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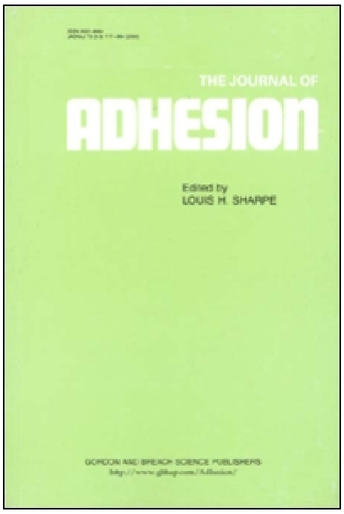

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The Effect of Etching on Ti6A14V Interfacial Chemistry and Adhesion to Evaporated Gold and a Commercial Adhesive

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(*Received February 4, 1980*)

Titanium 6-aluminum 4-vandium alloys were etched for varying periods of time in aqueous solution of hydrofluoric acid and ammonium dihydrogen 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 pressure sensitive tape peel tests and lap shear tests using a commercial adhesive. The uncoated specimens were evaluated by lap shear tests. Adhesion of Ti6A14V 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 increasing exposure of the beta phase. Heating of the gold on Ti6A14V resulted in improved adhesion, probably by diffusion mechanisms. Exposure to steam resulted in bond degradation in both gold/Ti6A14V and in adhesive/Ti6A14V systems. The adhesive bonding results for the etched specimens were compared to performance based on "attachment site" theory. Excellent agreement for both gold on Ti6A14V and commercial adhesive on Ti6A14V was observed. Degradation of the bond due to steam followed the same form in both systems, suggesting H_2O transport along the interphase.

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 Ti6A14V 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.

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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), 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.

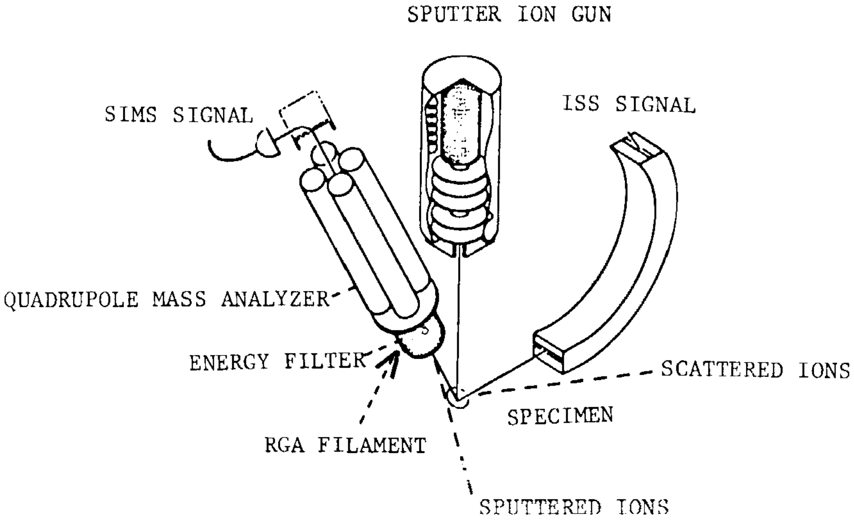

FIGURE 1 The experimental setup for ISS-SIMS (90° scattering).

† B. F. Goodrich Company.

ISS is based on the principle that when a surface is bombarded with low energy gas ions (^{3}He, ^{4}He, ^{20}Ne, or ^{40}Ar), the measurements 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_0, where E is the energy of the rebounding ion and E_0 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 Z 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 ions 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.

