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AFML-TR-79-4178 - PT-2
Part II

# FAILURE MECHANISMS AND INTERPHASE CHEMISTRY OF GOLD FILMS ON Ti6Al4V

## Part II. Etching of Ti6Al4V and Its Effect on Evaporated Gold and Commercial Adhesive Adhesion

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JANUARY 1980

TECHNICAL REPORT AFML-TR-79-4178, Part II
Final Report for period July 1978 to October 1979

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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This technical report has been reviewed and is approved for publication.


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| 1. REPORT NUMBER<br><br>AFML-TR-79-4178. Part II | 2. GOVT ACCESSION NO.<br><br>$AO\mathcal{S}/727$ | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle)<br>Failure Mechanisms and Interphase Chemistry<br>of Gold Films on Ti6Al4V<br>II. Etching of Ti6Al4V and Its Effect on<br>Evaporated Gold and Commercial Adhesive | | 5. TYPE OF REPORT & PERIOD COVERED<br>Internal<br>July 1978 to October 1979 |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| 7. AUTHOR(s)<br><br>W. L. Baun | | 8. CONTRACT OR GRANT NUMBER(s) |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Air Force Materials Laboratory<br>Air Force Systems Command<br>Wright Patterson Air Force Base, Ohio 45433 | | 10. PROGRAM ELEMENT, PROJECT, TASK<br>AREA & WORK UNIT NUMBERS<br>Project 2419, Task<br>241902, WU # 44 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>Air Force Materials Laboratory (AFML/MBM)<br>Air Force Wright Aeronautical Laboratories<br>Wright Patterson Air Force Base, Ohio 45433 | | 12. REPORT DATE<br>January 1980 |
| | | 13. NUMBER OF PAGES<br>37 |
| 14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) | | 15. SECURITY CLASS. (of this report)<br><br>Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING<br>SCHEDULE |

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

18. SUPPLEMENTARY NOTES

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

Adhesive Bonding, Ti6Al4V, Surface Treatments, Surface Chemistry,
Gold, Vapor Deposited, Failure Mechanisms, Weak Boundary Layer,
Locus of Failure

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

This work is part of a program which looks at the effects of sur-
face treatments on surface chemistry and morphology of titanium
alloys with reference to adhesive bonding. Here gold is vapor de-
posited on Ti6Al4V which was prepared to simulate conditions of
etching and aging which might be encountered during processing and
use. Although this model system of gold on Ti6Al4V is not a direct
analogy to adhesive bonding, certain similarities do exist and the
(cont'd)

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system provides interesting information on bond failure mechanisms

Titanium 6 aluminum 4 vanadium alloys were etched for varying periods of time in aqueous solution of hydrofluoric acid and ammonium phosphate.  Following etching, one-half of the specimens were covered with vacuum evaporated gold while the other half were bonded with a commercial adhesive.  Gold adhesion to the alloys was evaluated by peel tests and lap shear tests using the same commercial adhesive.  The uncoated specimens were evaluated by lap shear tests.  Adhesion of Ti6Al4V to gold and to the commercial adhesive was directly proportional to the length of time the specimen was etched.  Although etching in $HF/NH_4H_2PO_4$ resulted in a rather rough surface, there were only subtle differences with increasing time. Surface chemistry changes suggest selective etching of the alpha phase and subsequently larger influence of the β phase in bonding.  Heating of the gold on Ti6Al4V resulted in improved adhesion, probably by diffusion mechanisms.  Exposure to steam resulted in bond degradation in both gold/Ti6Al4V and in adhesive/Ti6Al4V systems.  The adhesive bonding results for the etched specimens were compared to expected performance based on "attachment site" theory.  Excellent agreement for both gold on Ti6Al4V and commercial adhesive on Ti6Al4V was observed.  Degradation of the bond due to steam followed the same form in both systems.

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, "Non Metallic 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.

Valuable discussion with N. T. McDevitt is acknowledged.
Gary Fugate and Donald Thomas are thanked for careful experi-
mental work. Some bonding and testing of specimens was capably
carried out by A. K. Behme, Jr.

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## INTRODUCTION

Many chemical etches are used in the treatment of metals and alloys for adhesive bonding. Each of these chemical pretreatments affect the composition of the surface either by introducing impurities or by increasing or decreasing the concentration of alloy elements at the surface. Commercial adhesives may be a very complicated proprietary mixture which can contain resins, curing agents, rubber-forming components, fillers, scrim cloth and impurities. The combination of commercial alloys and commercial adhesives can present an extremely complicated chemistry at the interface in adhesive bonded joints. This work reports on the interaction of the commercial adhesive PL 729-3* studied on Ti6Al4V which had been exposed to varying amounts of etching. It was hoped that the change in the length of etching time would provide different numbers or quality of "attachment sites"[1] for adhesive bonding. In order to simplify the study of the effect of etching on titanium 6 aluminum 4 vanadium, a concurrent study of the adhesion of gold to this alloy was also carried on. It was felt that the gold/alloy surface would provide a less complicated interface or interfacial volume compared to the commercial adhesive, while still modeling the behavior of adhesive-adherend interphase.

* B. F. Goodrich Co.

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# SECTION II
## EXPERIMENTAL

ISS/SIMS analysis of surfaces was carried out using commercial ion scattering instruments (3M Co., St. Paul, Minn.) Model 520, equipped with a Model 100C quadrupole mass spectrometer (UTI), Sunnyvale, CA), equipped with a simple three element cylindrical energy analyzer in front of the quadrupole filter. The experimental set-up for both techniques is shown in Figure 1. ISS is based on the principal that when a surface is bombarded with low density gas ions ($^3$He, $^4$He, $^{20}$Ne, or $^{40}$Ar), the measurement of the energy distribution of the back scattered ions will show energy losses which can be predicted by a simple binary elastic collision theory.[2,3] An elemental composition of the first atomic layer may be obtained by scanning the energy ratio $E/E_o$, where E is the energy of the rebounding ion and $E_o$ is the energy of the ion before encountering the surface. Sufficient resolution usually may be achieved for mass ranges for masses up to 83 by changing the probing noble gas ions. That is, heavy element ion beams are used for high elements. Spectra shown in this work were obtained at 2500 v ion energy, using two probe ions, $^4$He or $^{20}$Ne. The SIMS system analyzes the mass of positive ions sputtered from the surface[4] by the same beam used for ion scattering and is capable of detecting masses up to mass 300 with a resolution of at least one mass unit over the entire range. A typical set of ISS/SIMS data is seen in Figure 2. Here one can see that in the ion scattering spectrum, only peaks due to oxygen and titanium are observed. In the background region between the oxygen and the titanium peaks, it is obvious some impurity elements are also giving rise to signals. Therefore, this spectrum illustrates one of the problems of ion scattering, not being able to resolve close elements in the periodic table, especially in certain materials where high backgrounds may exist. In the SIMS spectrum elements appearing nearby in the periodic table may easily be separated. Here we can see in addition to the alloying

elements (titanium, aluminum, and vanadium), small amounts of sodium, magnesium, zinc and calcium. Note that molecular species are observed in SIMS spectra such as $TiO^+$ and may give important clues into the structure of the ions on the surface. In addition to using surface Chemistry analytical techniques to examine surfaces following failure, visual and microscopic inspections were also used. In this phase of work tensile lap shear specimens were analyzed following testing. Conventionally, after testing, visual or sometimes microscopic examination of the surface is made to determine the mode of failure. If adhesive remains on each adherend and failure appears to have occurred in the adhesive itself, the failure is termed cohesive failure. If the failure appears to have occurred at the interface between the adhesive and adherend, it is termed adhesive failure. It is unlikely that any pure adhesive failures take place where true wetting of the surface has occurred. Frequently, it is not simple using visual examination to determine following testing whether an apparent adhesive failure occurred at an interface due to improper wetting or at some new interface leaving behind a thin layer of adhesive. ISS/SIMS has been used to provide useful information on the locus of failure in an adhesive joint even when the failure occurs near the original interface and includes parts of both the adhesive and adherend.[5] Surface Chemistry techniques are especially applicable when failure takes place in a weak boundary layer.[6] Gold was chosen to study for numerous reasons, one of which was the high sensitivity of ion scattering for gold on the titanium surface following apparent interfacial failure at the gold/ alloy interface.

Gold films of 500nm (measured by quartz crystal) were deposited from a molybdenum boat in an ultrahigh vacuum chamber which was pumped to an initial vacuum of at least $1 \times 10^{-7}$ Torr. Table I shows the sample designation and the preparation steps including cleaning with an abrasive pad and detergent, etching for different periods of time with $HF/NH_4H_2PO_4$ (25 ml/50g in 1 ℓ. aqueous solution) evaporation of the gold, first tape test, the bonding of the commercial adhesive at $300°F$ followed by the second tape test. The

duplicate specimens were then tested in tension and diagnostics performed on the failure surfaces. The entire procedure was repeated. Substantially the same results were obtained. The single overlap specimens were tested in a Tinius Olsen testing machine using a crosshead speed of 0.02 in/min.

