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APPLICATIONS OF SURFACE ANALYSIS TECHNIQUES TO STUDIES OF ADHESION

W. L. BAUN
MECHANICS & SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

SEPTEMBER 1979

TECHNICAL REPORT AFML-TR-79-4126
Final Report for period March 1979 – July 1979

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

(14) 1. REPORT NUMBER
AFML-TR-79-4126

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

(6) 4. TITLE (*and Subtitle*)
Applications of Surface Analysis Techniques to Studies of Adhesion.

5. TYPE OF REPORT & PERIOD COVERED
Final Mar 79-July 79

6. PERFORMING ORG. REPORT NUMBER

(10) 7. AUTHOR(s)
William L. /Baun

8. CONTRACT OR GRANT NUMBER(s)
Inhouse Report

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, OH 45433

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
(16) 2419 241902 (17)
WUD #44

11. CONTROLLING OFFICE NAME AND ADDRESS
(12) 38

(11) 12. REPORT DATE
Sept[redacted]79

13. NUMBER OF PAGES

14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)

15. SECURITY CLASS. (*of this report*)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release; distribution unlimited.

(9) Final rept. Mar – Jul 79,

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

62102F

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Adhesion	Adherend	ISS
Adhesive Bonding	Adhesive	SIMS
Surface Characterization	AES	SEM
Surface Analysis	XPS	

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

The question is often asked, "Which is the best surface chemistry tool for research on adhesive bonding?" This question is difficult to answer because it depends on the aspect of adhesion which is being studied. Often a combination of instruments must be used to take advantage of the strong points of each. In metal-to-metal bonding there are many facets of adhesive/adherend interaction. Elemental characterization

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of adherends, especially when composition with depth is desired, is often best accomplished with Auger Electron Spectroscopy (AES). When information of chemical bonding is required, X-Ray Photoelectron Spectroscopy (XPS) is the choice of most workers. Extremely thin layers of material (when first layer surface sensitivity is needed) requires Ion Scattering Spectrometry (ISS). The high sensitivity of Secondary Ion Mass Spectrometry (SIMS) to many elements important in adhesive bonding makes this technique useful, especially coupled with other methods, such as ISS and AES. Modern surface analysis along with Scanning Electron Microscopy (SEM) provides information on failure surfaces to allow unequivocal determination of the mode of failure. Problems such as charging and decomposition under the probing beam are encountered when characterizing the part of the failure surfaces containing the adhesive.

Although original surfaces and failure surfaces following testing are relatively routinely analyzed, the characterization of the intact bond is not so easy. The interphase region between adherend and adhesive is smaller than the probe, exhibits charging and is unstable. Although no one technique adequately characterizes the bond interphase region, the SEM, the AES microprobe, and special techniques using Transmission Electron Microssopy (TEM), may be used to gain some information about the bond. The more fundamental study of the interaction of polymers and polymer precursors with metals and alloys is carried out by surface energetics measurements, infrared and Raman spectrometries, XPS, and electron tunneling spectroscopy.

FOREWORD

This technical report was prepared by W. L. Baun of The Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright-Patterson Air Force Base, Ohio. This work was initiated under Project 2419, "Nonmetallic and Composite Materials," and Work Unit Directive Number 44 "Improved Materials, Processes, and Life Prediction Methodology for Adhesive Bonding." The Work Unit Monitor was Dr. T. W. Haas.

This report covers work performed inhouse during the period March 1979 to July 1979 and represents material contained in an invited presentation at The Symposium on Applied Surface Analysis 13-15 June 1979 at The University of Dayton, Dayton, Ohio. The meeting was sponsored by the Air Force Office of Scientific Research.

Valuable discussion with N. T. McDevitt, J. S. Solomon, and T. W. Haas are acknowledged. Douglas Hanlin and Donald Thomas are thanked for careful experimental work.

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SECTION I
INTRODUCTION

In an effort to develop strong, light, and corrosion resistant structures, the aerospace industry has gone more and more to adhesive bonding. The automotive industry is quickly following along using different structural alloys. In these fields, bonded structures must be strong and possess long-time durability. Both strength and durability depend on many factors of bond preparation and fundamental properties of the adhesive and adherend. One important influence in the formation of a good adhesive bond is surface or interfacial chemistry. In the broader sense, in which two substances are held together by interfacial forces, adhesion is of importance in many technologies such as in thin films and semiconductors. It is the purpose of this report to discuss methods of surface characterization applicable to the broad area of adhesion with emphasis on adhesive bonding.

SECTION II
DISCUSSION

The question is often asked, "Which is the best surface chemistry tool for research on adhesive bonding?" This question is difficult to answer because it depends on the aspect of adhesion which is being studied. Often a combination of instruments must be used to take advantage of the strong points of each. Table I shows the facets of bonding and some of the characterization methods which are applicable in these areas. Table II is a list of surface techniques from the work of Powell,[1] and the familiar acronyms by which they will be referred to in this work. Many of these methods were described by Park,[2] in a comprehensive review in which he categorized the techniques according to the kind of information they provide. This discussion included what is being probed, such as vibrational states, the probe itself, such as monoenergetic electrons, and what was actually being measured, such as the electron emission.

1. CHARACTERIZATION OF THE ADHEREND

A determination of the chemistry of metallic adherends presents problems of each of the areas discussed here. Many of the surface chemical techniques are applicable to the analysis of adherends, and because of the stability and good conductivity, decomposition, and surface charging are not problems. Surface chemical analysis is usually devoted to (1) determining the amount and distribution of elements purposely placed on the surface to impart a desirable property, and (2) detection and monitoring of impurity elements which may be deleterious to the adhesive bond. Many chemical etching and oxidizing treatments are used on metal and alloys to enhance adhesive bonding of the surface. Enhancement comes about by roughening of the surface and by changing the surface chemistry. In addition, some thermal treatments, such as the bond cure in adhesive bonding, may affect

TABLE I

ASPECTS OF ADHESIVE BONDING AND APPLICABLE SURFACE CHARACTERIZATION METHODS

ADHEREND CHEMISTRY

AEAPS, AEM, AES, APS, BIS, CIS, CL, EM, ES, EXAFS, IIRS, IIXS, IMMA, IS, ISS, LMP, PES, RBS, SIMS, SXAPS, SXES

ADHEREND STRUCTURE AND MORPHOLOGY

AEM, ELL, EM, HEED, IMMA, LEED, SEM, SIIMS, SRS, STEM, TEM, XEM, XRD

ADHESIVE CHEMISTRY

AES, AIM, ASW, ATR, ESR, HA, IRS, ISS, LS, PES, SIMS, UPS, XPS

ADHESIVE STRUCTURE AND MORPHOLOGY

ATR, IR, UV, RAMAN, SEM

INTERACTION OF POLYMERS WITH METALS

AES, AIM, ASW, CPD, ELL, EELS, ESDI, ESDN, FD, FDS, HA, IRS, IR, ISS, ISD, LEED, LS, PD, SC, SIMS, UPS, XPS, RAMAN

FAILURE SURFACES (LOCUS OF FAILURE)

