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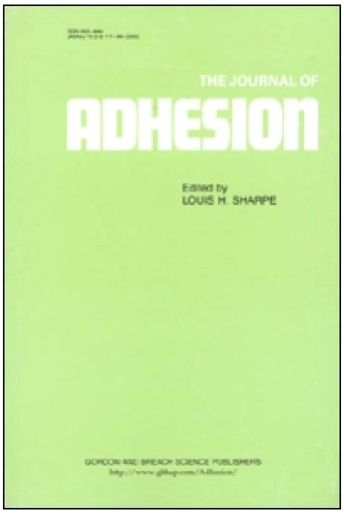

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Use of Ion Scattering and Secondary Ion Mass Spectrometry to Characterize Apparent "Adhesive" Failure in an Adhesive Bond

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Use of Ion Scattering and Secondary Ion Mass Spectrometry to Characterize Apparent "Adhesive" Failure in an Adhesive Bond

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Frequently it is not easy using visual or even microscopic examination of an adhesive joint to determine after physical testing whether an apparent adhesive failure occurred at the original interface due to improper wetting or at some new interface leaving behind a thin layer of adhesive. Elemental analysis techniques such as ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS) are easily capable of determining the locus of failure in an adhesive joint. The use of these two techniques in combination is shown for investigating adhesive bonding phenomena. The operating parameters as well as advantages and disadvantages of each are summarized. ISS–SIMS data are shown for two adherend surfaces which broke in a lap shear test by apparent cohesive failure in both the adhesive and adherend.

INTRODUCTION

The strength of an adhesive joint is assessed by means of physical tests such as single lap shear, double lap shear, peel, etc., in which an increasing load is placed in the joint until failure occurs. Following failure, visual (or sometimes microscopic) examination of the surfaces is made to determine the mode of failure. If adhesive remains on each adherend and the joint appears to have failed 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, the failure is termed "adhesive".

Bikerman[1] says that "rupture so rarely proceeds exactly between the adhesive and an adherend that these events (that is 'failure in adhesion') need not be treated in any theory of adhesive joints". He points out that apparent failures in adhesion are quite common but they take place so near the interface that the adhesive remaining on the adherend after the rupture is not visible. Good[2] has analyzed adhesive joint failure and reports that interfacial separation is highly improbable when true wetting of the surface has taken place.

Frequently it is not simple using visual or even 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. Even scanning electron micrographs are not definitive for very thin layers of adhesive. Often surface features of the original adherend are closely reproduced by a surface covered by a thin film of adhesive. Further, there is a resolution limitation of about 100 Å for most scanning electron microscopes which makes very thin films difficult to detect, especially when the adhesive is a pure polymer containing no fillers of higher atomic number than the polymer to increase contrast. Optical and staining methods have been reported[3] to determine the presence of adhesive films. However, the optical technique uses the interference phenomenon which is only applicable to fairly thick films, certainly not films only a few Angstroms thick. Staining techniques are sensitive only to specific compounds present in the usually complex adhesive systems.

RESULTS AND DISCUSSION

Ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS) provide useful information on the locus of failure in an adhesive joint even when the film is 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. ISS uses a relatively low energy ion beam to probe just the first atomic layer at the surface.[4] SIMS uses the same ion beam to sputter and mass analyze secondary ions from the surface.[5] Both techniques result in an elemental profile with depth as the surface is slowly eroded away by the primary ion beam. A summary of the operating features and advantages and disadvantages of both techniques is shown in Table I. These comments in Table I are offered for the combined technique using low energy (as shown) inert ion beams from the commercial ISS instrument. Some comments are very generalized, such as indicating that a combination of positive and negative SIMS is applicable to *all* elements. In practice there are a few elements which have extremely low positive or negative ion yields. Further, each point in the table may not be valid for sputtering with high energy active gases, such as oxygen, used with the ion microprobe technique. The system used here is the commercial ion scattering equipment Model 520 manufactured by 3M company[6] to which a modified UTI[7] model 100C quadrupole mass filter has been added.

