APPLICATION OF INELASTIC ELECTRON TUNNELING TO THE
STUDY OF ADHESION

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The problem of devising meaningful and reliable methods for nondestructive evaluation of adhesively bonded joints has been the subject of considerable effort for many years. It remains an important and unsolved problem. The use of conventional NDT methods involving ultrasonics is not entirely satisfactory because the thickness of a bond line is small compared with typical acoustic wavelengths and, perhaps more importantly, because the strength and service life of an adhesive bond is dependent on its chemical as well as mechanical properties. That is, an adhesive bond that is mechanically perfect may fail because of chemical degradation initiated at the adhesive/adhered interface.

Figure 1 is a schematic of a typical metal/adhesive bond. Any metal employed in a practical situation will have a thin oxide layer on its surface and consequently any adhesively bonded metal joint will involve an oxide/polymeric interface.

The dashed line in Fig. 1 represents a typical fracture line (or fracture surface) which occurs in failure. It is well known that the fracture line is very rarely limited to the glue line (adhesive/oxide interface). The final morphology of a fracture line and the position of the initial crack may be only weakly related if at all. Once a critical sized-crack is formed the development of the line is usually determined by the mechanical properties of the component materials.

In addition to mechanical mechanisms of failure such as large stress concentrations associated with voids and residual stress, chemical and physico-chemical mechanisms associated with interface phenomena are frequently involved in the initiation of bond failure.

An interface consists of an organic or polymeric substance in intimate contact with a non-stoichiometric metal oxide. Many of the metal oxides are excellent catalysts. The oxides of many common metals such as Al, Mn, Cr, Fe, Ni or Zn are well known for their ability to catalyze reactions in organics. TiO$_2$ is an excellent catalyst and its action in oxidizing a polymeric binder is well known to be the cause of "chalking" of paints. Black and Blomquist reported that adhesive joints employing phenolic and epoxy resins were critically degraded by the metal adherend when heated in air due to catalytic oxidation of the adhesive. Such effects were observed for numerous common metals. The results of Black and Blomquist are illustrated in Table 1:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Shear Strength (bars) before heating</th>
<th>after heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>122</td>
<td>65</td>
</tr>
<tr>
<td>Mn</td>
<td>118</td>
<td>72</td>
</tr>
<tr>
<td>Cr</td>
<td>112</td>
<td>63</td>
</tr>
<tr>
<td>Fe</td>
<td>99</td>
<td>38</td>
</tr>
<tr>
<td>Ni</td>
<td>111</td>
<td>47</td>
</tr>
<tr>
<td>Zn</td>
<td>127</td>
<td>78</td>
</tr>
<tr>
<td>Cu</td>
<td>96</td>
<td>0</td>
</tr>
<tr>
<td>Ag</td>
<td>146</td>
<td>80</td>
</tr>
<tr>
<td>Ce</td>
<td>130</td>
<td>82</td>
</tr>
</tbody>
</table>

The role of H$_2$O in degrading an adhesive bond is not understood in detail but its action in accelerating detrimental chemical reactions is well documented.

The initiation of chemical degradation of an adhesive bond takes place at the microscopic interface between the metal oxide and the adhesive (or primer). We are concerned in our project with possible new measurement techniques for detecting and monitoring the chemical state of this microscopic interface. The technique of inelastic electron tunneling spectroscopy (on IETS) offers a potential tool of incredible sensitivity and great versatility for investigating, in situ, the chemical state of a metal oxide/adhesive interface. It should be made clear that at the present time it is not obvious how IETS can be employed as a
practical, "on-line", NDE tool. However, it seems clear that knowledge of the oxide/adhesive interface chemistry would be extremely valuable in developing new types of NDE measurements.

With this point of view we initiated, in January of this year, a small exploratory project to assess the feasibility of utilizing IETS to monitor the properties of an aluminum oxide/adhesive interface.

Inelastic Electron Tunneling Spectroscopy

In order to describe our progress a brief review of inelastic electron tunneling spectroscopy is needed. We are concerned with a metal/insulator/metal thin film junction as illustrated in Fig. 2. A typical tunnel-junction is fabricated by evaporation of a thin Al film onto a glass substrate. The film is oxidized to form an aluminum oxide layer 30 to 100 Å in thickness; similar to the natural oxide on any aluminum surface. A molecular substance such as an adhesive is then deposited on the oxide by a variety of "doping" techniques. In most cases the molecular layer is 5 to 20 Å in thickness. Finally, a second metallic film (often Pb) is deposited over the molecular layer forming a four terminal thin film MIM junction as shown in Fig. 2.