AES, ATR, ELL, ISS, SIMS, PES, XPS, SEM, SXES, SXAPS, SRS, UPS

TABLE II

SURFACE CHARACTERIZATION METHODS

(Ref. 1)

AEAPS	Auger-electron appearance potential spectroscopy
AEM	Auger-electron microscopy
AES	Auger-electron spectroscopy
AIM	Adsorption isotherm measurements
APS	Appearance-potential spectroscopy
ASW	Acoustic surface-wave measurements
ATR	Attenuated total reflectance
BIS	Bremsstrahlung isochromat spectroscopy
CIS	Characteristic isochromat spectroscopy
CL	Cathodoluminescence
COL	Colorimetry: IR, visible, UV, X-ray, and γ-ray absorption spectroscopy
CPD	Contact potential difference (work-function measurements)
DAPS	Disappearance-potential spectroscopy
EL	Electroluminescence
ELL	Ellipsometry
EELS	Electron energy-loss spectroscopy
EM	Electron microprobe
ES	Emission spectroscopy
ESDI	Electron-stimulated desorption of ions
ESDN	Electron-stimulated desorption of neutrals
ESR	Electron-spin resonance
EXAFS	Extended X-ray absorption fine structure
FD	Flash desorption
FDM	Field-desorption microscopy
FDS	Field-desorption spectroscopy
FEM	Field-emission microscopy
FEES	Field-electron energy spectroscopy
FIM	Field-ion microscopy
FIM-APS	Field-ion microscope - atom prope spectroscopy
FIS	Field-ion spectroscopy
GDMS	Glow-discharge mass spectroscopy
HA	Heat of adsorption
HEED	High-energy electron diffraction
IIRS	Ion-impact radiation spectroscopy
IIXS	Ion-induced X-ray spectroscopy
IMMA	Ion microprobe mass analysis
IMXA	Ion microprobe X-ray analysis
INS	Ion-neutralization spectroscopy
IRS	Internal reflectance spectroscopy
IS	Ionization spectroscopy
ISD	Ion-stimulated desorption
ISS	Ion-scattering spectroscopy
ITS	Inelastic tunneling spectroscopy
LEED	Low-energy electron diffraction
LMP	Laser microprobe
LS	Light scattering
MBRS	Molecular-beam reactive scattering
MBSS	Molecular-beam surface scattering
MOSS	Mössbauer spectroscopy
NIRS	Neutral impact radiation spectroscopy
NMR	Nuclear magnetic resonance
NRS	Nuclear reaction spectroscopy
PD	Photodesorption
PEM	Photoelectron microscopy
PES	Photoelectron spectroscopy
RBS	Rutherford backscattering spectroscopy
RHEED	Reflection high-energy electron diffraction
SC	Surface capacitance
SDMM	Scanning desorption molecule microscopy
SEE	Secondary-electron emission
SEM	Scanning electron microscopy
SEXAFS	Surface extended X-ray absorption fine structure

TABLE II (Continued)

SURFACE CHARACTERIZATION METHODS
(Ref. 1)

SI	Surface ionization
SIIMS	Secondary-ion imaging mass spectroscopy
SIMS	Secondary-ion mass spectroscopy
SLEEP	Scanning low-energy electron probe
SRS	Surface reflectance spectroscopy
STEM	Scanning transmission electron microscopy
SXAPS	Soft S-ray appearance - potential spectroscopy
SXES	Soft X-ray emission spectroscopy
TE	Thermionic emission
TEM	Transmission electron microscopy
TL	Thermoluminescence
UPS	Ultraviolet photoemission spectroscopy
XEM	Exoelectron microscopy
XES	Exoelectron spectroscopy
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffraction (glancing incidence)

the composition of the surface, either by introducing impurities or by increasing or decreasing a concentration of alloying elements at the surface. McDevitt and co-workers used a number of complementary modern surface analysis tools to analyze several aluminum alloys following chemical treatment for adhesive bonding.[3,4,5] They found a number of interesting phenomena, including the one illustrated in Figure 1, where the formation of an interfacial region rich in copper is shown on 2024 aluminum alloy. The concentration and width of this potential weakened boundary layer is found to vary depending on the etching conditions of the chromic acid-sodium dichromate solution. This solution is related to the surface preparation method known as the FPL etch. Similar results were obtained more recently by Sun and co-workers.[6] The formation of such potential weak boundary layers may influence both the initial bondability and the long time durability of the adhesive bond. Baun, et al.[7] used ISS, SIMS, and AES to analyze a variety of metal and alloy adherends. These authors also used several surface treatments on titanium and titanium alloys and analyzed them by surface techniques such as ISS, SIMS, AES, and SEM.[8,9,10] Large differences in chemistry were observed on titanium and its alloys depending on the surface treatments. An example similar to the phosphate fluoride treatment on titanium commercial purity is shown in Figure 2. This ISS and positive SIMS data indicate that substantial amount of fluorine is present on the surface. The cluster or fingerprint spectra in the SIMS data suggests that titanium fluoride is actually present on the surface. The cleanliness and wetability of adherend surfaces may be inferred by classical methods such as contact angle measurements,[11] ellipsometry,[12] and contact potential difference measurements.[13] A combination of these techniques was used by Smith in a program related to the analysis of adhesive bonding materials.[14]

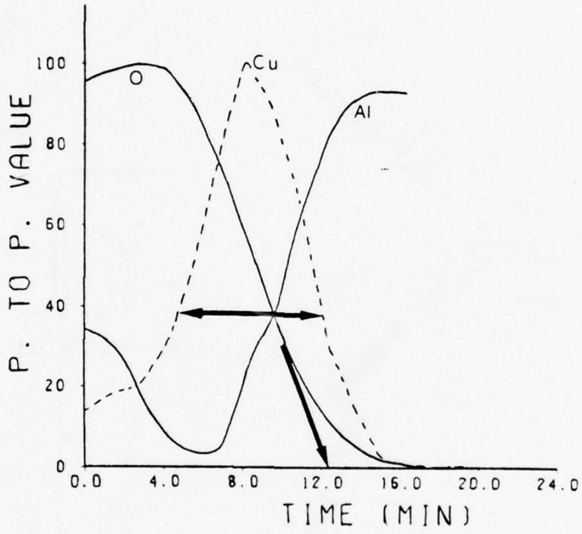

Figure 1. Normalized elemental profiles for aluminum, oxygen, and copper from 2024 aluminum alloy treated with FPL etch.