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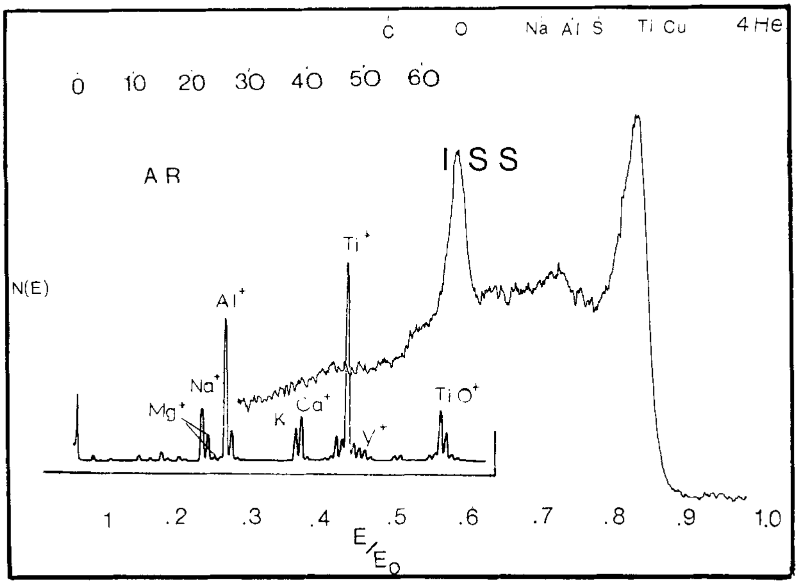

FIGURE 2 Typical ISS/SIMS data from a titanium surface.

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 such as TiO^+ are observed in SIMS spectra and may give important clues to the structure of the ions on the surface.

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 film was only on the order of atomic dimensions or 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 500 nm (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 1×10^{-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/

TABLE I

Tape test results for Ti6A14V etched for different periods of time before evaporation of gold

Sample	Clean	Etch (min)	Evap Au	Tape Test No. 1	Bond Lap Shear	Tape Test No. 2
014–1	Ab. Pad + Det, dil NaOH	0	X	1	729–3 (300°F)	1
014–2	+ Det, dil NaOH	0.5	X	1	729–3	2
014–3	+ Det, dil NaOH	1.0	X	2	729–3	3
014–4	+ Det, dil NaOH	3.0	X	3	729–3	4

Tape Test Code: Interfacial, Au/TiO_2 = 1; mixed (some Au remains) = 2; interfacial, adhesive/Au = 3; cohesive in adhesive, (adhesive remains on Au) = 4.

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50 g in 1 liter 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.

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°) 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 and are illustrated in Figure 3.

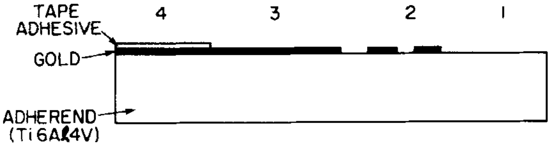

FIGURE 3 Four types of failure observed in gold peel tests using commercial transparent tape.

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°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

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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°F, the adhesion of the tape adhesive to the gold and the gold to the alloy has improved 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.

Mittal,[8] reviewing unpublished work of Beno, reports that peel tests using pressure sensitive tape are limited to adhesion of about 5×10^5 Pa. A rough estimate on films evaporated on unetched Ti6A14V (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°F, the ultimate strength of the bond was determined by testing of the single overlap specimens (1.0 in × 0.5 in overlap). This method uses tangential shear stresses, but in practice the stresses at the interphase appear very complex due to variation 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°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 vanadium 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 condensing steam. It can be seen that the trend here is the same as in the gold coated specimens; that is,

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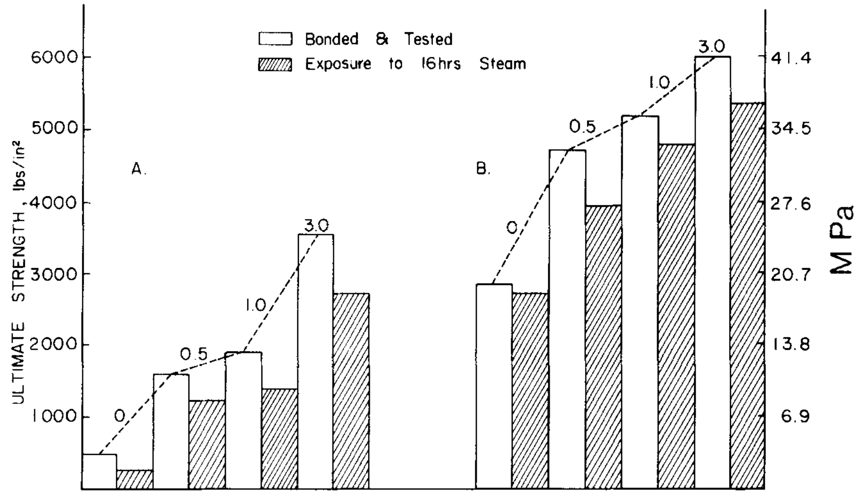