A variable bias is applied across two of the junction terminals and the current is measured across the second two terminals. Since the oxide is a good insulator only a small current of the order of $5 \times 10^{-9}$ amperes flows across the junction. This current is due principally to electrons which, in the quantum mechanical sense, tunnel through the oxide barrier. A schematic of the tunneling process is shown in Fig. 3. Fig. 3a illustrates the elastic electron tunneling process in which an electron tunnels through the insulating barrier from below the Fermi level of the Al film to an empty state above the Fermi level in the Pb film with no loss of energy. Fig. 3b illustrates the inelastic process. In this case the tunneling electron collides with one of the molecules on the oxide and excites one of the vibrational modes of the molecule having a characteristic energy $hv_m$ where $v_m$ is the vibrational frequency.
An inelastic tunneling process produces an abrupt change in the slope of the current-voltage characteristic at an applied voltage equal to the vibrational frequency $h \nu_m$. The effect is shown schematically in Fig. 4a. The effect can be greatly enhanced in two ways. First, by making measurements at very low temperatures thermal smearing effects can be greatly reduced. Usually measurements are made at liquid helium temperatures so that the Pb film is superconducting. Second, by using electronic modulation methods the junction conductance $G = dI/dV$ and the second derivative $d^2I/dV^2$ can be recorded. Structure due to excitation of molecular vibrational modes of the molecular layer are easily observed in $d^2I/dV^2$ versus $V$ curves. The characteristic shapes of these curves are illustrated in Fig. 4b and c. The structure due to inelastic tunneling processes appears in $d^2I/dV^2$ curves is remarkably similar to infrared absorption by the molecular substance. However, the tunneling method is different in several respects. First, the sensitivity to small quantities of material is fantastic: A monolayer of material on a junction with an area of $10^{-2}$ cm$^2$ is very easily detected. Second, all vibrational modes are detected by tunneling. That is, there are no selection rules and both infrared and Raman modes are seen in the same spectrum.

Figure 4a. Current-voltage curve characteristic of inelastic tunneling process.

Figure 4b. First derivative of 4a.

Figure 4c. Second derivative of 4b.

As an example of IETS we show in Fig. 5 the tunneling spectrum of the organic compound phenylalanine. The upper panel is the tunneling spectrum obtained by Simonsen and Coleman and the lower panel is the infrared transmittance reported by Hugol Mull. A large number of characteristic vibrational modes are easily identified and the IETS spectrum is quite similar to the IR spectrum. The IETS spectrum can be used to monitor the chemical state of the molecular layer. It is this property that is the basis of employing IETS for the study of an oxide/adhesive interface.

Figure 5. Tunneling spectrum of organic compound phenylalanine.

Application of IETS to Adhesives

The purpose of our project is to assess the feasibility of utilizing IETS as a tool for the study of the chemical state of a metal oxide/adhesive interface. Our immediate objectives are to determine if measurable changes in the tunneling spectrum can be correlated with processes involved in adhesive setting, curing, and degradation.
Setting of a typical adhesive involves cross-linking polymerization, chemical addition or condensation. In the cross-linking process for example, C=O bonds may be replaced by C-C bonds as illustrated in Fig. 6. This cross-linking can be accelerated by heating of the joint. It may be possible to monitor the cross-linking process by recording the IETS spectrum before and after heat treatment of the junction. The question of interest here is whether the diminution of the intensity of the vibrational stretching mode of the carbon-carbon double bond and the change in the distribution of vibrational modes can be observed as the cross-linking increases.

In the setting of epoxy resins such as illustrated by the addition reaction in Fig. 6 three molecules are joined in the curing process. Many epoxy adhesives cure slowly and at elevated temperatures. It may be possible to monitor the curing process by recording the IETS as a function of time or by performing isochronal heating of the tunnel junction.

**CROSS LINKING**

\[
\begin{align*}
-O\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH} & \quad \text{HC-CO-CH}_2\text{-CH}_2\text{-O-} \\
-O\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH} & \quad \text{HC-CO-CH}_2\text{-CH}_2\text{-O-}
\end{align*}
\]

**ADDITION REACTION**

\[
\begin{align*}
-O\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH} & \quad \text{HC-CO-CH}_2\text{-CH}_2\text{-O-} \\
-O\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH} & \quad \text{HC-CO-CH}_2\text{-CH}_2\text{-O-}
\end{align*}
\]

Figure 6. Schematic bonding configurations that may be observed with IETS.

By heating junctions in oxygen or in a high humidity environment, it may be possible to observe the catalytic oxidation of the adhesives at the interface. Catalytic interface reactions may produce chemisorption bonds between the adhesive and the oxide and intermediate chemical species such as O₂ and excited O₂ which are known to be reactive. It may be possible to detect and identify these species with IETS. Excited state (singlet) oxygen is known to accelerate the degradation of polymeric material. New vibration modes associated with the formation of chemisorption bonds may also be observable using IETS.