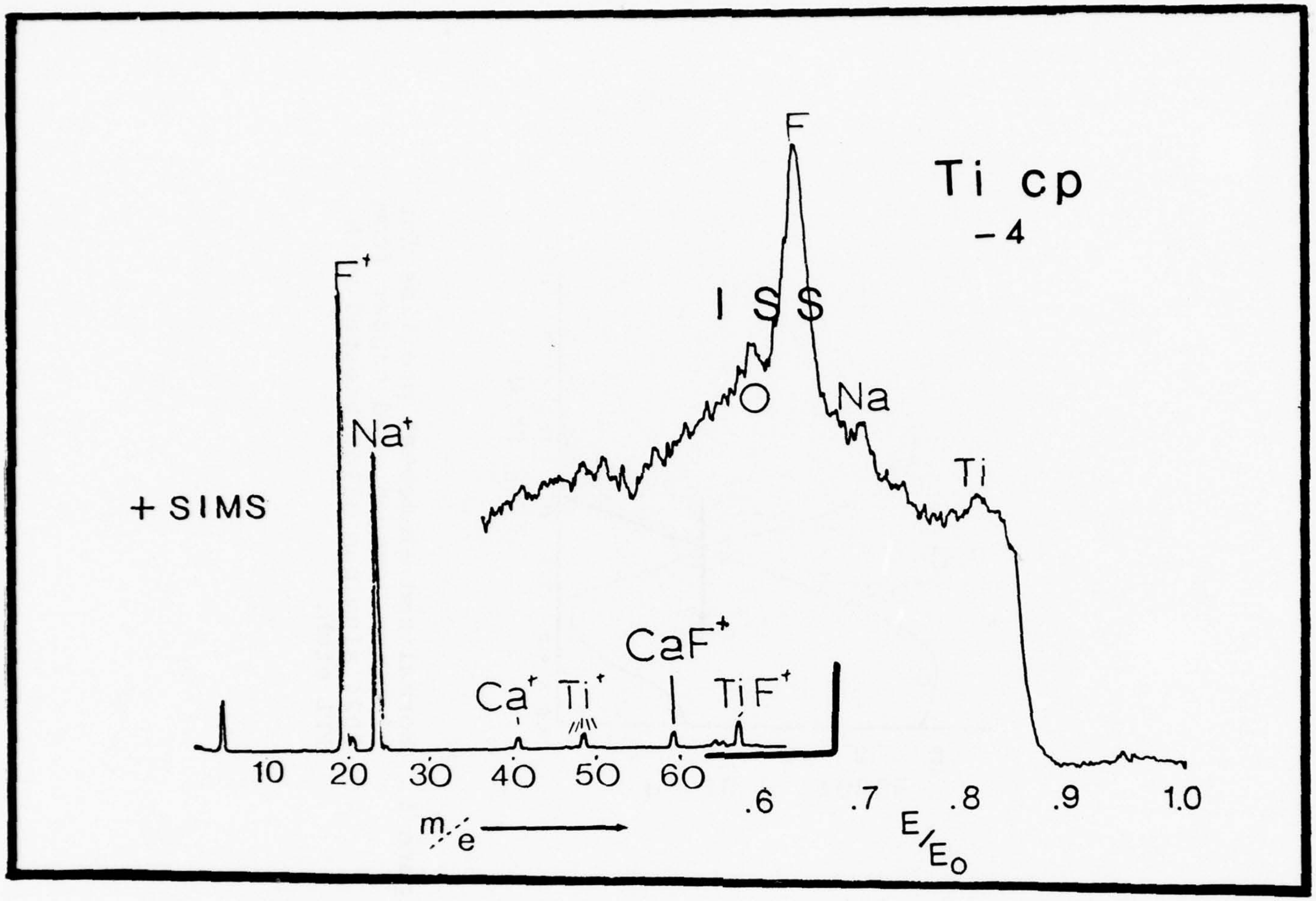

Figure 2. ISS-SIMS data for titanium treatment as follows: Sample submerged in a solution of 50 grams sodium orthophosphate, 9 grams sodium fluoride, 26 milliliters of hydrofluoric acid and distilled water to make 1 liter. Rinse in running tap water and deionized water.

Generally, the metallic adherend is covered by a layer of oxide on the surface. Since this layer of oxide is the surface to which the adhesive comes in contact, the structure and thickness of this oxide is extremely important. Several methods are available for determining the thickness of oxides on metals. An extremely accurate method when surfaces are very flat and smooth, is the ellipsometer. Optical interference methods are very simple and provide accurate answers for many materials. More recently, scanning electron microscopy has been applied to the measurement of thicknesses by bending the specimen until the oxide film breaks and then observing the broken film. Such work is illustrated by the research done by Remmel which provided not only the thickness of oxides on aluminum alloys but also an acceptance classification for the oxide.[15] A very useful method which both chemical data and thickness information is gained is the sputter-etching method. This technique uses a beam of noble or active ions to slowly etch away the surface. The same beam or another sampling beam provides chemical information with depth. Rastering and gating techniques of the ion beam minimize crater edge effects. An AES elemental profile for titanium and oxygen from commercial purity titanium is seen in Figure 3. The sputtering time as shown in this figure can be equated to oxide thickness by the use of standard oxide samples prepared by anodization methods.

Some elemental analysis techniques allow the determination of electronic structure of the solid surface by probing core level electrons.[16] These methods include characteristic isochromat spectroscopy, soft x-ray appearance potential spectroscopy, and x-ray photoelectron spectroscopy. By far, the most popular of these techniques has been XPS. The XPS technology allows core level binding energies to be routinely measured and line shapes studied to allow the determination of chemical bonding