FIGURE 4 Single overlap shear test results for etched specimens held in condensing steam. A. Ti6A14V with gold coating bonded with 729–3 adhesive. B. Bare Ti6A14V (with no gold coating) bonded with 729–3 adhesive.

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 3×10^5Pa for Au on glass, which compares to the value measured here of 7×10^5Pa on the unetched Ti6A14V specimen. With etching, adhesion improved about 30 × to 2.0×10^7Pa.

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 vanadium content is observed. The probability of small changes in hydrocarbon type and content and in alkali emission are also observed.

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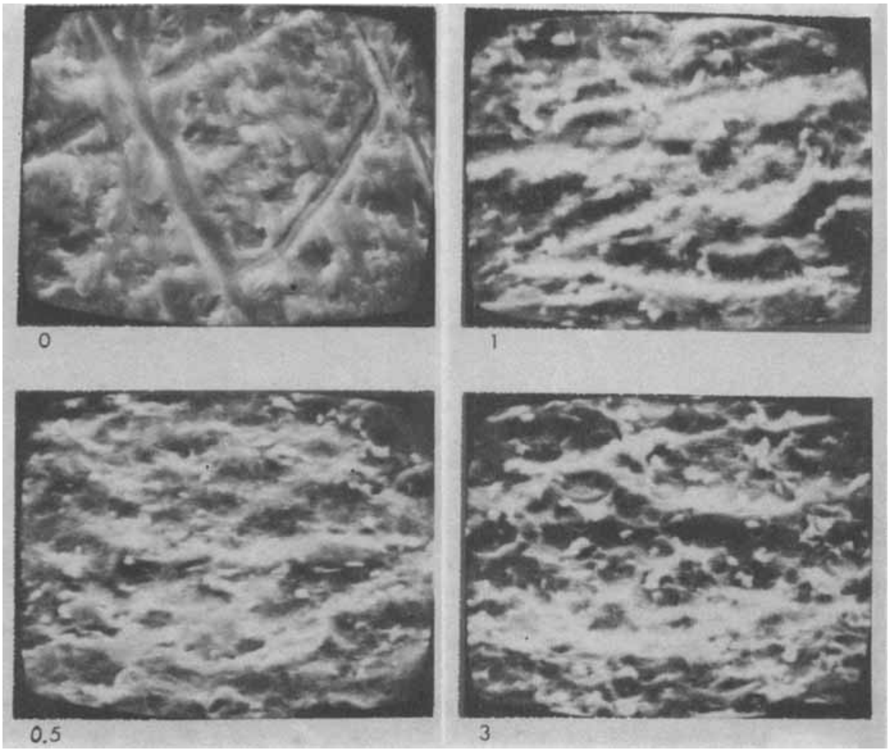

FIGURE 5 Scanning electron micrographs of specimens of Ti6Al4V which were etched in $HF/NH_4H_2PO_4$ for 0, 0.5, 1.0, and 3.0 minutes.

