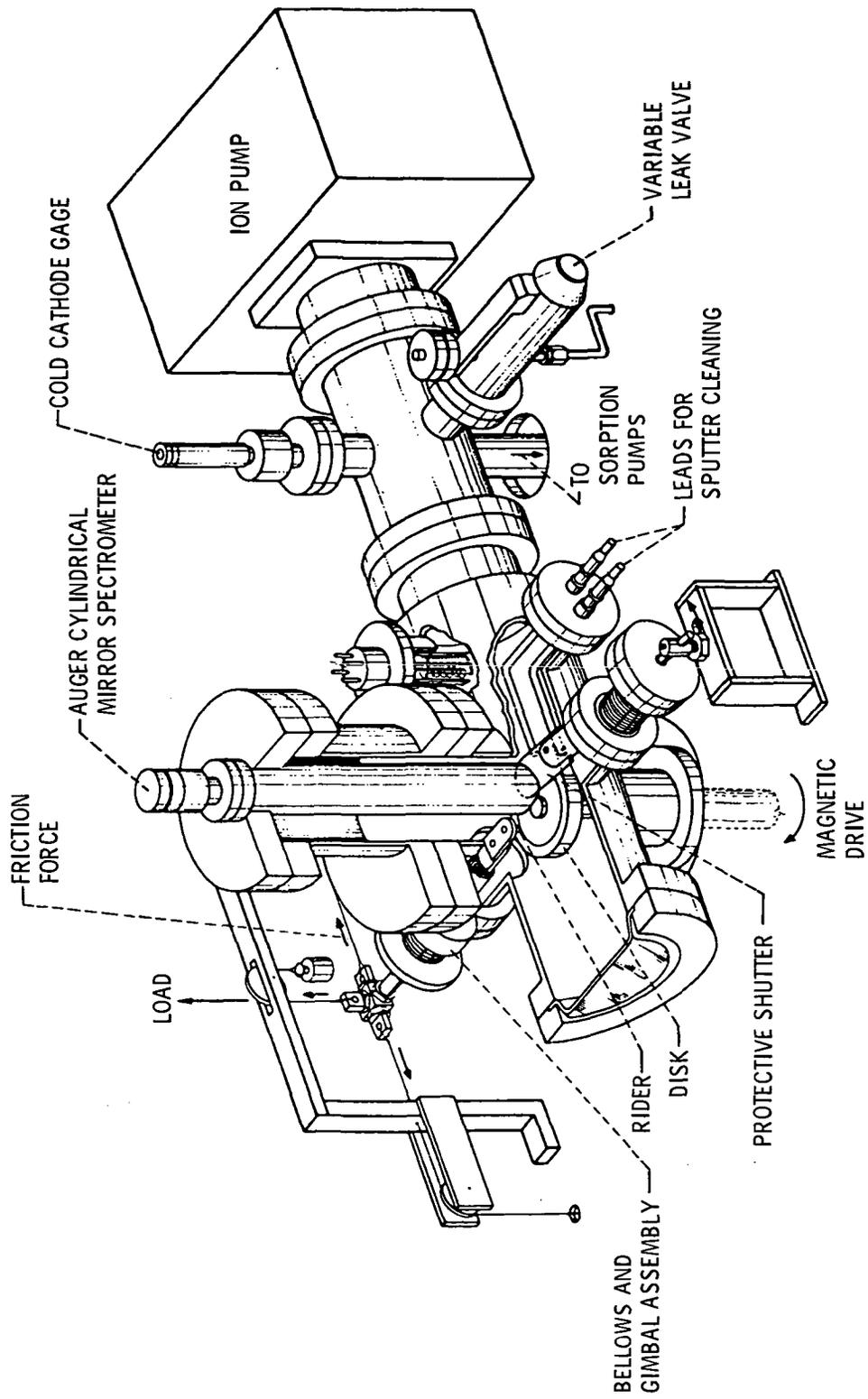


Figure 2. - AES analyzer incorporated in pin-on-disk friction test apparatus.