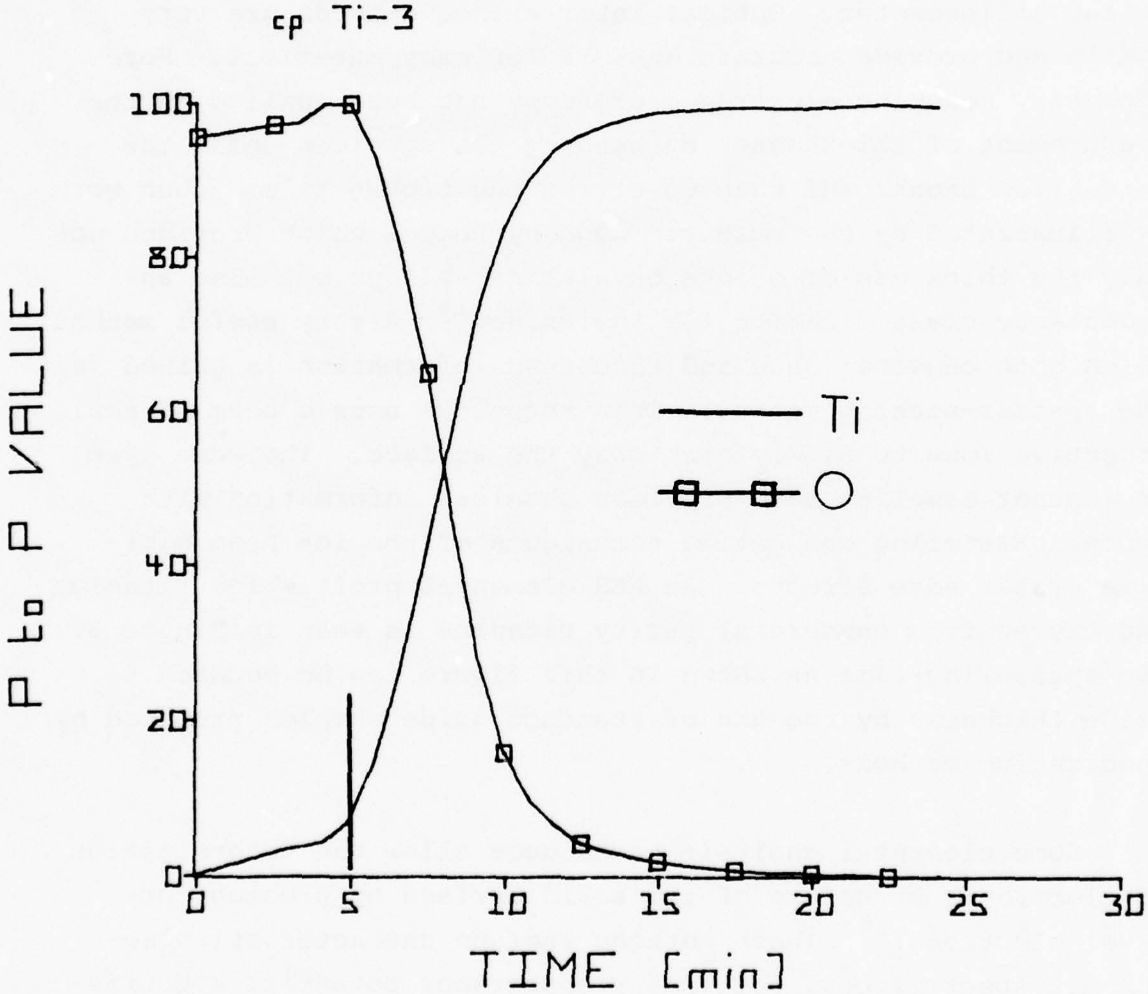

Figure 3. AES elemental profile for Ti and O from TiC.P. given nitric/hydrofluoric acid etch.

at the surface. Practical use of this technique is shown in Table III from work of Van Ooij.[17] Here the XPS results were used for the development of an adhesion model of rubber to brass. They were combined with quantitative data on adhesion of samples with different properties or compositions. Some experiments were conducted to evaluate the adhesive properties of materials other than brass. A summary of these results is given in this table. The conclusion that was reached was that high adhesion level can only be obtained with brass of 60-70% copper, with pure copper layer of thickness less than 50 nm or with a thin copper sulfide layer.

In many adhesive bonding systems, the morphology of the oxide on the adherend is all important. Such is the case with the phosphoric acid anodize for aluminum used for commercial adhesive bonding in the aerospace industry. It has been found that the formation of a porous structure is necessary for good bondability and durability. Determination of oxide morphology is best accomplished by scanning electron microscopy. An example of the columnar or porous structure seen in phosphoric acid anodized on 2024 aluminum alloy is shown in Figure 4.[18]

Although oxide growth morphology is relatively easy to determine using the scanning electron microscope, the determination of actual structure is not that simple. Most oxides formed at low temperature and particularly oxides formed in anodizing solutions tend to be very poorly crystalline (nearly "amorphous"). They may be very highly impurity stabilized and contain many defects. Therefore, conventional methods of analysis which depend on highly crystalline lattices, such as electron diffraction, do not provide much information on thin oxide films used in adhesive bonding. Likewise, x-ray diffraction provides little information on thin films because of the high penetration. Special

TABLE III

ADHESION OF SOME SELECTED MATERIALS TO RUBBER[a]

	Material	Adhesion level[b]	XPS of interface	Remarks
1.	iron, steel	0	-	no adhesion
2.	copper sheet	0	excess Cu_2S	some adhesion if undercured
3.	copper-plated steel[c]	700-900	-	good adhesion if plating thickness <50 nm
4.	steel + Cu_2S coating[d]	700-800	-	good adhesion for fresh Cu_2S layer (<50 nm)
5.	zinc sheet	100-200	ZnS formation	poor adhesion
6.	copper-plated zinc[c]	700-800	Cu_2S formation	good adhesion if plating thickness <50 nm
7.	70/30 brass sheet	700-1000	formation of Cu_2S and ZnS	good adhesion; level depends on surface preparation

[a] Vulcanized at 150°C for 25 min.

[b] In N/64 mm^2.

[c] By electroless immersion plating.

[d] Prepared from sample 3 by reaction with sulfur in liquid paraffin at 180°C.

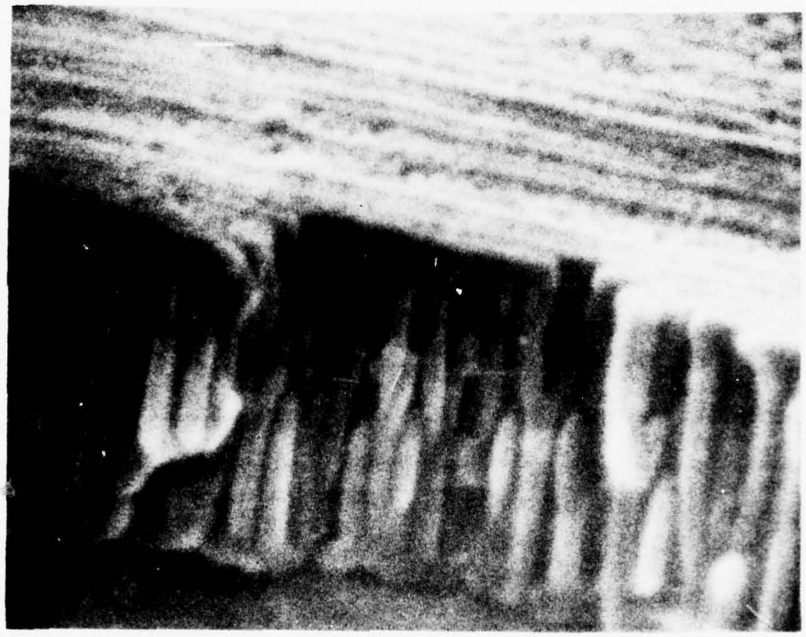

Figure 4. Scanning electron micrograph showing oxide columnar structure of phosphoric acid anodized aluminum.

techniques utilizing grazing incidence and focusing methods, such as the Seeman-Bohlin method may be used to improve surface sensitivity, but the lack of crystallinity of most films still poses problems. Such conventional techniques as x-ray diffraction should not be abandoned, however, since some effects such as stress due to mechanical working of the surface may show up in fine features of the diffraction pattern, such as peak broadening or intensity variations.