TABLE I

Comparison of depth profiling techniques

Parameter	Profiling technique: Ion scattering spectroscopy ISS	Profiling technique: Secondary ion mass spectroscopy SIMS
Principle	Elastic binary collision with surface ion	Sputtering of surface atoms by ion beam
Probe	~1–3 KeV ions	~1–3 KeV ions
Signal	Ion current *vs* energy	Ion current *vs* mass
Applicable elements	$>Z = 3$	All (if positive and negative SIMS)
Sensitivity, general	High	Variable
Sensitivity, low Z	Low	High
Resolution (spectral)	Low	High
Spectral shift	Possible, but generally no	No
Information on chemical combination	No	In some cases usually no
Quantitative anal	Yes	Probably no maybe with similar standards
Influence of operating conditions and matrix	No	Yes
Isotopic analysis	Yes, in principle but generally no because of resolution limits	Yes
Beam induced surface changes	No	No

An example of the use of ISS–SIMS for analysis of adhesive bonded surfaces is shown in Figures 2 and 3. Data here are from a titanium, commercially pure adherend which was anodized, bonded, subjected to lap shear testing, and appeared to fail in an adhesive mode. That is, there appeared to be failure at the interface of the oxide and adhesive. The adhesive was a modified epoxy with a magnesium silicate filler. Therefore, there are several elements such as C, N, Mg and Si to search for to determine whether failure was truly adhesive or whether in fact failure occurred along a new interface. As can be seen by the ISS spectra in Figure 2, the titanium scattered peak exhibits long tailing to low energy which obscures C and N to low E/E_0

of the oxygen peak and both Mg and Si between the oxygen and titanium peaks. In this figure the ISS spectrum is shown for the anodized failure surface and for a reference area on the end of the adherend which had not been anodized. Note the change in oxygen to titanium peaks when going from a metallic surface to the anodized oxide surface. Because of the high solid solubility of oxygen in titanium, some oxygen is nearly always visible,

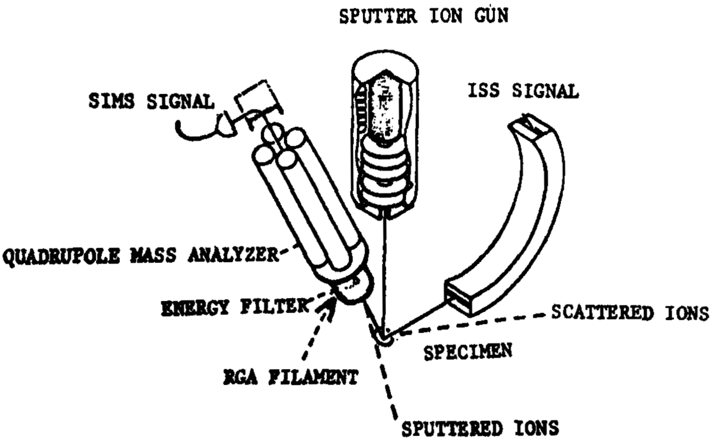

FIGURE 1 Essential components in ultra high vacuum for combination ISS-SIMS characterization of surfaces.

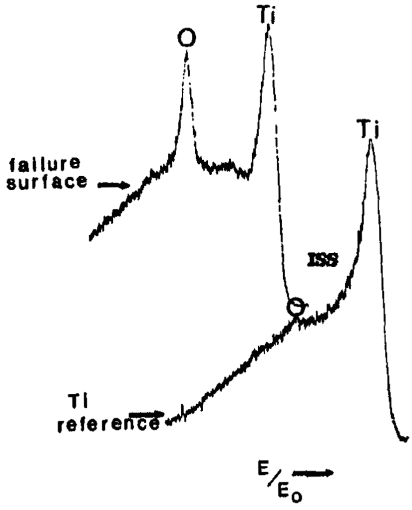

FIGURE 2 ISS spectra from titanium adherend following testing. From anodized failure surface. From reference point on end of adherend.

even in pure vacuum evaporated films which have been sputtered to remove surface oxide. Even though in this case little information is gained on the locus of failure, the data may be used to determine oxide thickness and homogeneity.

The SIMS spectra in Figure 3 taken simultaneously with the ISS spectra of Figure 2 do not suffer the limitations of ion scattering. Each of the elements of interest along with titanium is observed on the failure surface, indicating breakage on a new interface. Note the increase in +ion efficiency from the oxide failure surface compared to the unbonded surface shown for reference. Note also the great increase in sodium and potassium on the failure surface compared to the unbonded surface. Migration of these mobile monovalent ions to the interface is commonly seen especially in adherend–adhesive systems requiring a heat cure to effect a bond. In this adhesive joint failure, first SIMS traces before erosion into the surface took place showed elements from both adhesive and adherend. Failure probably occurred near the original interface. If the interface is considered to be an interlocking of "mountains and valleys" on the adherend with the adhesive, then we must be seeing cohesive failure of the adherend in the "mountains" as well as cohesive failure of the adhesive filling the "valleys", although these results do not rule out also some possible adhesive failure.