# SECTION III
## EXPERIMENTAL RESULTS

Table I shows, in addition to the specimen preparation techniques, the tape test results for gold adhesion by a tape peel test ($180^{\circ}$) on titanium 6 aluminum 4 vanadium. This simple technique using pressure sensitive tape is usually attributed to Strong[7] who first used the method to evaluate cleaning procedures for substrates on which Al films were deposited for telescope mirrors. The test as applied here is purely qualitative. When used in this qualitative way, adhesion is usually classified according to whether the film is wholly or partially removed from the substrate or not removed at all. Normally only these preceding three failure conditions are considered in peel testing.[8,9] Four types of failures were observed here and are illustrated in Figure 3. It was found that when no surface preparation other than cleaning was performed on the as-received alloy, that the peel test removed all of the gold from the oxide surface and is noted here as interfacial failure (type 1, on figure). Even after the specimen was heated to $300^{\circ}$F, all of the gold still was removed interfacially from the specimen surface. When the specimens were etched one-half minute, a point at which hydrogen evolution just begins and etching is very light, all of the gold is again removed in the initial tape test. Similarly, prior to the second peel test the titanium and gold film was heated to a temperature approximating the temperature used in adhesive bonding. Following the heating and tape test some of the gold remains on the titanium surface (Type 2). When the specimen is etched for one minute, definite etching takes place and the initial tape test shows some gold remaining on the surface. When this specimen is heated, the adhesion further improves and all of the gold is left on the surface (type 3), the tape and adhesive being removed from the gold. When the titanium alloy specimen is etched for three minutes, the initial tape test shows all of the gold remaining on the surface. Following heating to $300^{\circ}$F, the adhesion of the tape adhesive to the gold and the gold to the alloy has improved to the

point where cohesive failure in the adhesive is observed. That is, a film of adhesive remains on the gold surface following peel. This is noted in the table and the figure as condition number 4. This sequence of specimens has gone from complete interfacial failure of the gold on the titanium surface to the point where adhesion is sufficiently good that the adhesive on the tape is removed and remains on the gold. Apparently, the peel strength of the gold on titanium exceeds the peel strength of the adhesive on the tape or the cohesive strength of the adhesive. Mittal,[8] reviewing unpublished work of Beno, reports that peel tests using pressure sensitive tape are limited to adhesion of about $5 \times 10^5$ Pa. A rough estimate on films evaporated on unetched Ti6Al4V (all Au removed) indicated values of the same magnitude. The sequence of cleaning, etching and evaporation, followed by moderate heating always resulted in the best adhesion of the gold to the alloy surface. Heating of the films may result in annealing stress in the film or the formation of a desirable interface[10] by diffusion mechanisms. Such improvement with heating or aging at ambient conditions has been observed for many metals[11] on a variety of substrates.

Following bonding and curing of the adhesive for one hour at $300^{\circ}$F, the ultimate strength of the bond was determined by testing of the single overlap specimens (1.0 in x 0.5 in overlap). This method uses tangential shear stresses, but in practice the stresses at the interphase appear in a very complex manner due to variations in the bulk properties of the materials and inhomogeneities at the interphase.[12]

Results of lap shear tests from duplicate samples from two separate experiments are shown in Figure 4. Here the open bars show results from samples which were prepared and aged at room temperature previous to the testing. The shaded bars show results from the specimens which were prepared and held for 16 hours at elevated temperature ($90^{\circ}$C) and 100% relative humidity. Results in Figure 4A show that the titanium 6 aluminum 4 vanadium adherends coated with gold increase in strength with an increase in time of etch in the HF/$NH_4H_2PO_4$. Similarly, it can be seen that exposure to the high relative humidity

decreases the lap shear strength in an appreciable amount.  In
Figure 4B, results are shown for bare titanium 6 aluminum 4 vana-
dium alloys which were subjected to the same etch conditions as the
alloys which were used in the vacuum evaporation studies.  Also
shown here are results from specimens held for 16 hours in condens-
ing steam.  It can be seen that the trend here is the same as in
the gold coated specimens; that is, the samples increase in lap
shear strength with an increase in etch time.  The trend of the
appreciable drop in strength following exposure to condensing
steam also is similar to the results for samples which were coated
with gold.

No data were found in the literature for shear of gold on
titanium but Lin[13] measured the adhesion of several metal films on
glass and MgO by tangential shear and obtained a value of $3 \times 10^5$
Pa for Au on glass, which compares to the value measured here of
$7 \times 10^5$ Pa on the unetched Ti6Al4V specimen.  With etching, adhesion
improved about 30X to $2.2 \times 10^7$ Pa.

Although increasing etching time on the adherends appreciably
improved adhesion, the corresponding changes in morphology and
chemistry were very subtle.

Since the original as-received material is somewhat rough, an
increase in roughness with longer etching periods is not greatly
obvious as seen in Figure 5.  Scratches are visible on the unetched
specimen which disappear upon etching.  Note that the light colored
phase here is usually identified as the beta phase.  Some changes
in surface chemistry are observed with increasing etching, but again
these are not gross changes as seen in the ISS spectra in Figure 6.

SIMS data for the same samples are seen in Figure 7.  The
definite drop in aluminum concentration is noted from the very light
etch to the heavier etch, and the corresponding increase of the vana-
dium content is observed.  The probability of small changes in hydro-
carbon type and content and in alkali emission are also observed.

As was mentioned earlier, sometimes it is difficult using
visual or microscopic examination to determine after testing whether

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an apparent adhesive failure occurred at the interface due to improper wetting or at some new interface leaving behind a thin layer of adhesive. When studying the interaction of the evaporated gold with titanium surfaces, one does not have this problem since it is very visible. However, it is still difficult visually to quantify the amount of gold remaining in patches on the surface following failure. Ion scattering provides an excellent method of quantifying the gold remaining on the surface since it is extremely sensitive to gold, and the beam may be rastered over a large area to give an averaged analysis. A typical set of ISS spectra are seen in Figure 8 for a) the original surface, and b) the surface following the peel test on the gold for a specimen etched for 30 sec. Even higher sensitivity for the gold on the surface may be achieved by switching to the heavier probe gas $^{20}Ne$. The corresponding SIMS data are shown in Figure 9. Here the most striking feature is the great increase in $Na^+$ on the failure surface and its effect on the total yield of the other ions. Also obvious is the virtual disappearance of $F^+$. SIMS proved exceptionally useful for looking at the gold failure surface in determining whether the weak boundary layer of impurity atoms continues to adhere to the gold failure surface. Such a weak boundary layer is commonly achieved when the surface is heated for a prolonged period in air previous to gold deposition. This weak boundary layer consists primarily of alkalis and oxygen. An example of a typical surface analysis of a gold surface is seen in Figure 10 where large amounts of sodium are seen in both spectra. Another simple weak boundary layer forming technique is washing or holding of the specimen in very hot tap water for long periods of time. This results in the concentration at the surface of the titanium alloy of the impurity elements in the water, particularly calcium, magnesium and sometimes iron. An example of ISS/SIMS data from such a weak boundary layer (WBL) on gold is seen in Figure 11 from an earlier report[14] where adhesion and failure surfaces were studied. The usual ISS counting rate on the peak was 100,000 counts/sec on pure gold. As can be seen, the coverage of weak boundary layer elements diminished this intensity approximately 10 times. Even though the Ti alloy surface visually appeared clean, some Au was still observed by ISS

on that surface.  The majority of WBL failures were not pure inter-
facial failures but rather a mixed mode similar to that illustrated
in Figure 12 in substantial agreement with the predictions and
theories of Bikerman.[15]

# SECTION IV
## DISCUSSION

The results for adhesion behavior of gold on Ti6Al4V and an adhesive on Ti6Al4V discussed above are compared in this section with the theory of attachment sites developed by Lewis and Natarajan. This new model says that depending upon the boundary or interphase[16] strength,intermediate joint strengths exist and follow a curve of the general form shown in Figure 13 (taken from Ref. 1).

This model for adhesive joint strength was proposed based on the hypothesis that the strength of the boundary layer is directly proportional to the number of mechanically effective "attachment sites", $Z_e$ in the interfacial area between the bulk adhesive and bulk adherend. Weak boundary layers are characterized by the existence of few or no operative attachment sites resulting in a low joint strength, $S_o$, exhibiting a boundary (adhesive) failure mode. As the number of effective attachment sites increases by chemical and/or physical modifications or treatment of the participating surfaces, the joint strength also increases accompanied by a change to a mixed mode of joint failure. At a certain saturation level of effective attachment site density $(Z_c)$, an optimum boundary layer strength is reached where the boundary layer strength is equal to or greater than the cohesive strength of the bulk adhesive. Increasing the number of attachments beyond this point does not increase the joint strength; the strength of the joint has reached a so-called Cohesive Plateau, $S_c$. In the application of this model, it is assumed that the thickness of the adhesive bond is much greater than the thickness of the boundary layer. In the attainment of the Cohesive Plateau, failure of the "bulk" adhesive (although constrained) must be possible; no direct perturbation by the boundary layers must exist.