2. CHARACTERIZATION OF THE ADHESIVE

Characterization of the chemistry and morphology of the adhesive is somewhat more difficult than for the adherend. Since the adhesive is generally nonconducting when it is bombarded with charged particles or electrons, the surface charges and causes problems in surface chemical analysis. Methods of charge neutralization are available which minimize this problem. For instance, in ISS and SIMS a flood of low energy electrons removes the positive charge caused by the bombardment of ions on the surface. In techniques such as XPS, charging is not so severe but still remains a problem. XPS appears to be the technique most used for characterization of the adhesive because of the large amount of data which it provides. Table IV shows the principal features in the XPS spectra of polymers, and the information that can be gained from these features.[19] Numerous XPS results have established that absolute and relative binding energies and relative peak intensities are capable of elucidating many important aspects of polymer surface chemistry. New work on low intensity shake-up satellite peaks, located a few electron volts higher in binding energy than the main peak, have been assigned to $\pi \rightarrow \pi^*$ transitions. This is a new characteristic feature in the spectra of unsaturated polymers and offers a potential for new insight into π electron distribution. Dwight and co-workers have performed detailed analyses of photoelectron spectra of hydrocarbons and other complex molecules,[19] and of fluorocarbons.[21,22]

TABLE IV

PRINCIPAL FEATURES IN THE XPS SPECTRA OF POLYMERS (Ref. 19)

Spectral Feature	Information
I. Main Peak Position	Atom identification
II. Chemical shift	Oxidation state
III. Peak area ratios	Stoichiometry
IV. Shake-up satellites	$\pi \rightarrow \pi^*$ Transitions

Many polymers show PES features that are a combination of two or more valence states such as the example shown in Figure 5, the carbon ls levels from Mylar.[19] The main peak at 285 eV is assigned to the six carbons from the benzene ring, the peak at 286.8 eV to the two ester carbons, and the third peak at 289 eV to the two carboxyl groups. At 291.5 eV, a low intensity shake-up satellite arising from the aromatic ring can be resolved. By detailed analysis and deconvolution of such spectra, very small changes in polymer structure may be deduced.

The molecular spectroscopy techniques, infrared spectroscopy and Raman spectroscopy, are used to determine small changes in polymer surfaces by reflection techniques. Two major recent developments have improved the state of the art of molecular spectroscopy. One development was that of the Fourier transform in infrared spectroscopy, mostly due to the availability of computer techniques and the wide-spread use of interferometer methods in infrared. In Fourier transform infrared, all infrared signals are observed simultaneously and the resultant signal or interference pattern is transformed into a standard spectral distribution by Fourier analysis. The other development is that of the laser as a Raman source. The additional energy available in the laser source has enabled recording of the spectra from many solid surfaces. An example of the use of Raman spectroscopy is seen in Figure 6 where the 1096 cm^{-1} line is shown from Mylar. The effect of crystallinity is seen here by a narrowing of the band in the crystalline polymers.[23] Similar effects are observed in reflection infrared spectra. Reflection-absorption infrared spectra coupled with ellipsometry has been used to study epoxy films on metals.[24] The spectra from this work suggests that the thin films deposited on the metal from solution probably were adsorbed with a vertical confirmation with only a single bond to the surface. The latter work is an

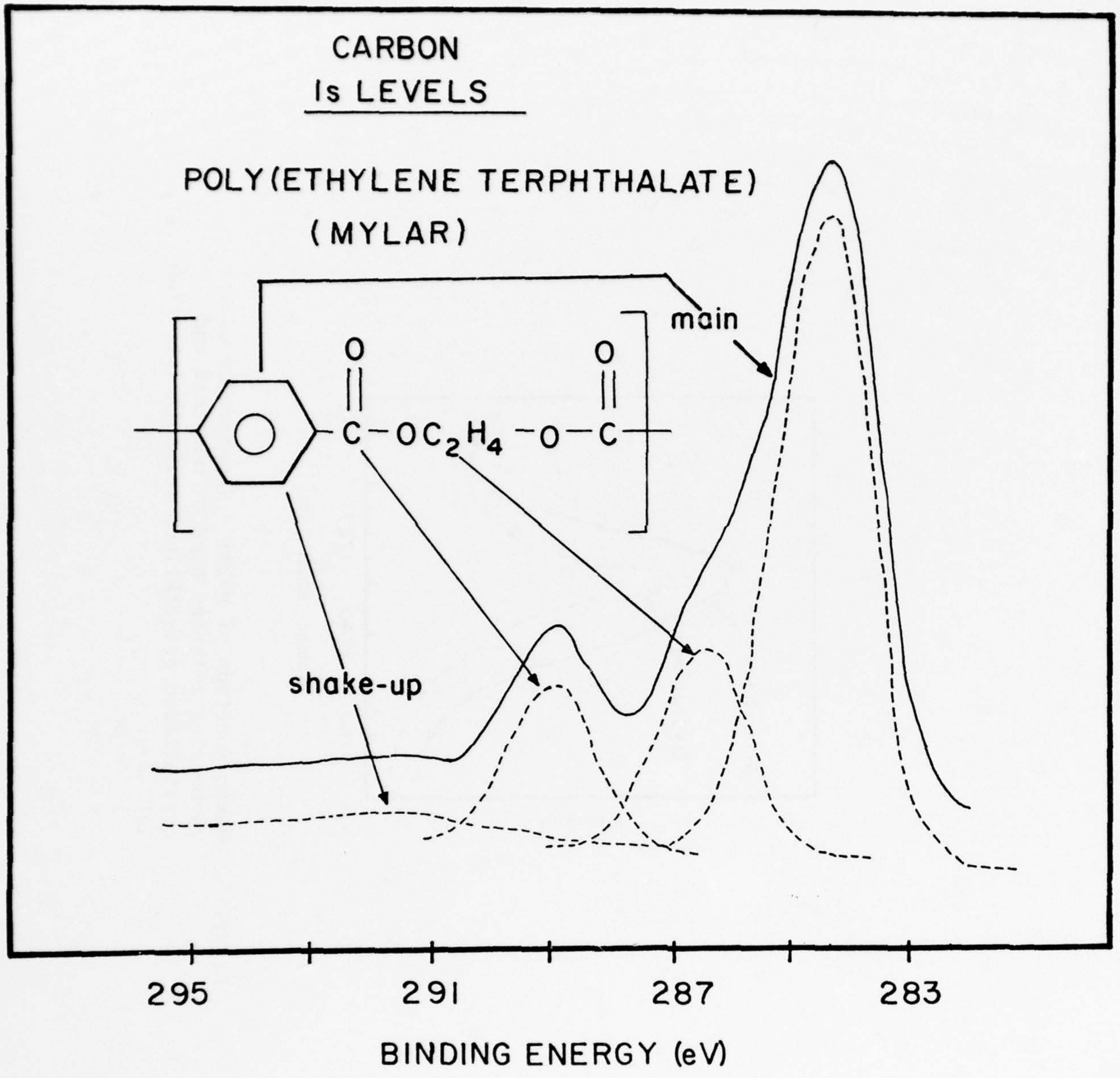

Figure 5. Carbon 1s XPS spectrum from polyethylene terephthalate (Mylar) film.