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

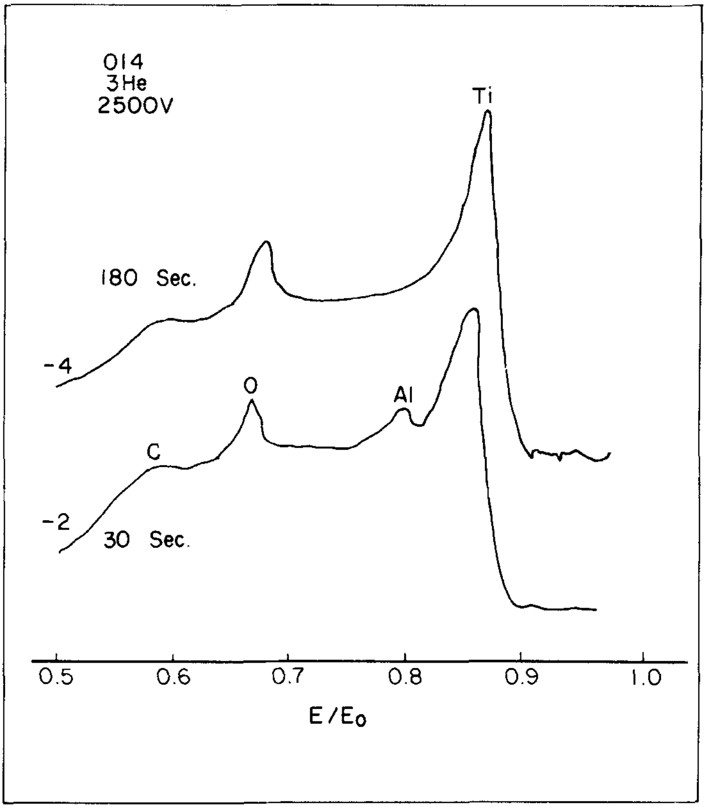

FIGURE 6 Ion scattering spectra from sample 014-2, Ti6A14V etched in $HF/NH_4H_2PO_4$ for 30 seconds and 014–4 Ti6A14V, etched in the same acid mixture for 180 seconds.

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 continue 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 prior 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, which results in the concentration at the surface of the titanium alloy of the impurity elements in the water, particularly calcium, magnesium and sometimes iron.

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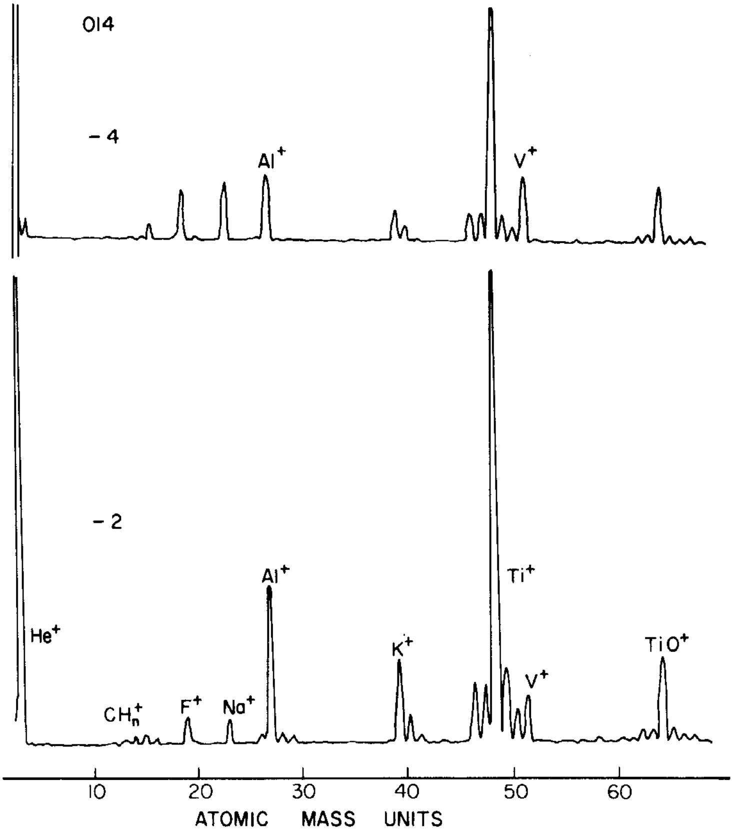

FIGURE 7 Secondary ion mass spectra for the same specimens shown in Figure 6.