The nature of these "attachment sites" cannot yet be described in quantitative terms other than that they are believed to be of morphological size rather than molecular size. These boundary layer attachment sites can best be described as being microscopic areas of attachment at the interface that are capable of contributing to the mechanical strength of an adhesive joint.

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The model of adhesive joint strength proposed in Ref. 1 has the following features that must be examined, verified cr modified and finally established by way of future theory and experimentation:

1. The attachment site theory proposed that adhesive joint strengths are controlled by the degree of interfacial attachment at the boundary layer and the rheological strength of the adhesive material.

2. An equation of state for adhesive joint strength is proposed which can be analyzed in terms of the molecular characteristics of the materials that constitute the adhesive joint. The application of an interaction matrix analysis to this equation has been demonstrated.

3. It is proposed that the model of adhesive joint strength can be used to describe the environmental behavior of adhesive joints by considering that the deterioration of the joint is a result of the destruction of attachment sites in the boundary layer (by interfacial corrosion, thermal degradation, etc.) as seen in Fig. 14 where there is a conversion of $Z_e$ sites to $Z_o$ sites in a stressed bond in a hostile environment. The diagram shows the number of attachment sites are being destroyed at a rate $dZ_e/dt$. In time, when the effective number of Z's remaining reach a critical value, the boundary layer can no longer support the bond, and failure occurs.

The joint strength for single overlap shear specimens is plotted in Fig. 15 vs. etch time. Here it is seen that both gold on Ti6Al4V and commercially adhesive bonded Ti6Al4V follow qualitatively the form of the attachment site theory. The fact that the all cohesive failure area (high joint strength) does not show zero slope may suggest a continuing effect on the polymer boundary area by the adherend even after sufficient sites have been created to cause 100% adhesion (and subsequently cohesive failure). The area shown as B, or boundary failure, does not occur in these specimens and is shown as a dashed line in an area of "negative etch", suggesting such a surface might be obtained if attachment sites were

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destroyed. The mixed failure surfaces B/C and C/B were observed with the cohesive component increasing with increasing joint strength. Interfacial (Au/TiO$_2$) failure was observed on all gold coated specimens.

Exposure to condensing steam showed a similar decrease in joint strength in both series. Many workers have studied the degradation of adhesive bonds and polymer/metal interfaces[17-20]. The fact that in this work the adhesive/alloy bond and the gold/alloy bond is degraded similarly may be extremely significant, pointing to the alloy (oxide) surface as the region in which attachment sites are being destroyed rather than to a degradation of the polymer sites.

# SECTION V

## CONCLUSIONS

These experiments show that initial adhesion of both gold and a commercial adhesive of Ti6Al4V are increased with increasing etching time of the titanium alloy. Exposure of the bond to steam resulted in a similar decrease of the bond strength, perhaps suggesting degradation mechanisms at the interphase rather than in the adhesive. Heating of the evaporated Au/Ti alloy always resulted in improved adhesion, presumably by stress relief and diffusion mechanisms. The change in roughness with increased etching was subtle, perhaps indicating a dependence on surface chemistry and/or other aspects of the interface. A comparison of these experimental results and attachment site theory showed good agreement.

## TABLE I
### TAPE TEST RESULTS FOR Ti6A14V ETCHED FOR INCREASING
### PERIODS OF TIME BEFORE EVAPORATION OF GOLD

| SAMPLE | CLEAN | ETCH TIME | EVAP AU | TAPE TEST #1 | BOND LAP SHEAR | TAPE TEST #2 |
|--------|-------|-----------|---------|--------------|----------------|--------------|
| 014-1 | Ab. Pad | 0 | X | 1 | 729-3 | 1 |
| | + Det, dil NaOH | | | | $(300^{\circ}F)$ | |
| 014-2 | " | 0.5 | X | 1 | PL 729-3 | 2 |
| 014-3 | " | 1.0 | X | 2 | PL 729-3 | 3 |
| 014-4 | " | 3.0 | X | 3 | PL 729-3 | 4 |

TAPE TEST CODE:
INTERFACIAL, $Au/TiO_2$ = 1
MIXED (Some Au Remains) = 2
INTERFACIAL ADHESIVE/Au = 3
COHESIVE IN ADHESIVE, = 4
(adhesive remains on Au

## TABLE II
### LAP SHEAR TEST RESULTS OF Au COATED
### AND UNCOATED Ti-6Al-4V/729-3
### SINGLE OVERLAP SPECIMENS

| Specimen | Etch time, min | Expose to 16 hr. steam | Au Coated Ultimate Strength MPa | $lbs/in^2$ | Mode of Failure |
|---|---|---|---|---|---|
| 014-1 A | 0.0 | | 0.83 | 120 | $Au/TiO_2$ |
| B | 0.0 | X | 0.48 | 70 | $Au/TiO_2$ |
| 014-2 A | 0.5 | | 12 | 1740 | $Au/TiO_2$ |
| B | 0.5 | X | 7.9 | 1140 | $Au/TiO_2$ |
| 014-3 A | 1.0 | | 16.8 | 2430 | $Au/TiO_2$ |
| B | 1.0 | X | 13.1 | 1900 | $Au/TiO_2$ |
| 014-4 A | 3.0 | | 21.9 | 3180 | $Au/TiO_2$ |
| B | 3.0 | X | 17.2 | 2500 | $Au/TiO_2$ |
| Uncoated | | | | | |
| 014-5 A | 0.0 | | 18.2 | 2650 | interfacial[*]/ cohesive |
| B | 0.0 | X | 18.2 | 2650 | interfacial[*]/ cohesive |
| 014-6 A | 0.5 | | 30.8 | 4470 | mostly cohesive |
| B | 0.5 | X | 26.3 | 3820 | mostly cohesive |
| 014-7 A | 1.0 | | 33.7 | 4900 | cohesive[**] |
| B | 1.0 | X | 31.6 | 4590 | mostly cohesive |
| 014-8 A | 3.0 | | 39.9 | 5780 | cohesive[**] |
| B | 3.0 | X | 37.4 | 5430 | mostly cohesive |

[*] failure interfacial at adhesive/$TiO_2$

[**] adhesive itself fails cohesively

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SPUTTER ION GUN

ISS SIGNAL

SCATTERED IONS

SPECIMEN

SPUTTERED IONS

SIMS SIGNAL

QUADRUPOLE MASS ANALYZER

ENERGY FILTER

RGA FILAMENT
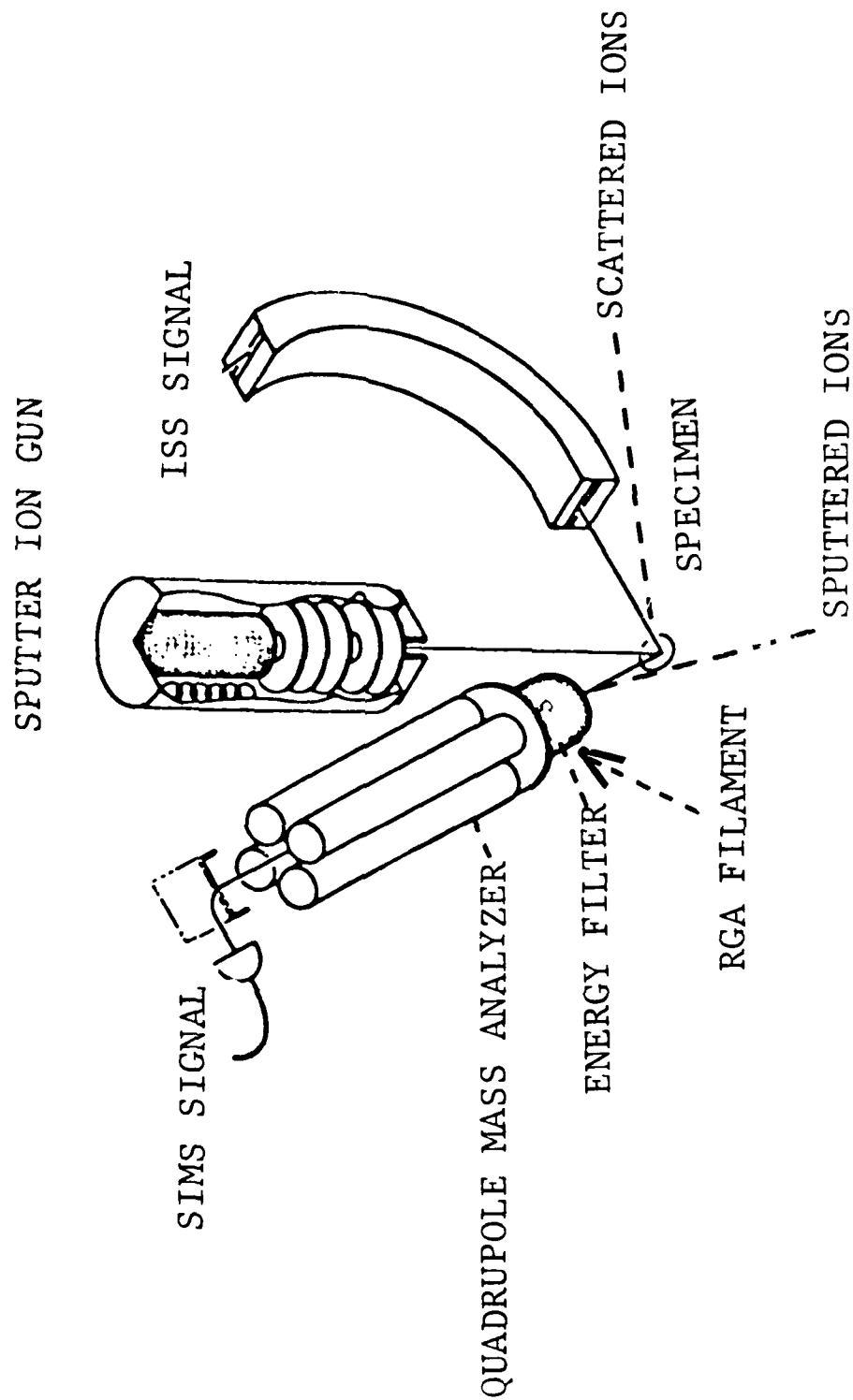
Figure 1. The Experimental Setup for ISS-SIMS (90° Scattering).