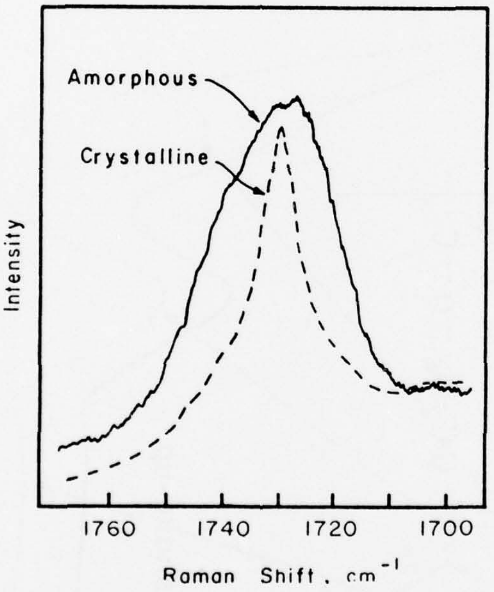

Figure 6. Raman Spectrum of Mylar - (Appearance of the carbonyl stretching band of quenched and crystallized polyethylene terephthalate from Ref. 23).

example of the study of the structure of the adhesive and its alteration upon interaction with the adherend. This interaction of the polymer with the metal or alloy is studied or indirectly inferred by adsorption, desorption, contact angle, XPS, electron tunneling, x-ray excited AES, and radioactive tracer methods. It appears that XPS provides the most powerful method for determining bonding of organic materials on oxidized surfaces. An example of such work is the research of Anderson and Swalen,[25] who studied the bonding of various organic monolayers on oxidized surfaces. They found that with successive applications of different amounts of soap films applied by the Langmuir-Blodgett technique to oxidized metal surfaces that progressive changes were observed in the x-ray photoelectron spectra from the elements in the oxides. They also found that the binding energies and peak shape changed in the soap film overlayers, suggesting partial transfer of charge, such as an acid-base interaction.[25]

Although there are numerous methods to study the interaction of the adhesive with the adherend, there are very few methods which allow the direct study of the intact bond. Even the SEM methods are not simple because the adhesive area is an insulator and tends to charge. In order to obtain good SEM pictures frequently the adhesive bond must be coated with a thin film of a conductor, such as gold or gold-palladium alloy. Nondispersive x-ray emission analysis may be performed either in a microprobe or in the SEM, but generally the elements which may be determined are limited to elements heavier than fluorine. Elements such as carbon and oxygen which are of considerable interest in adhesive bonding studies give x-ray emission spectra which are of too long a wavelength to be detected by conventional detectors. The AES microprobe which usually allows spacial analysis of surface elements of approximately 5 μm, also is plagued by the problem of surface charging on intact bonds. Special TEM methods using ultra microtomy may provide some structural information but do not provide any chemical data. Conventional replication methods on intact bonds may be used to study the interaction of adhesive and adherend as illustrated in Figure 7. Here it appears that the adhesive has not penetrated the pores of the phosphoric acid anodized oxide on 2024 aluminum alloy.

3. FAILURE SURFACES

The strength of an adhesive joint measured by means of numerous physical tests which place the joint in shear or tension or a combination of the two. These tests, in which an increasing load is placed on the joint until failure occurs, give some idea of the initial bondability of an adhesive-adherend combination. Similar tests in which the bond is under load but at high temperatures and humidity are accelerated tests of bond durability. In the past, following joint failure, visual or sometimes microscopic examination of the failure surfaces was made to determine the mode of failure. A major consideration in identifying the mechanics of adhesive joint failure is the locus of fracture, whether the joint failed by (1) cohesive fracture of the adhesive, (2) adhesive failure interfacially between the adhesive substrate interface, or (3) a complex mixture of possible failure modes. A long-time theory held by Bikerman[26] says that true interfacial failure occurs so seldom that this failure mode need not be treated in any theory of adhesive joints. He says that apparent failures in adhesion are quite common but they take place in a weak boundary layer so near the interface that the adhesive remaining on the adherend after the rupture is not visible. Such failures at a weak boundary layer have been analyzed by ISS-SIMS.[27,28,29] In that work it was shown that when the SEM and spectro-chemical tools are used to determine the morphology and the chemical species on the surface there still may be difficulties in interpreting the location of failure.