The penetration of water into the interface will be easily detected by inelastic tunneling since both the O-H bending and stretching modes are known to be quite intense. On the investigation of water permeation, D₂O may be used so that water entering from the environment may be easily distinguished from residual water contained in or on the oxide film.

We may also investigate the catalytic properties of the interface by looking for the appearance of C-D stretching and bending modes. If H atoms are exchanged with the D atoms of the permeating water it would be suspected that such an exchange reaction would require the action of a catalyst. In this case the oxide would be the catalytic agent.

**Progress**

In the remainder of this report we review our progress towards investigating adhesive properties using IETS.

**Equipment**

A large oil diffusion pumping system was modified for use in preparing tunneling junction. This system together with suitable cold traps was utilized in obtaining the data presented below. The system must be replaced by an oil-less "vac-ion" system in order to reduce junction contamination. The components of a vac-ion system are now available and after suitable modification will be assembled and utilized in future work.

An electronic (lock-in) modulation system capable of measuring and recording I-V, dI/dV-V, and d²I/dV²-V curves was built and employed in our experiments. The D.C. sweep unit was designed to provide voltage sweeps from 10 sec to 24 hours. Long sweep times are necessary to obtain good spectral resolution. Noise in the system with 10⁻¹ V modulation was reduced to within 3 Db of the Johnson noise limit.

Two dewar systems were constructed. One allowed the junction to be immersed directly into a storage dewar for measurements made at 4.2 K. The second is a He ⁷ glass dewar which can be pumped to 1.3 K and can accept several junctions. A special holder with leads and shielding and grounding was constructed.

**Results**

Al/O₃/Pb junctions were fabricated and data taken at 4.2 K. Measurements of I-V, dI/dV and d²I/dV² recorded. Initial measurements were made on "clean" (undoped) junctions. A typical dI/dV curve is shown in Fig. 7 with V in the range from ±40 x 10⁻³ ev. The sharp peaks near zero bias are due to the super-conducting density of states of the Pb film at 4.2 K. This response is characteristic of elastic tunneling and serves to document that the current flow is due to tunneling and not to small electrical shorts in the oxide. The energy gap of Pb, 2Δ, corresponds to the separation between the peaks.
In Fig. 7 we show inelastic tunneling spectra obtained on two different junctions. Curve A is for a "clean" junction which was not doped with a molecular material. There is very little structure in the $d^2I/dV^2$ curve. The shoulder at about .15 V is due to the O-H stretching mode. These structures are associated with residual contamination on the junction acquired during the formation of the oxide in the vacuum system. Curve B is for a junction doped with one component of a commercial epoxy adhesive, "Chemlock 304." Several vibrational modes associated with the adhesive component are clearly evident. The most intense modes are the C-H stretching and bending modes. The O-H stretching and bending modes are also very intense.

The data presented in Fig. 8 is our first attempt to observe inelastic tunneling with the adhesive dopant. There are many other vibrational modes evident in the data but considerable improvement in the signal to noise must be accomplished before the data can be used quantitatively. A number of improvements in the fabrication and signal processing are currently being implemented.

Experiments are underway to look at the spectrum of the other component of Chemlock and at the mixed epoxy itself. Following this we shall attempt to monitor changes in the epoxy due to thermal setting and degradation of the adhesive due to water and/or heating in a gaseous environment. An assessment of the feasibility of using IETS to study the chemical state at an aluminum oxide/adhesive interface should be completed in the next few months.

REFERENCES

DISCUSSION

PROF. MAX WILLIAMS (University of Pittsburgh): We have time for any questions of points of fact. We won't have time for discussion of the paper, but are there any questions as points of fact?

DR. BILL BASCOM (Naval Research Laboratory): Can you distinguish between a hydroxyl of water and hydroxyl bonded to aluminum?

PROF. WILLIAMS: I think I must ask you to just reply either yes or no or maybe.

PROF. WOLFRAM: I suspect the answer is maybe.

PROF. WILLIAMS: I saw one other question of fact back here.

DR. G. GARDNER (Southwest Research Institute): At what temperature are these measurements?

PROF. WOLFRAM: Pardon?

DR. GARDNER: At what temperature are these measurements?

PROF. WOLFRAM: These measurements that you saw were performed at liquid helium temperatures. The technique itself does not require superconductivity. You increase your sensitivity or your resolution by going to low temperature. It also impedes any further chemical processes, so you can take a picture of it, then warm it back up, and then go back down and freeze in your particular chemical state. It doesn't really require superconductivity; it does require low temperatures to get resolution.

PROF. WILLIAMS: Thank you very much, Dr. Wolfram, particularly for meeting your shortened time for presentation.