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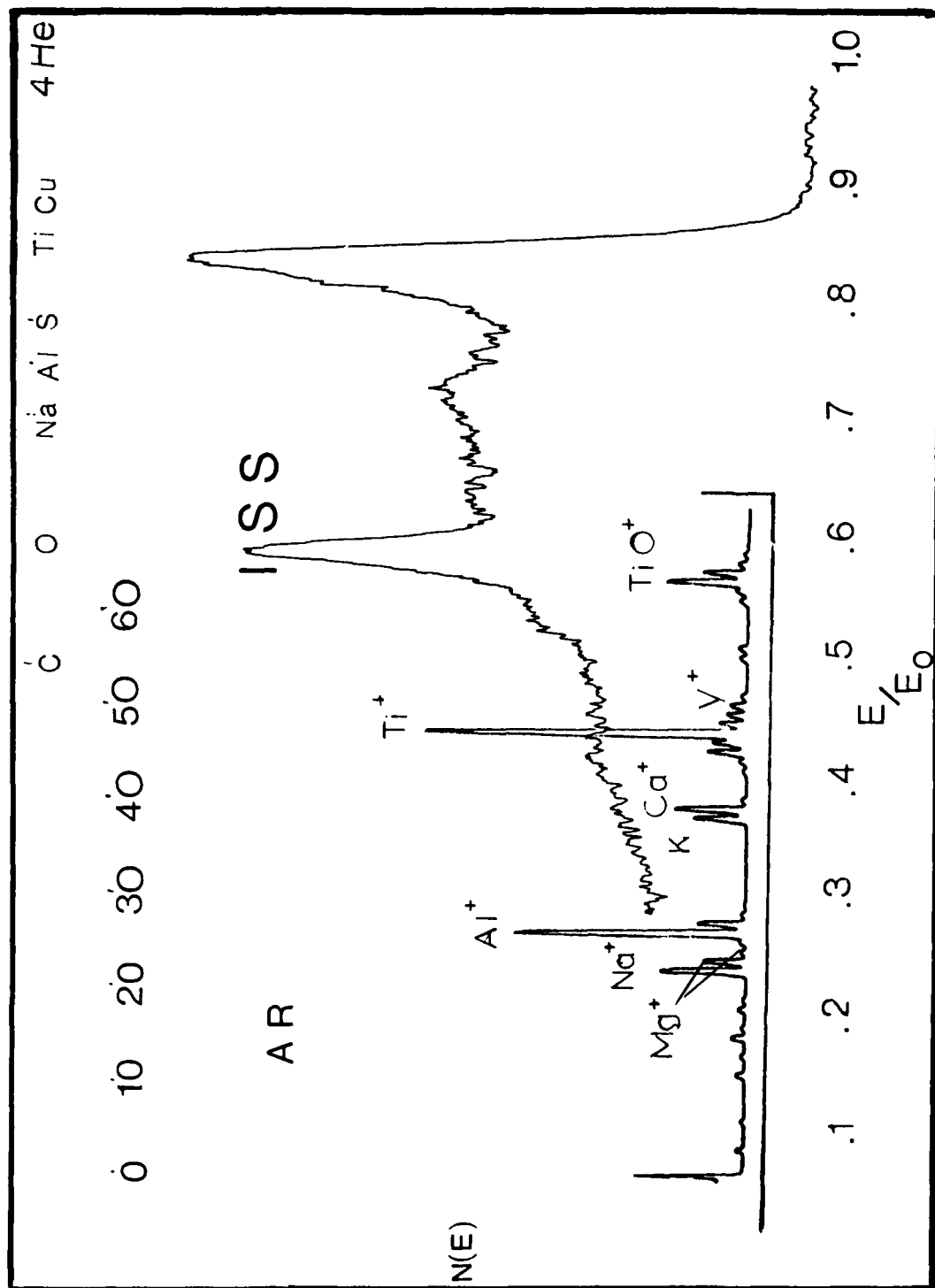
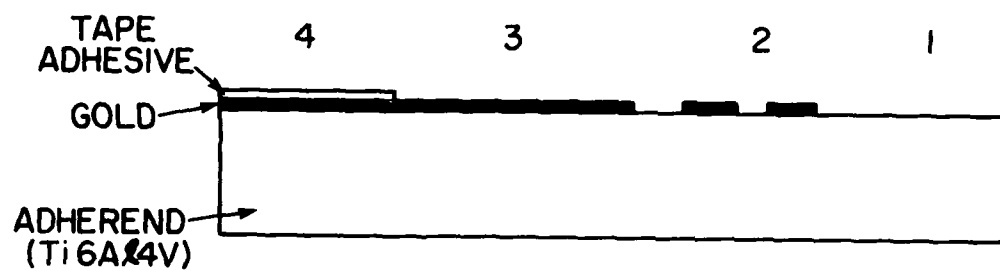Figure 2. Typical ISS/SIMS Data from a Titanium Surface.

Figure 3. Four Types of Failure Observed in Gold Peel Tests Using Commercial Transparent Tape.
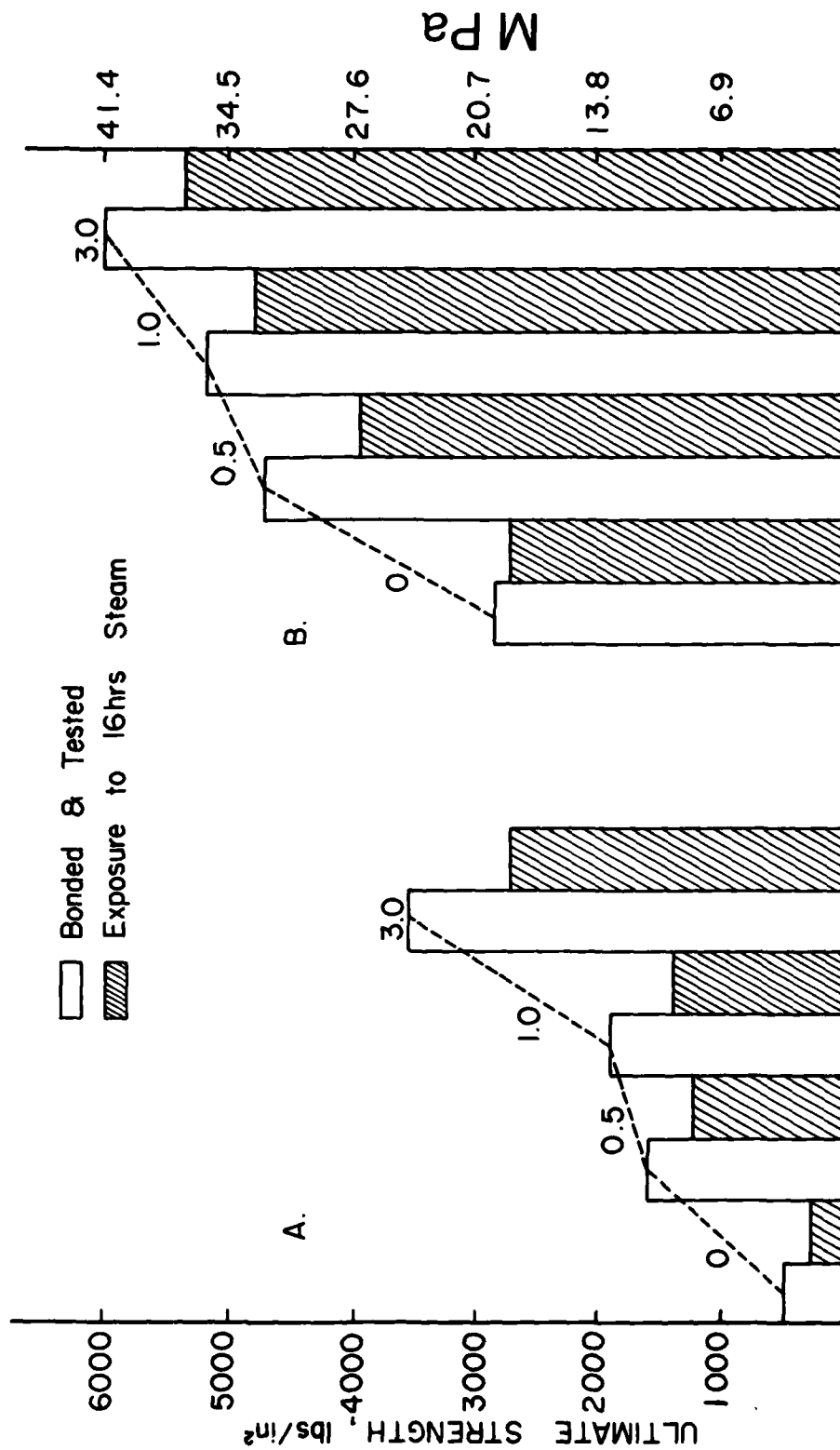
Figure 4. Single Overlap Shear Test Results for Etched Specimens Held in Condensing Steam A. Ti6Al4V with Gold Coating Bonded with 729-3 Adhesive B. Bare Ti6Al4V (with no Gold Coating) Bonded with PL 729-3 Adhesive.