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 interfacial failures but rather a mixed mode similar to that illustrated in Figure 12 in substantial agreement with the predictions and theory of Bikerman.[15]

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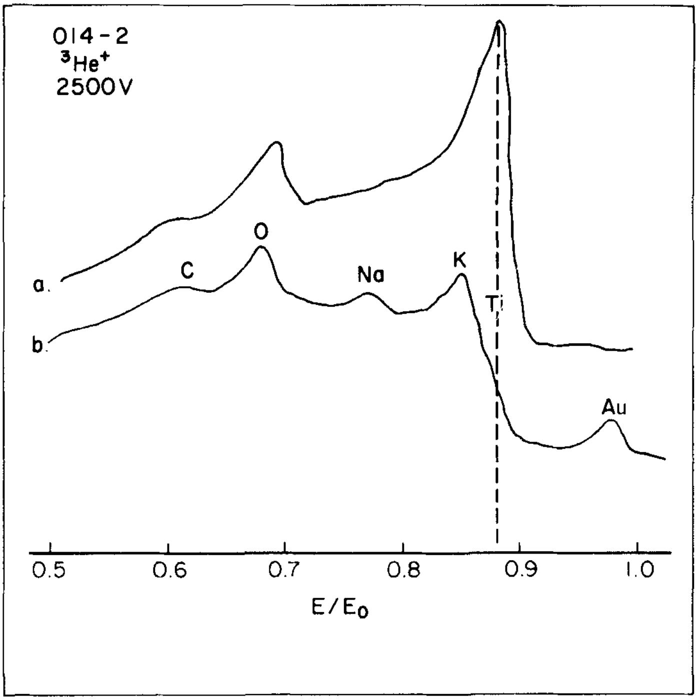

FIGURE 8 Ion scattering spectra from 014-2 from the original surface, a, and from the surface after stripping the gold, b.

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DISCUSSION

The results for adhesion behaviour of gold on Ti6A14V and an adhesive on Ti6A14V discussed above were compared with the theory of attachment sites developed by Lewis and Natarajan.[1] 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 Reference 1.

This model for adhesive joint strength is 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_0, 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

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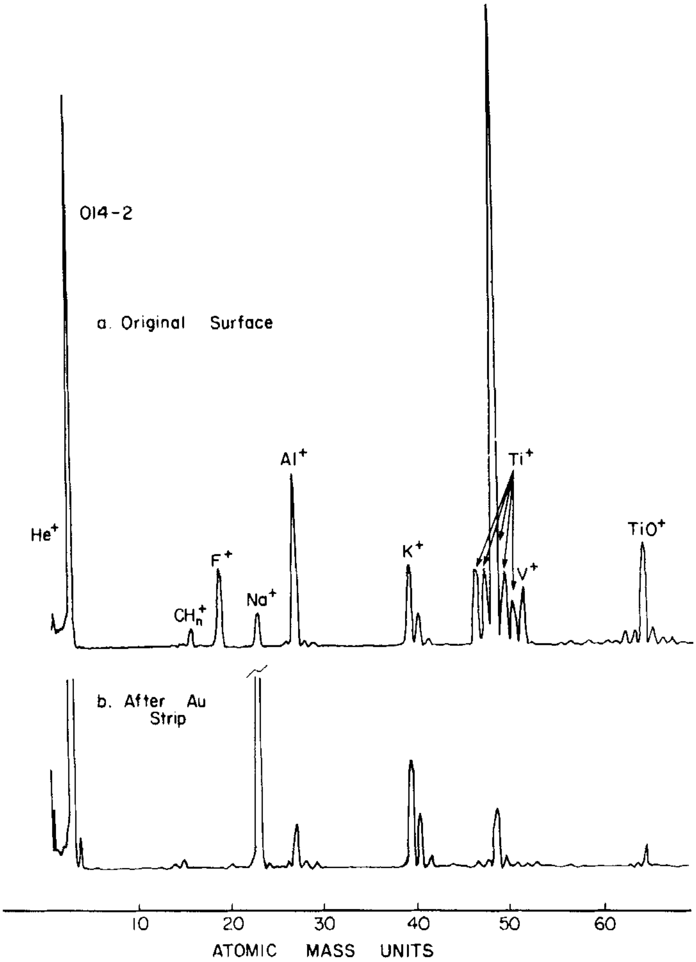

FIGURE 9 Secondary ion mass spectra for the same specimens shown in Figure 8.