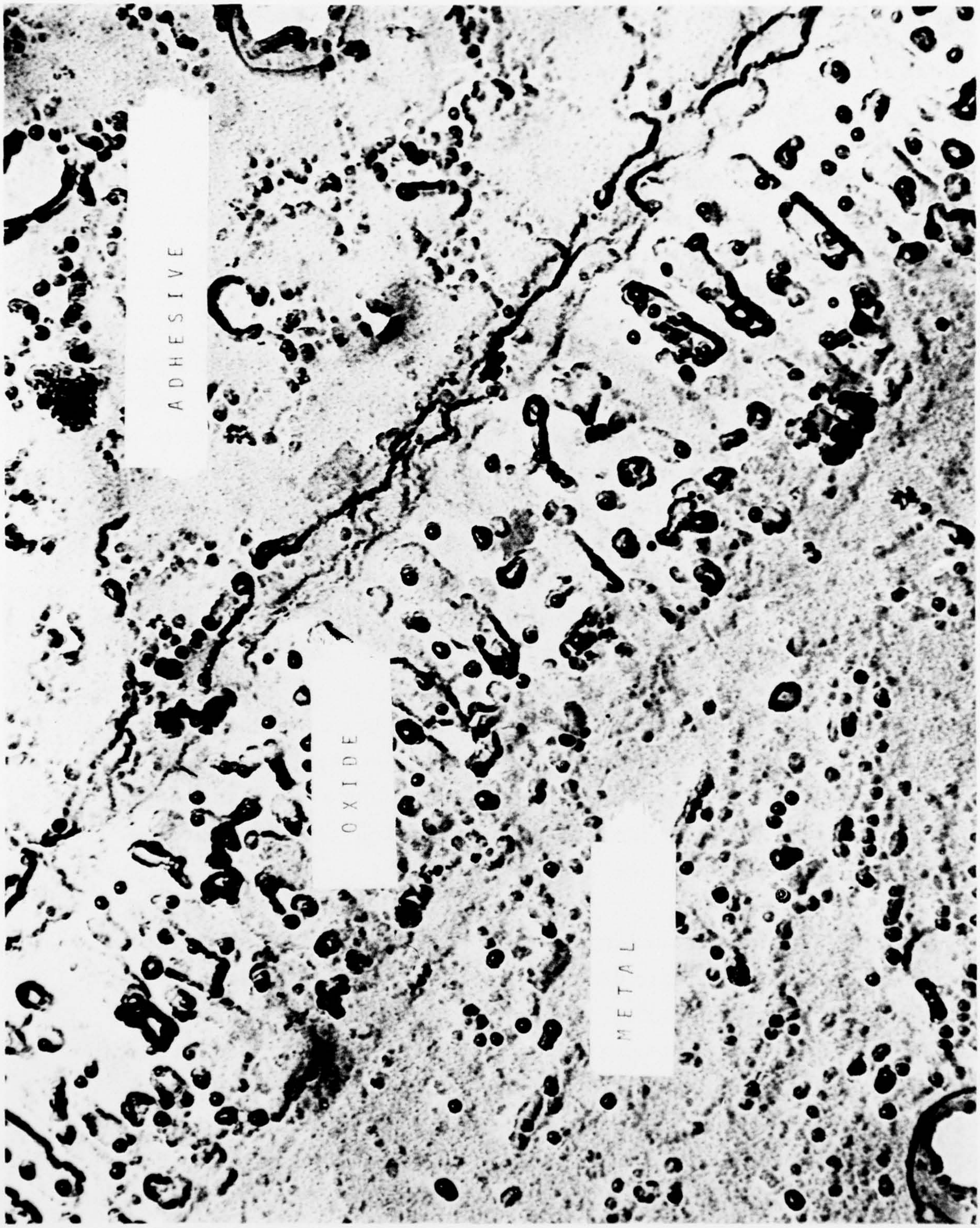

Figure 7. Transmission electron micrograph of a replicated surface of phosphoric anodized aluminum surface.

Some failures are very clear cut while in others, particularly mixed mode failures, the interpretation may not be as easy. Figure 8[28] shows a typical complex adhesive bonded system in which several interfacial regions exist. Each of the materials coming together to form these interfaces has its own individual chemical signature. The substrate, for instance, usually contains alloy elements which vary in content between the surface and the bulk. In addition to alloying elements, surface treatments leave behind elements characteristic of each treatment. For instance, the popular etch used for aluminum alloys, consisting of sulfuric acid and sodium dichromate in distilled water, leaves a detectable amount of chromium on the alloy surface. Primers often contain anion and cation which can be followed by spectro-chemical methods. Such additives, such as strontium chromate are usually placed in the primer to provide corrosion protection in the coating. The adhesive often contains fillers such as aluminum or aluminum oxide to provide conductivity or to match coefficient of thermal expansion. Using these differences in chemistry, it was possible[28] to determine a failure mechanisms occurring in a thick-thin wedge specimen designed to concentrate stresses along the interface. This work showed an initial locus of failure which changed during the period of testing at high temperature and humidity.

In addition to determining what elements exist on failure surfaces, it is most important to look at these surfaces using optical microscopy and SEM. Dwight and co-workers[30] have used the SEM extensively, especially in cohesive failures to attempt to understand the mechanism by which failure occurs. Plastic and brittle failure mechanisms are easily differentiated in the polymer surface. Initial and final flaws and voids may be determined and are of importance in evaluating joint performance. Some of these features which may be observed by microscopic techniques are shown in Figure 8.

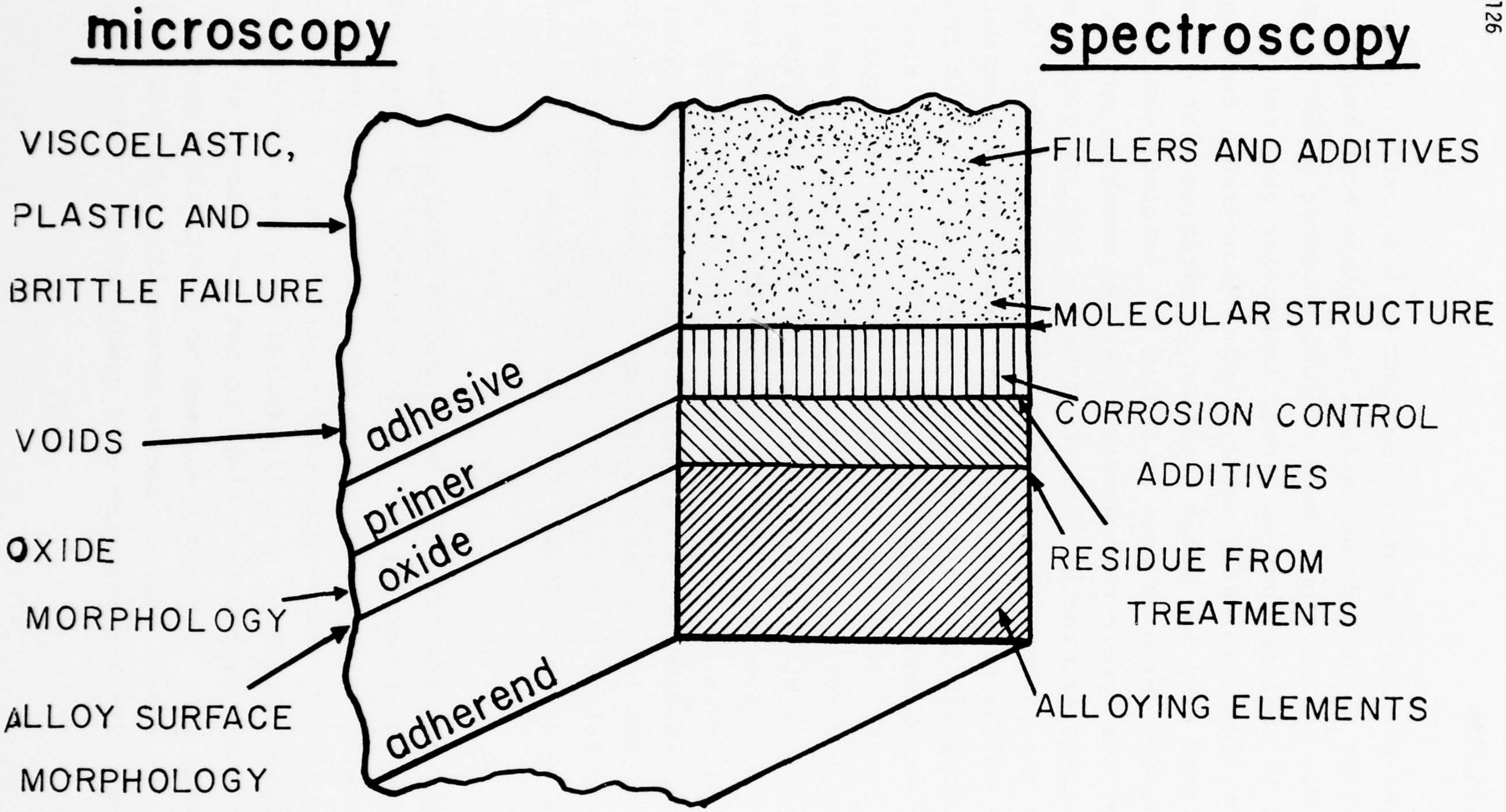

Figure 8. A typical complex adhesive bond and the role of microscopy and spectroscopy in the study of the materials and interfaces of that bond.