Figure 5. Scanning Electron Micrographs of Specimens of Ti6Al4V Which Were Etched in HF/$NH_4H_2PO_4$ for 0, 0.5, 1.0 and 3.0 Minutes.
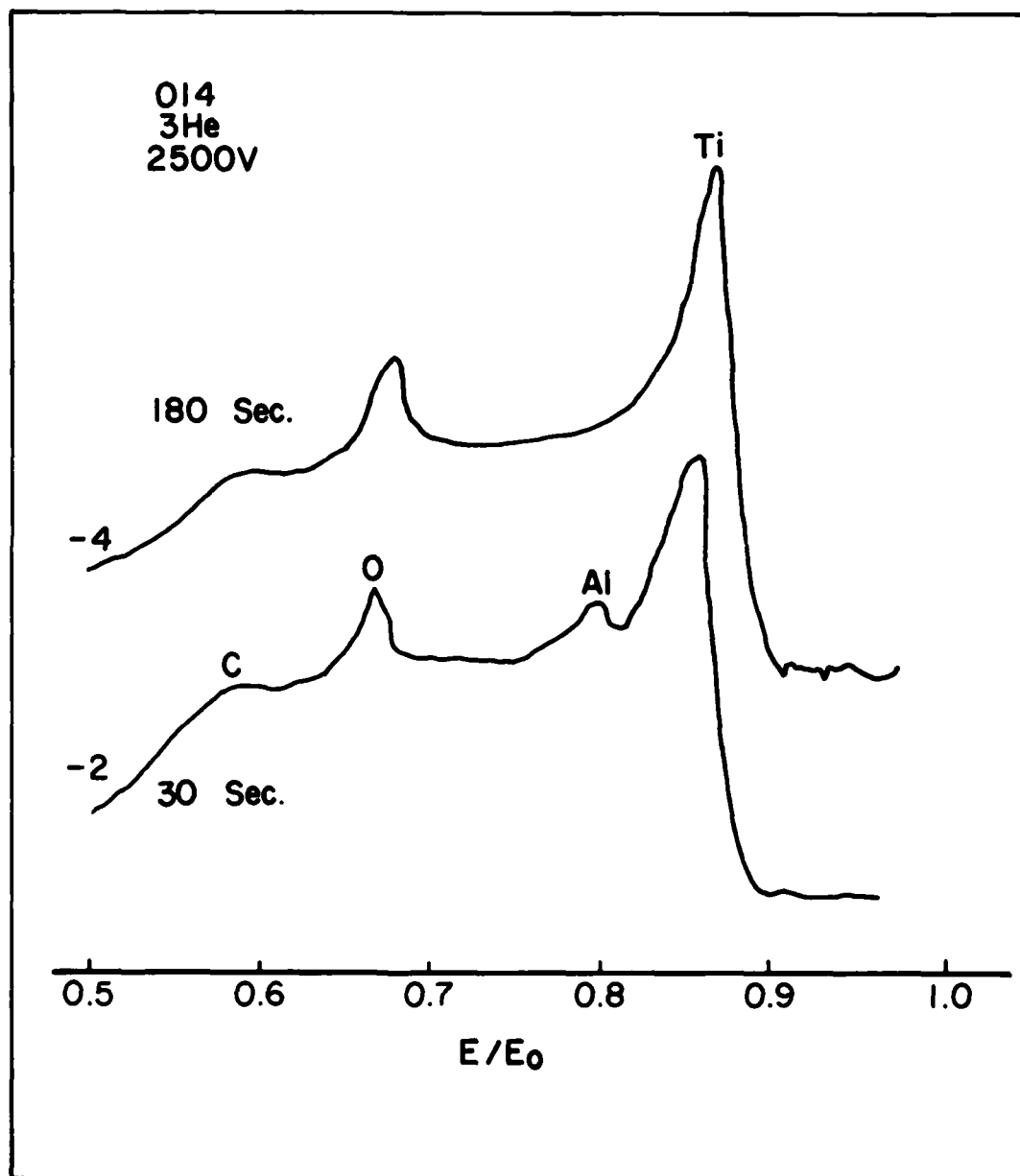
Figure 6. Ion Scattering Spectra from Sample 014-2, Ti6A14V Etched in HF/NH$_4$H$_2$PO$_4$ for 30 sec. and 014-4 Ti6A14V, Etched in the Same Acid Mixture for 180 sec.
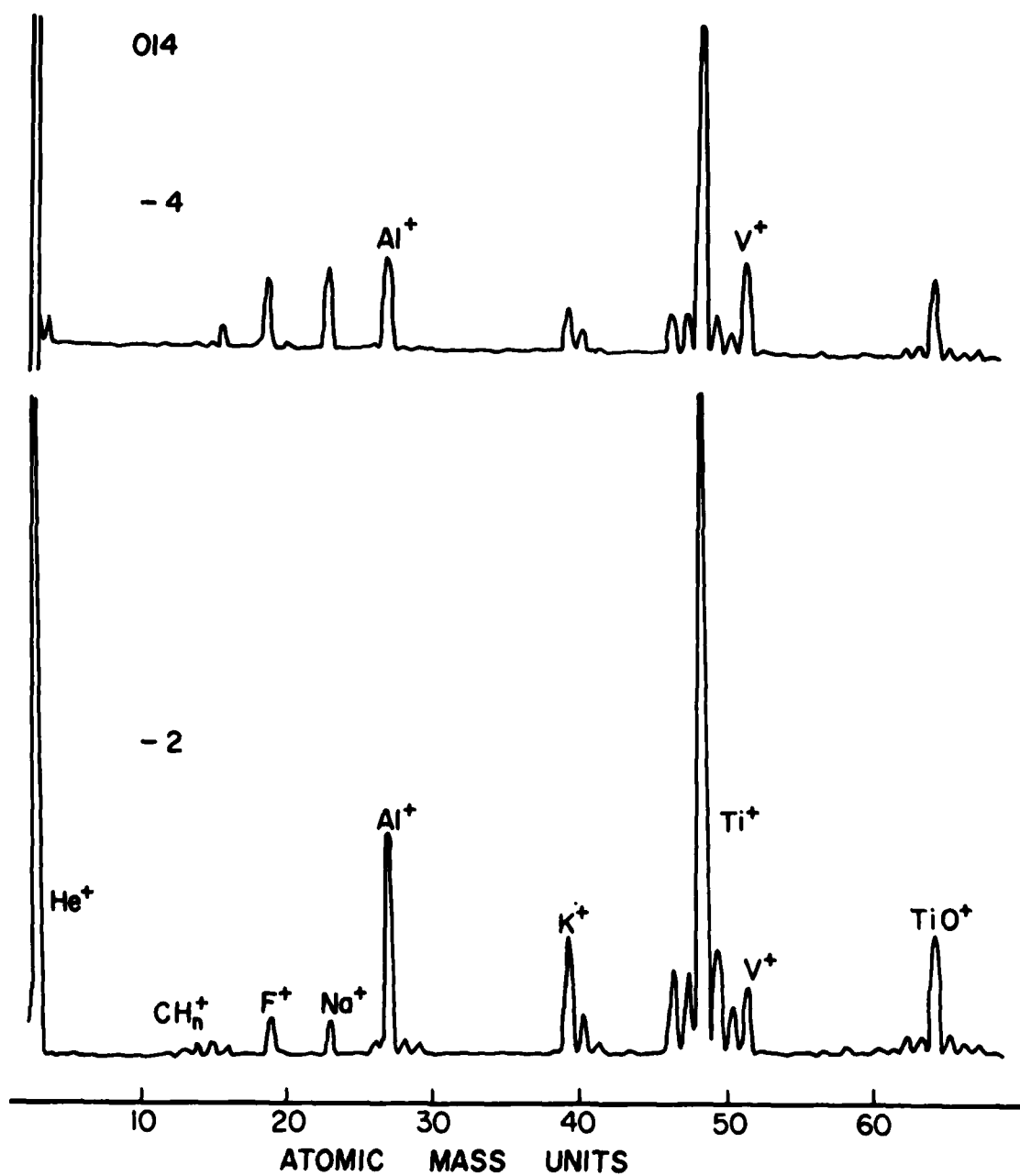
Figure 7.   Secondary Ion Mass Spectra for the Sare Specimens Shown in Figure 6.
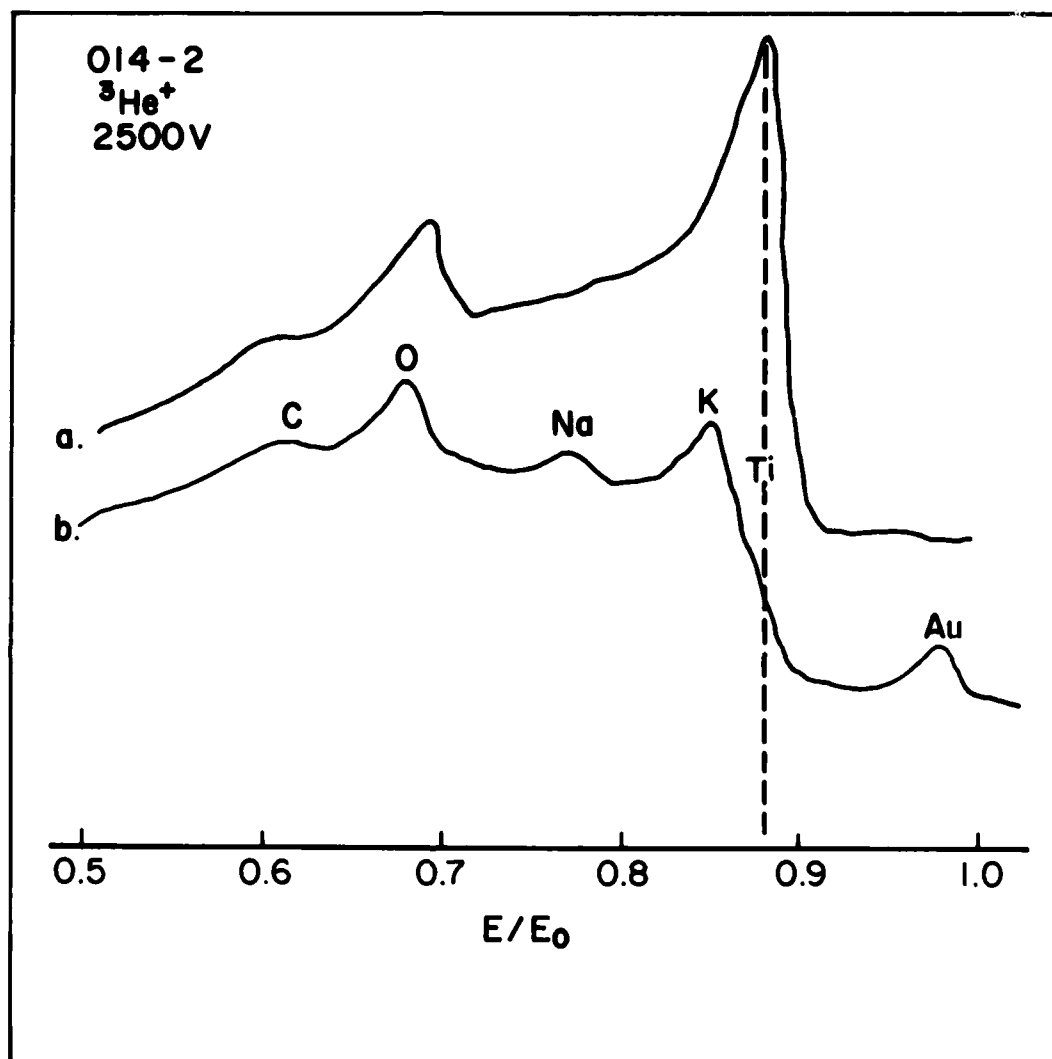