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

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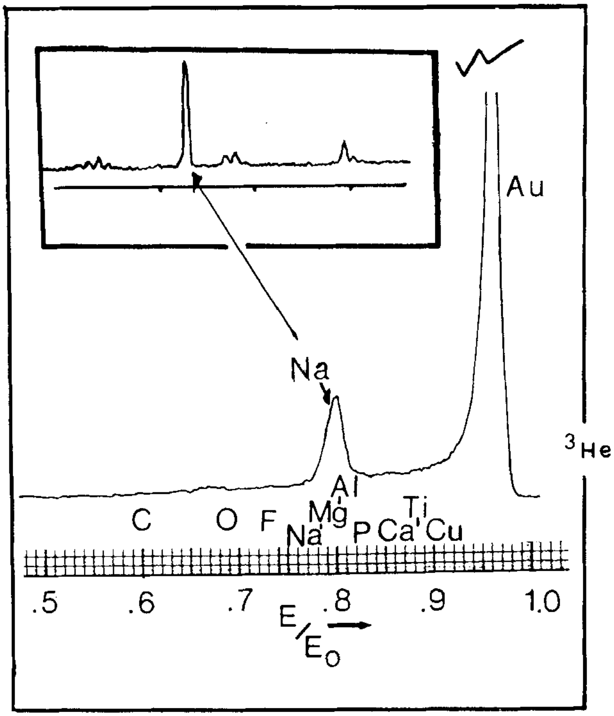

FIGURE 10 Ion scattering spectrum and secondary ion mass spectrum (inset) of a gold surface stripped from Ti6Al4V.

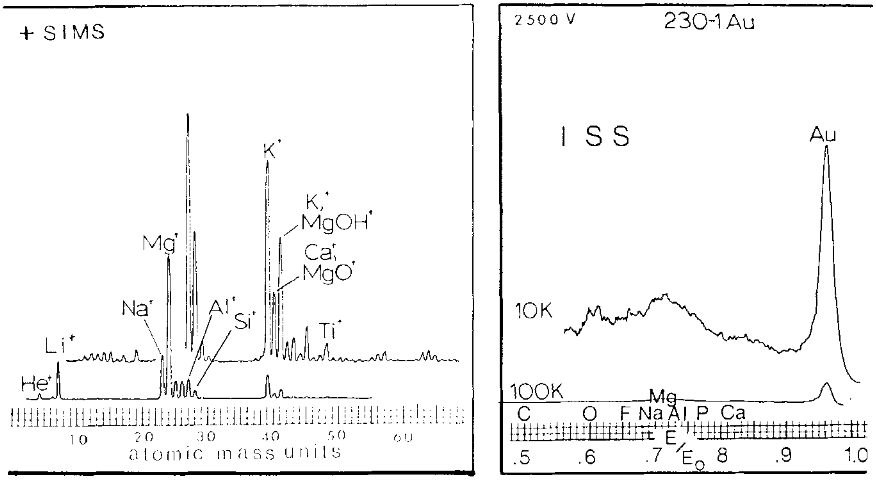

FIGURE 11 ISS/SIMS data from a gold failure surface.

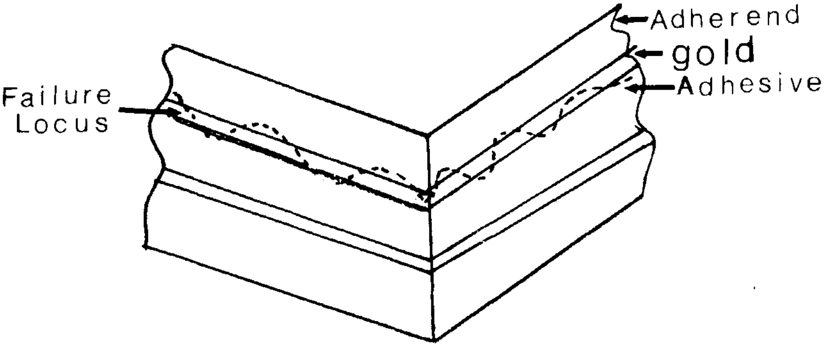

FIGURE 12 Model of a mixed mode failure near a weak boundary layer.