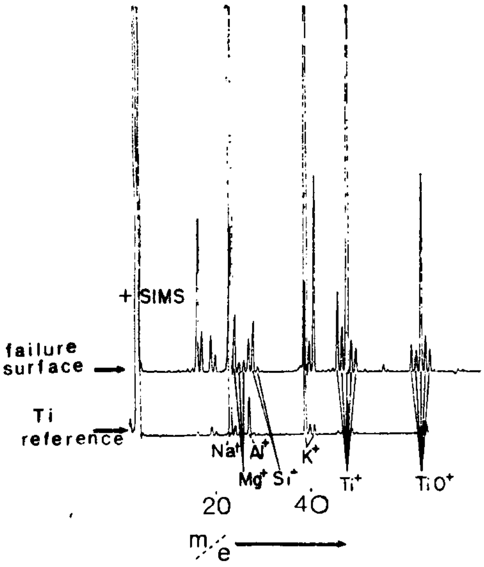

FIGURE 3 +SIMS spectra from same surfaces as in Figure 2.

Figure 4 shows ISS and SIMS data from an aluminum adherend which had been bonded with epoxy containing a TiO_2 filler. The ISS spectrum A of the failure surface shows carbon, oxygen, aluminum and titanium. Spectrum B is from TiO_2 and is shown for reference purposes. Such a reference spectrum may be subtracted from an "unknown" spectrum to enhance features which are normally obscured. The SIMS spectrum at the bottom of the figure corroborate the ISS results, indicating as in the earlier titanium adherend that failure did not occur cleanly at the Al_2O_3 surface, but rather in a complex region containing both adhesive and adherend.

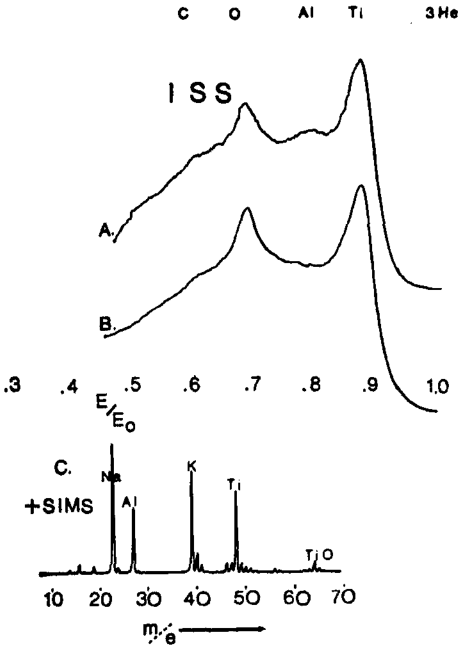

FIGURE 4 ISS and +SIMS from failure surface of anodized aluminum adherend bonded with TiO_2 filled epoxy. ISS (A), failure surface; ISS (B), TiO_2 reference; (C) +SIMS, failure surface.

The majority of failure surfaces examined which visually appeared to be adhesive failure, have been of the type shown in the examples where cohesive failure in both materials appears to have occurred. It is necessary to be able to determine by ISS, SIMS, Auger electron spectroscopy or some other elemental analysis method whether the surface contains both adhesive and adherend, since a test only for the adhesive on the adherend might cause an incorrect deduction of failure mode and location. For instance, a test for adhesive such as differential scanning calorimetry as performed by Bair and co-workers[8] to determine the amount of branched polyethylene adhering to a copper oxide surface does not in itself prove that the mode of failure was only cohesive in the polymer.

Some failures which could be classed as pure adhesive or cohesive have been examined by ISS–SIMS. Adherend surfaces which were obviously not wet by the adhesive showed no trace of the adhesive on the adherend. Often these surfaces were "dirty" and showed a thin layer of contaminating elements on the adherend. This kind of failure probably should not be considered "adhesive" if proper bonding between the two surfaces never occurred. Completely cohesive failures in which approximately the same amount of polymer remains on each adherend in a lap shear test have also been observed with no trace of adherend seen on either surface by ISS–SIMS.

SUMMARY

The combination of ISS–SIMS has proven valuable for analyzing the locus of failure in adhesive joints. Very thin adhesive films of near atomic dimensions may be determined. Mixed mode failure in both adhesive and adherend is easily determined.

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