Figure 8. Ion Scattering from 014-2 from the Original Surface, a, and from the Surface after Stripping the Gold, b.
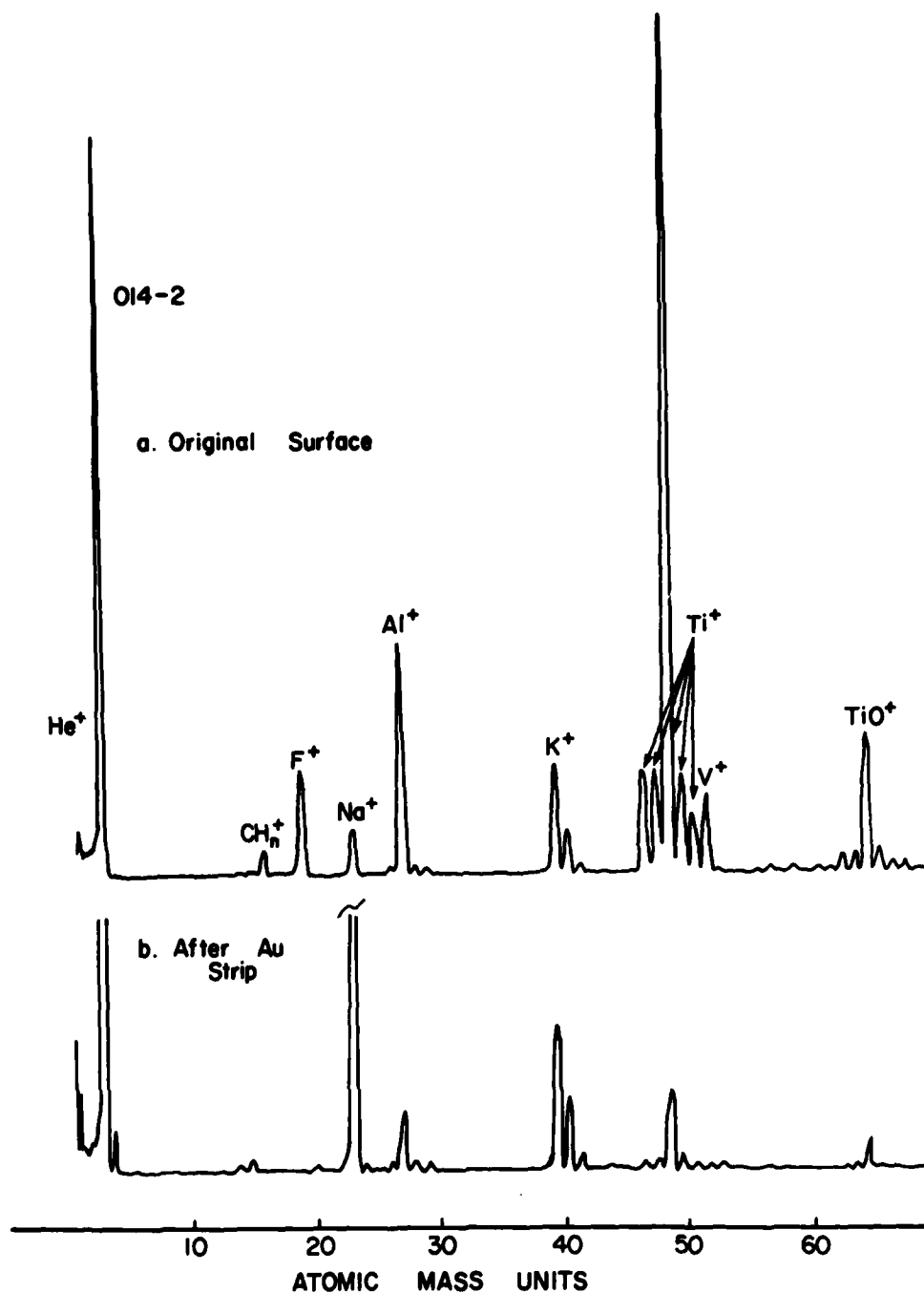
Figure 9.   Secondary Ion Mass Spectra from the Same Specimens
Shown in Figure 8.
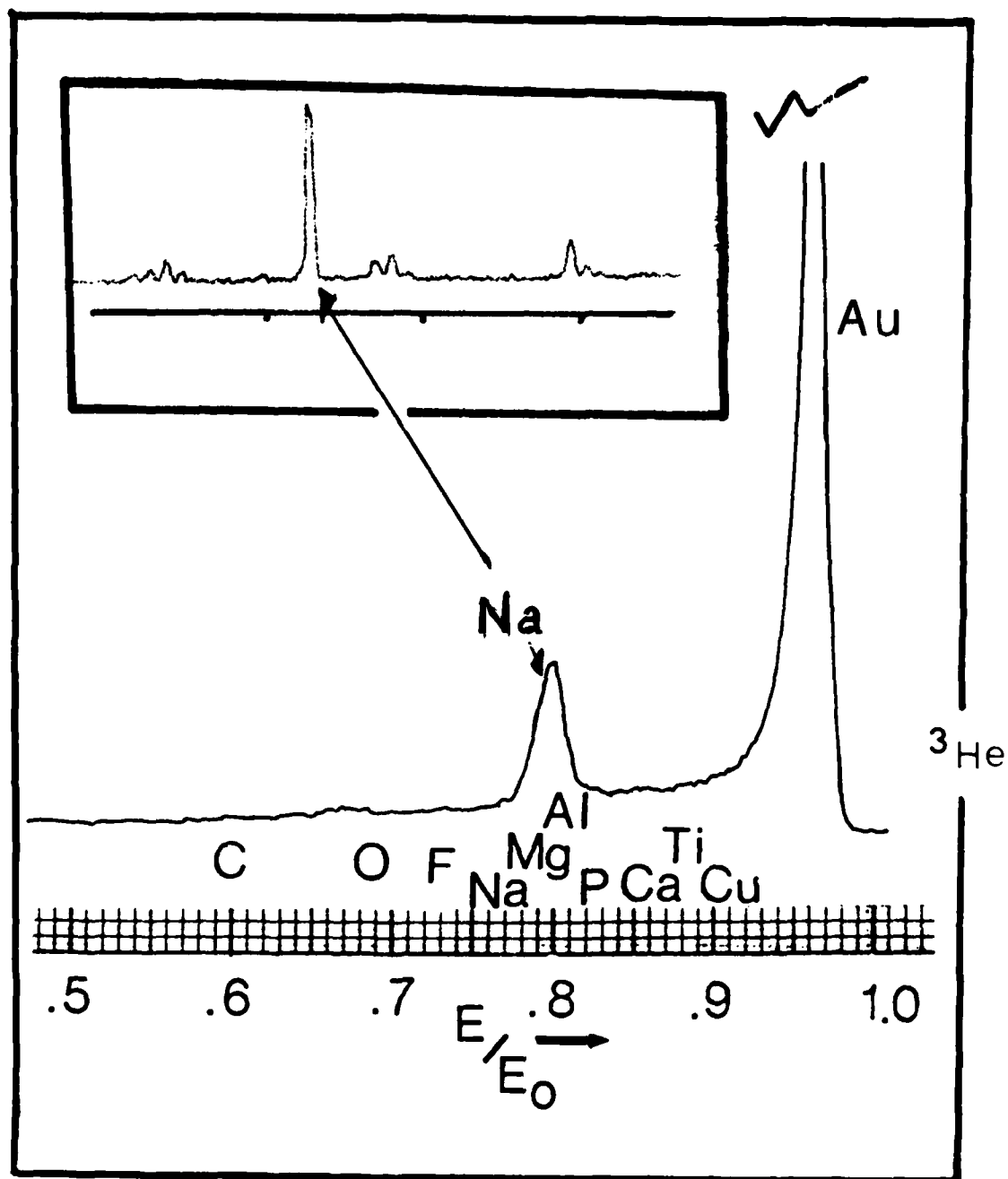
Figure 10. Ion Scattering Spectrum and Secondary Ion Mass Spectrum
(Inset) of a Gold Surface Stripped from Ti6Al4V.
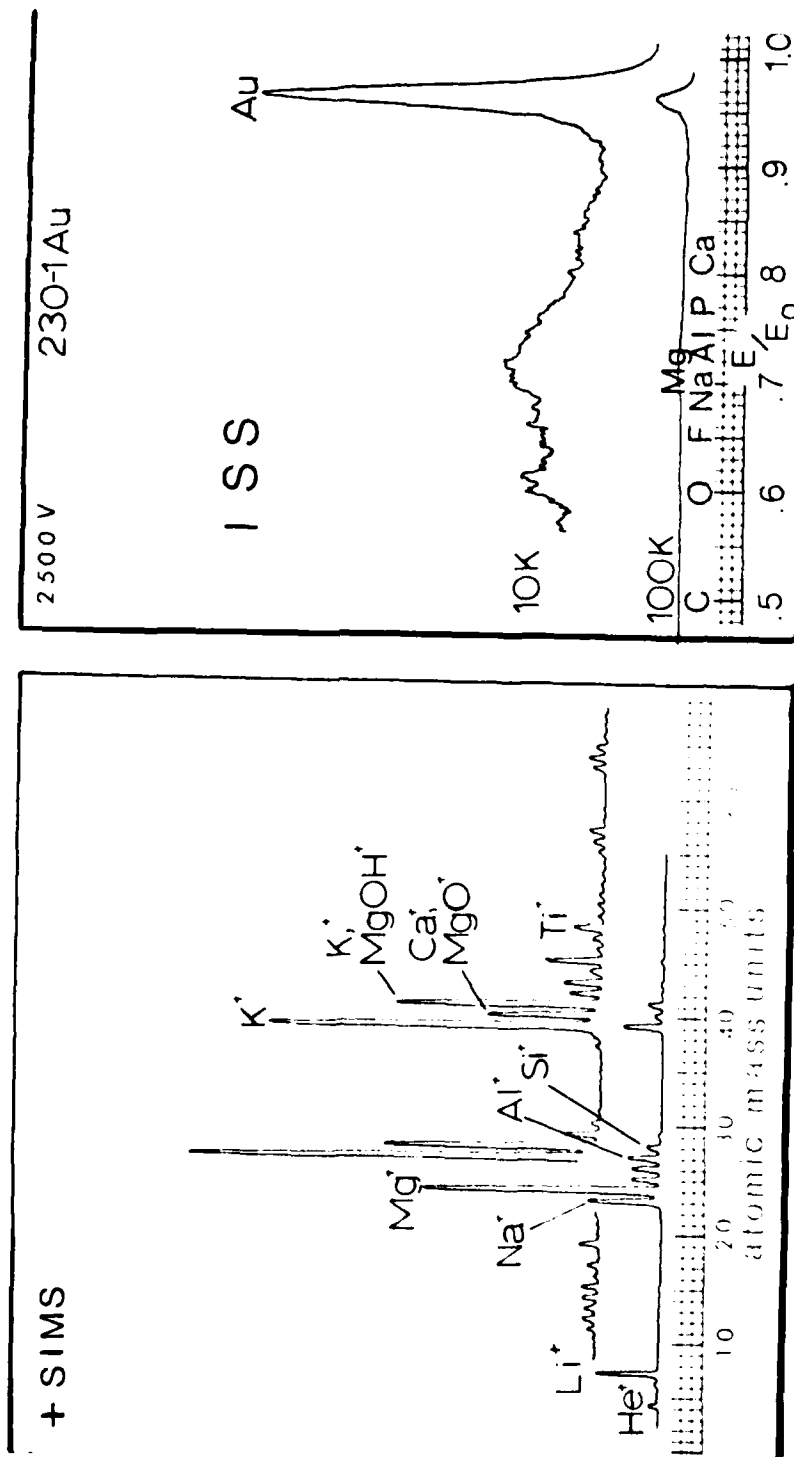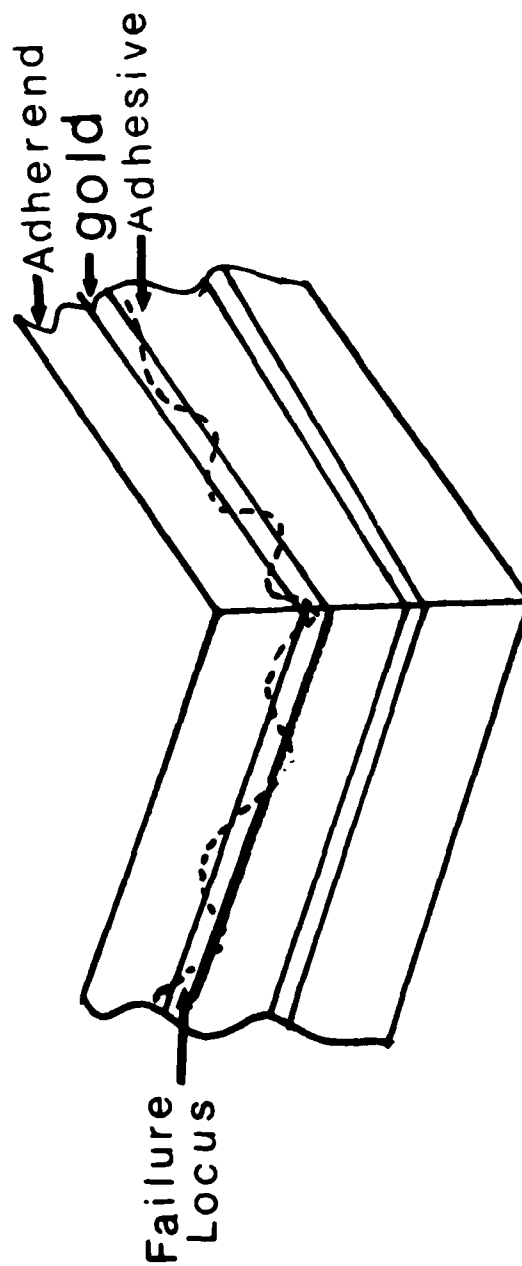
Figure 11. ISS/SIMS Data from a Gold Failure Surface.