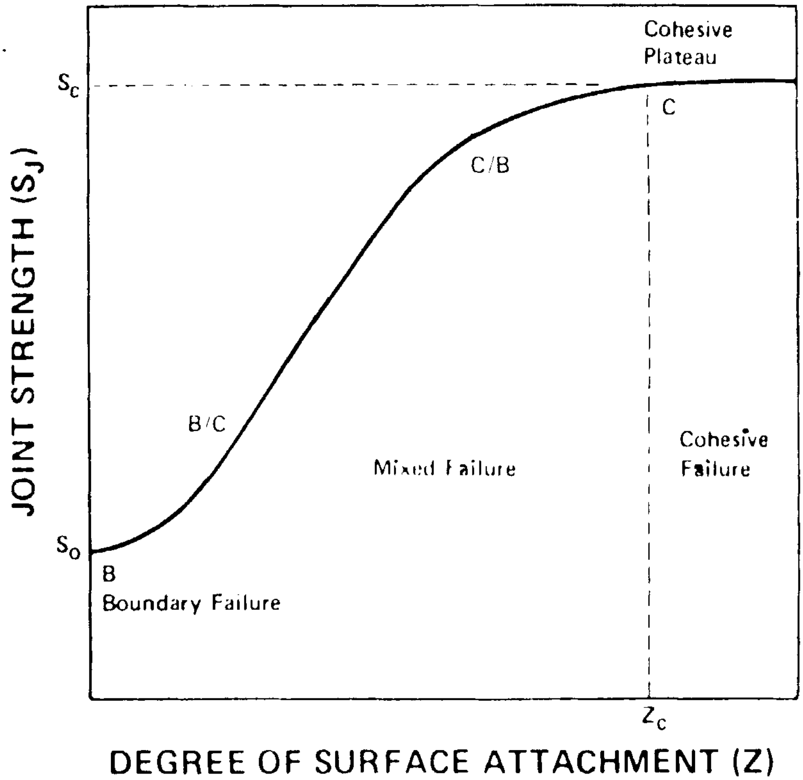

FIGURE 13 Schematic diagram of adhesive joint strengths as a function of the strength of boundary layer (Ref. 1).

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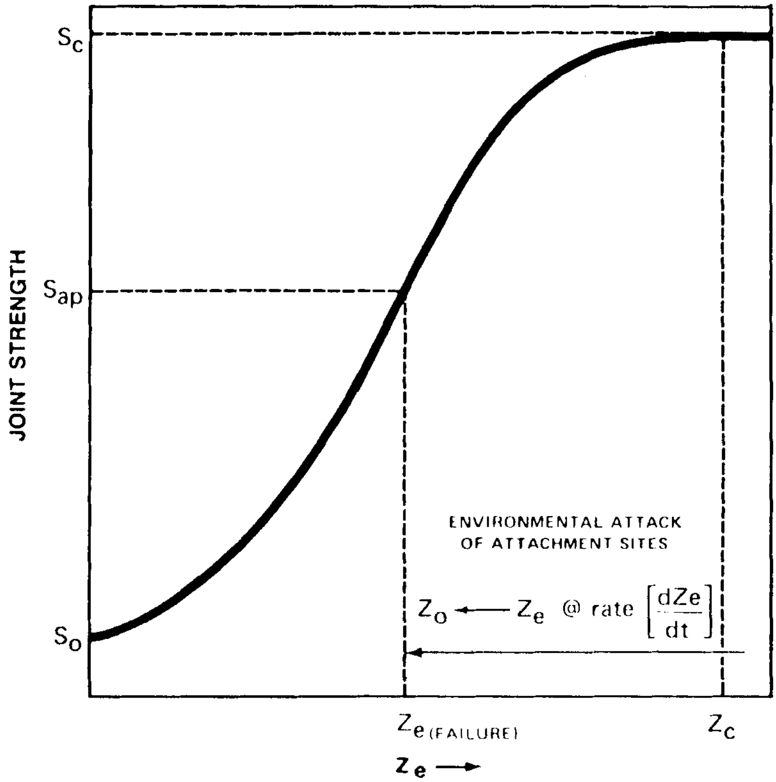