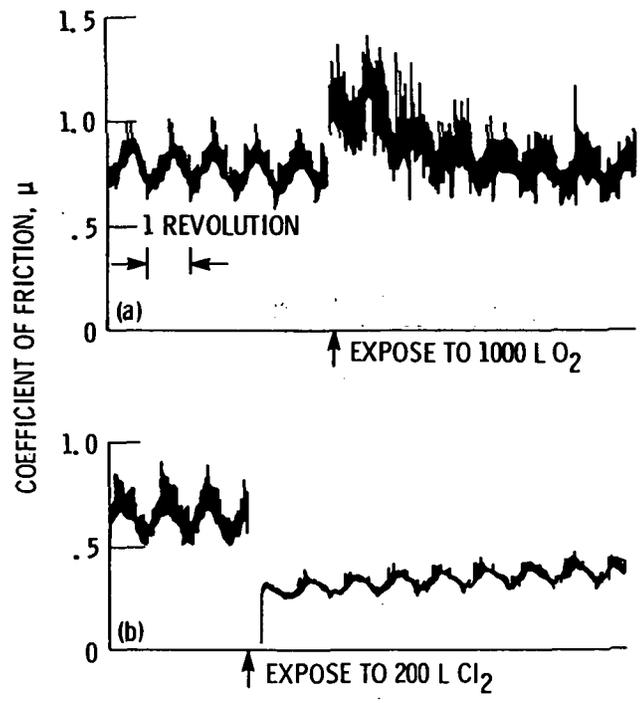


Figure 3. - Effect of oxygen and chlorine on the friction of Fe sliding on sapphire.

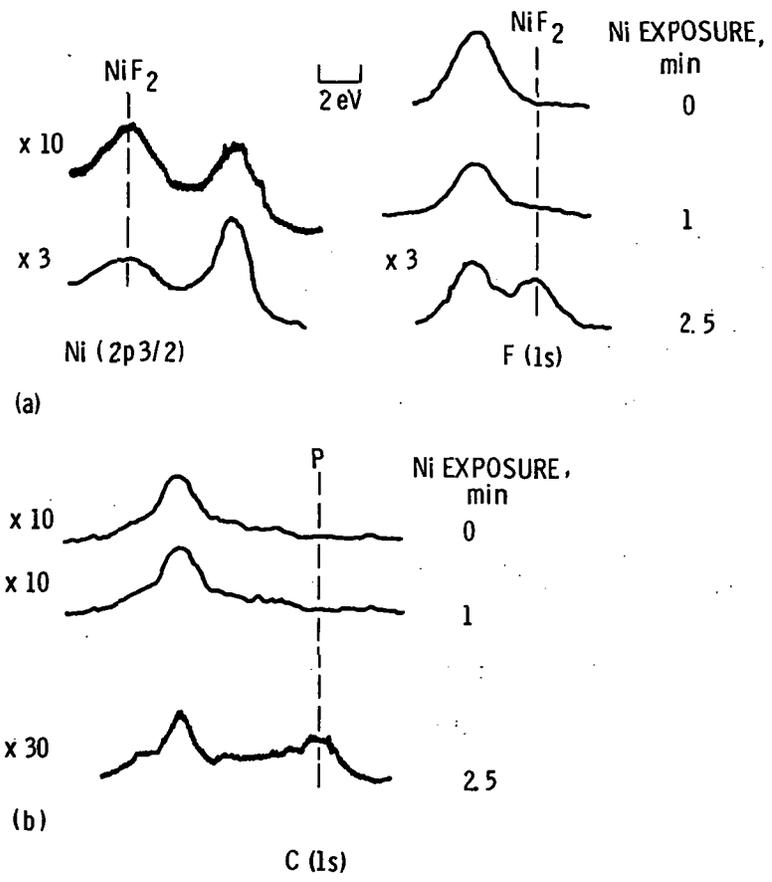
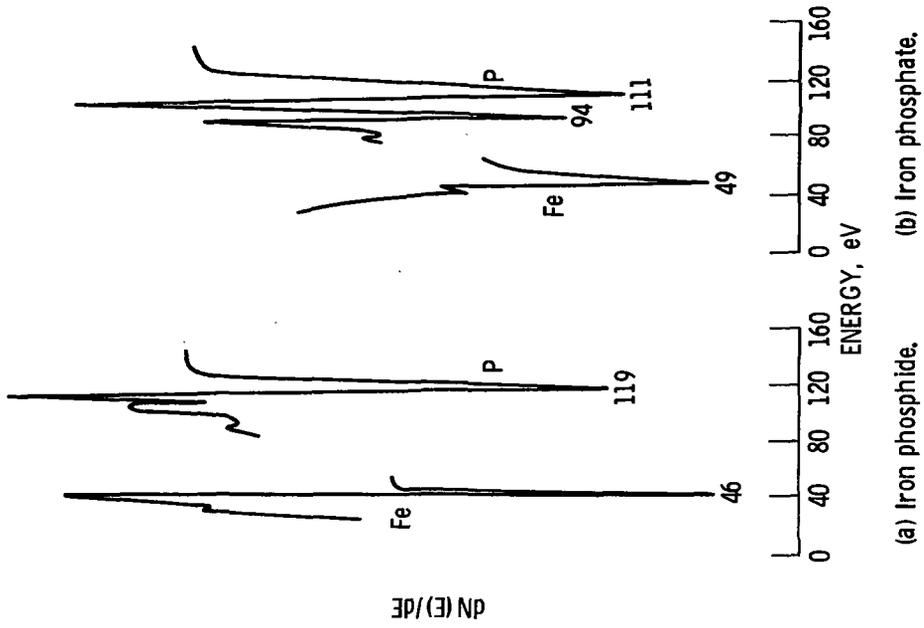