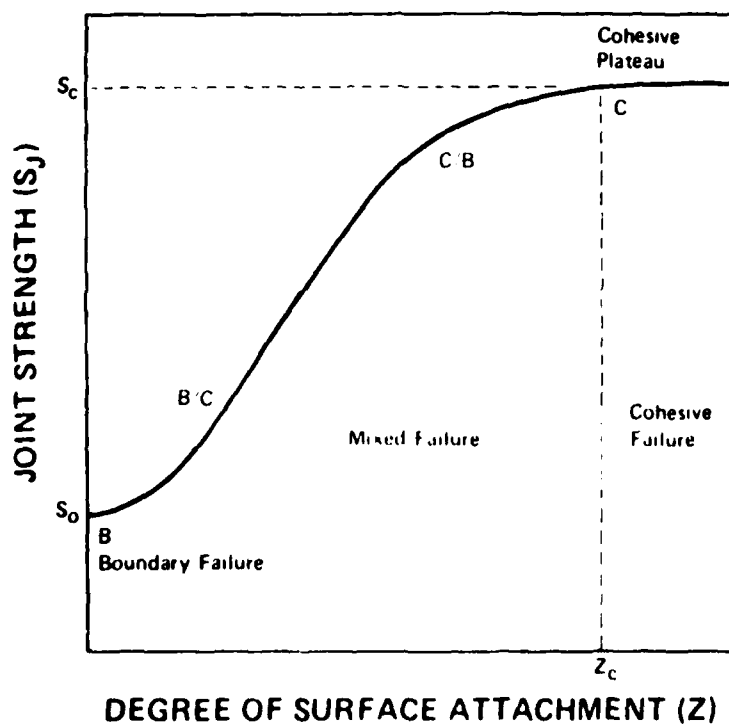Figure 12. Model of a Mixed Mode Failure Near A Weak Boundary Layer.