FIGURE 14 Environmental deterioration of a stressed adhesive joint as represented by the attachment site model (Ref. 1).

(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.

The model of adhesive joint strength herein presented has the following features that must be examined, verified or modified and finally established by way of future theory and experimentation:

1. The attachment site theory proposes 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

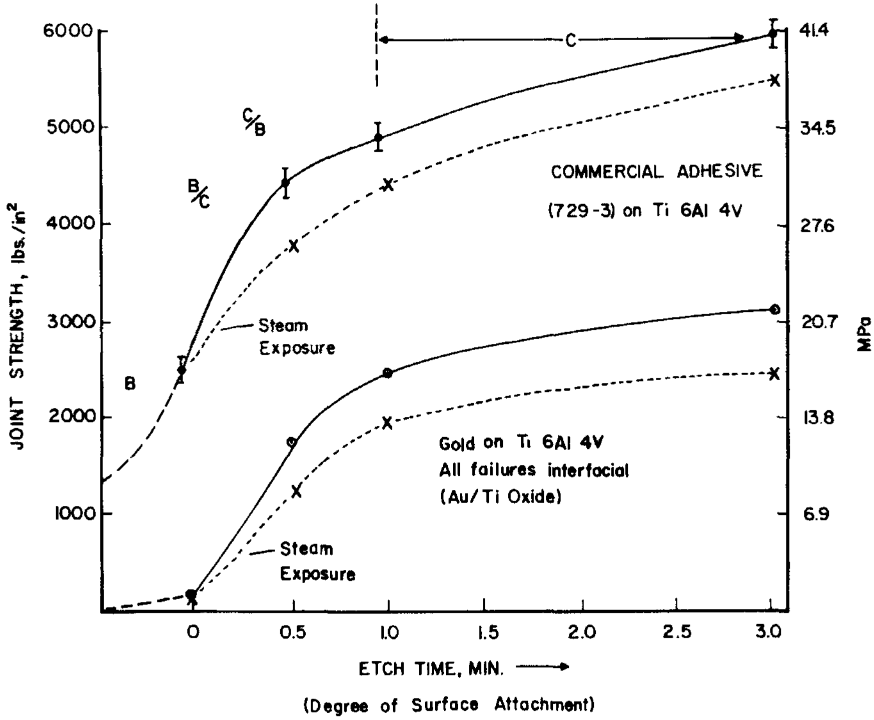

FIGURE 15 Bond strength plotted *v*. etching time of Ti6Al4V in $HF/NH_4H_2PO_4$. A. Gold on Ti6Al4V, and B. Ti6Al4V bonded with 729–3 adhesive.

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 Figure 14 where there is a conversion of Z_e sites to Z_0 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 reaches 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 Figure 15 *versus* 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

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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 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. The results also suggest by their similar

TABLE II

Lap shear testing of Au coated and uncoated Ti6A14V

Specimen	Etch time, (min)	Expose to 16 hr steam	M Pa	Ultimate strength lb/in^2	Mode of failure
		Au Coated			
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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behavior that water vapor transport may occur along the interphase rather than through the adhesive.

CONCLUSIONS

These experiments show that initial adhesion of both gold and a commercial adhesive on Ti6A14V 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, suggesting degradation mechanisms and perhaps H_2O transport at the interphase rather than in the adhesive. Heating of the evaporated Au/Ti alloy always resulted in improved Au adhesion, presumably by stress relief and diffusion mechanisms. The change in roughness with increased etching was stuble, 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.

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