Figure 4. - C (1s), F (1s) and Ni (2p) XPS spectra from a nickel film evaporated on PTFE substrate.



(a) Iron phosphate. (b) Iron phosphide.
 Figure 6. - Auger line shapes from iron-phosphide and iron-phosphate reaction films on steel surfaces (ref. 53).

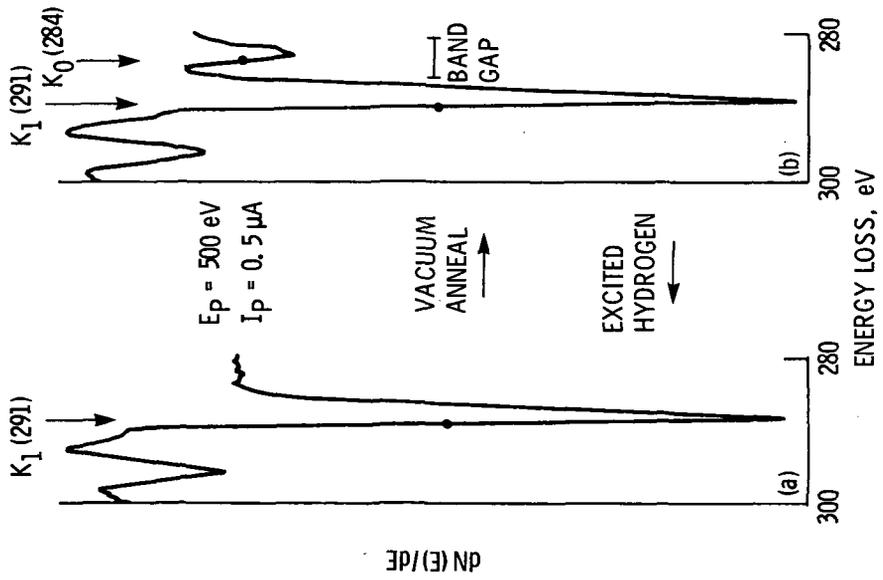


Figure 5. - EELS spectra of annealed and un-annealed diamond surface.

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16. Abstract For some years, surface analysis has been used in fundamental studies of solid-solid contacts as they exist in tribological systems. Analysis was used to detect material transfer in sliding contacts. It has also been used to monitor surface films in studies of the effects of such films on the adhesion of contacts. Finally electron spectroscopic analysis of interfaces has shed some light on the fundamental electronic nature of the interfacial bond. More recently, surface analysis has been applied to many tribological engineering problems. In particular, identification of chemical films formed during the sliding contact of lubricated systems and study of the surface chemistry of lubricant additives have been active areas of research. In all of these studies one or more of four properties of the analytical technique will be important in determining its utility. The four are: lateral resolution, specimen damage, depth resolution and the availability of chemical information. In each of the applications discussed here, the important factors are brought out.					
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