Figure 13. Schematic Diagram of Adhesive Joint Strength as a Function of the Strength of Boundary Layer (Reference 1).
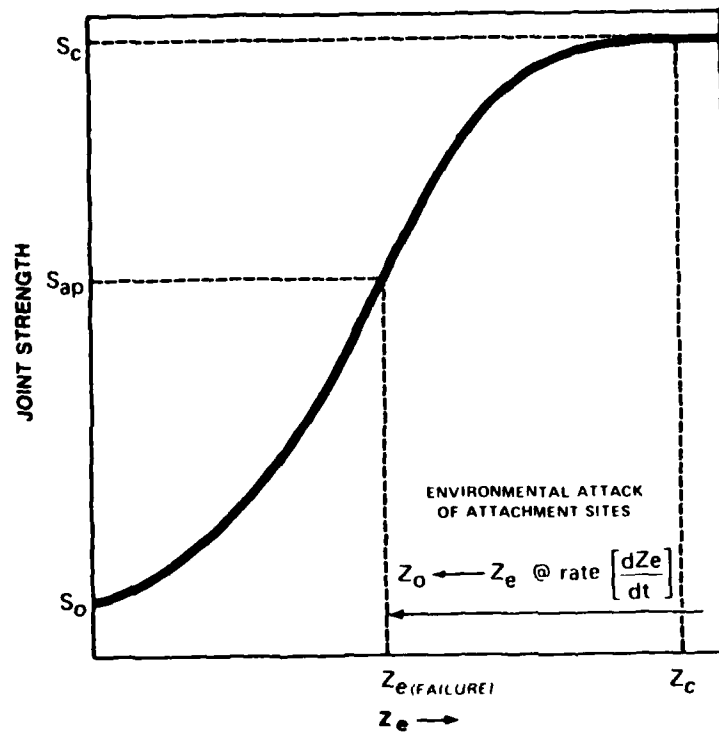
Figure 14.  Environmental Deterioration of a Stressed
Adhesive Joint as Represented by the Attach-
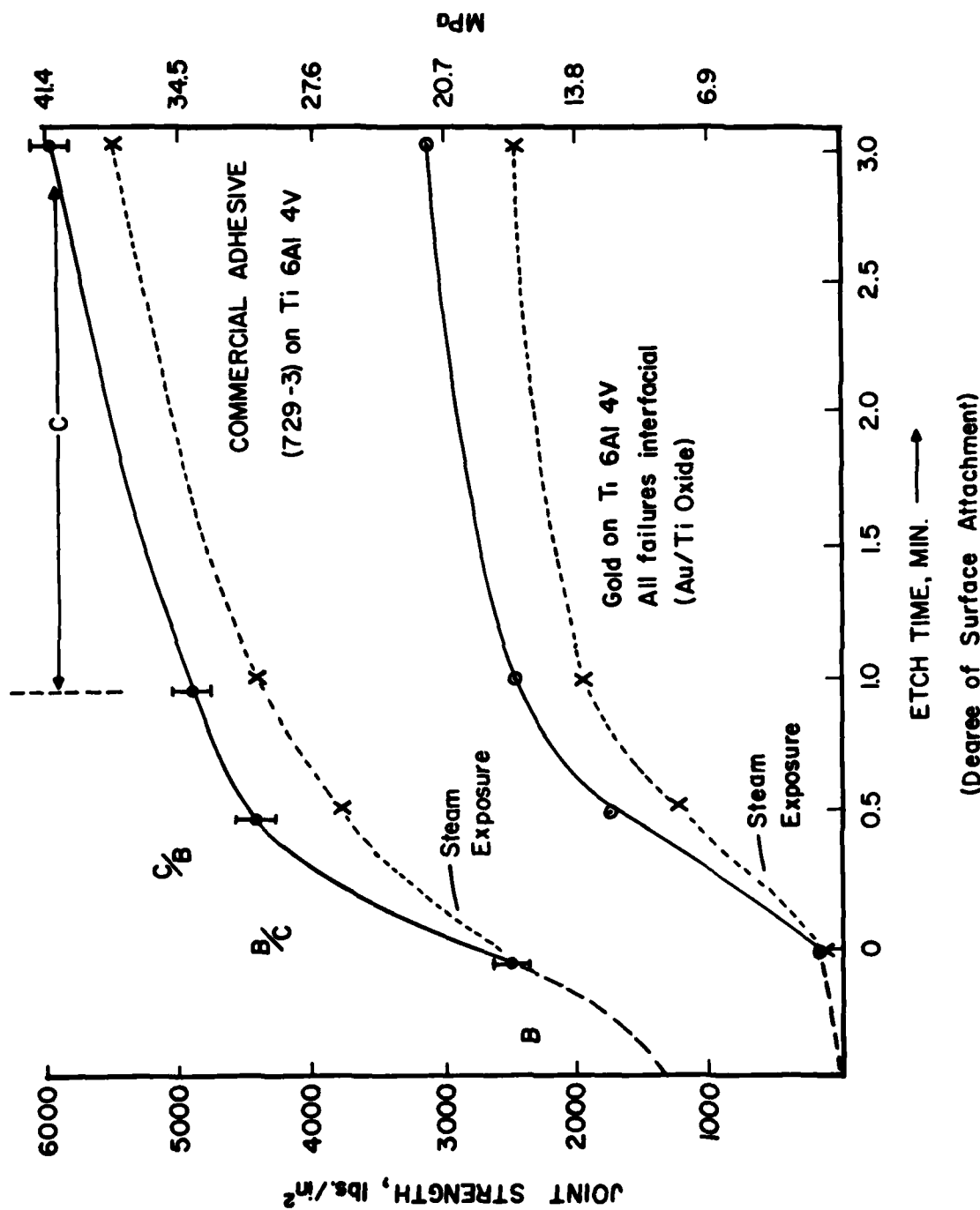ment Site Model (Reference 1).

Figure 15. Bond Strength Plotted vs. Etching Time for Ti6A14V Etched in HF/NH4H2PO4  A. Gold on Ti6A14V  B.  PL729-3 Adhesive on Ti6A14V