Detailed analysis of micrographs is frequently necessary to determine exact mode of failure and obtain most benefit from microscopic examination. Some failure surfaces appear simple and easy to analyze, but on closer inspection turn out to be different from originally anticipated. Micrographs from matching surfaces of a lap shear specimen of titanium with a commercial adhesive FM400 is seen in Figure 9. Original visual examination of the specimens suggested that the matching patterns on both sides originated from the adhesive pulling out in the areas of the pattern on the other side of the adhesive. Detailed analysis of the micrographs, however, shows that the actual joint contained nearly 50% void and that the pattern shown is from the adhesive which was originally along the knots of the tricot carrier cloth. Such air entrapment, especially on supported adhesives, is not unusual. Bascom and Cottington[31] have shown air entrapment with structural adhesive films using nylon support cloth. They have found that it is possible to increase bond strength as much as 30 percent by complete void removal. Microscopic examination of 14 typical adhesive bond joints obtained from aerospace industries showed varying amounts of void formation in adhesives with support cloth. Random support mats appeared to cause or foster less void formation in the bond line.

Other methods have also been used to determine the locus of failure in structural and adhesive joints. Gettings and co-workers,[32] using a combination AES and XPS, have demonstrated that the joints, which appeared visually to fail at the metal oxide-epoxy interface, actually failed in a far more complex way with the crack propagating close to but not exactly at the interface. When such joints are exposed to water, the fracture path is found to change and is exactly between the adhesive-metal interface. Similar research used complementary techniques, XPS

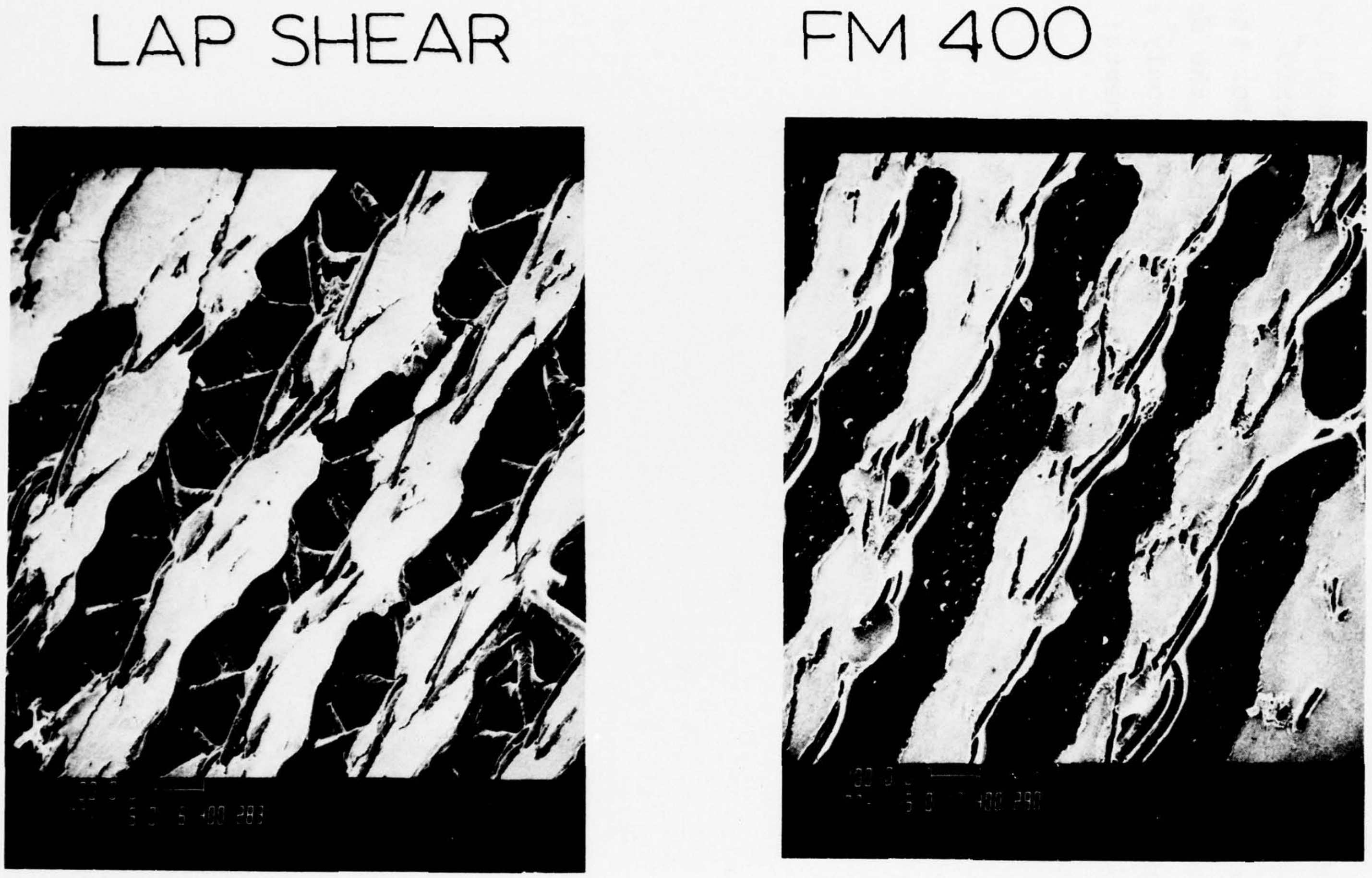

Figure 9. Scanning electron micrographs of matching failure surfaces from a lap shear specimen of Ti6Al4V - FM400 adhesive.

and SIMS, to study the interaction of polysiloxane-metal oxide interfaces.[33] Detection from the iron adherend of $FeSiO^+$ radicals from the primer has strong direct evidence for the formation of a chemical bond, probably Fe-O-Si, between the metal oxide and the polysiloxane primer. Such studies not only elucidate the locus of failure but also clarify the fundamental processes between adhesive and adherend.

SECTION III
CONCLUSIONS

Spectro-chemical techniques combined with microscopy can usually be used to analyze the adherend and adhesive surfaces and to gain a clear picture of where an adhesive joint failed during testing or service. Methods are also available for studying the fundamental interaction of polymers and polymer precursors with metals and metal oxide surfaces. The study of the undisturbed adhesive bond, however, is more difficult. Few techniques really tell very much about the intact bond, and a definite need exists for such methods.

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