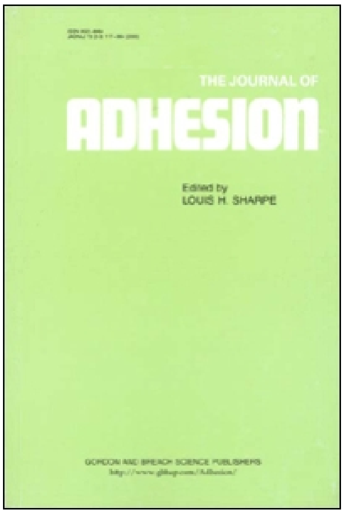

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Chemical and Thermodynamic Characterization of Metal Surfaces for the Adhesive Bonding of Metals

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Several complementary surface analysis techniques were employed to determine the properties of the polished surfaces of titanium-6Al,4V, 2024-T3 aluminum, and interstitial free steel. XPS indicated that the oxides were all approximately 50 Å thick and covered with a layer of carbon-containing compounds probably consisting of both hydrocarbons and more highly oxidized carbonaceous materials such as carbonates or bicarbonates. The calculation of wettability envelopes showed all of the surfaces to have similar energetics, possibly because these properties are determined largely by the adsorbed water and hydrocarbons present on all transition metal surfaces. The surface isoelectric points were estimated using indicator dyes and compared to published values. Finally, reflection–absorption infrared spectra were obtained from the aluminum surfaces, allowing the oxide structure to be determined and giving more information about the nature of the overlying carbon-containing compounds.

KEY WORDS Surface analysis; surface isoelectric point; metal oxides; surface contamination; reflection–absorption infrared spectroscopy; surface energetics.

INTRODUCTION

Knowledge of the chemical and physical structure of the first few atomic layers of a solid surface is of prime importance when dealing with the design of new adhesives or coatings systems. This information is also important when determining the performance capabilities of, or analyzing failure mechanisms that occur in, existing systems. Fortunately, many sensitive techniques that enable analysis of the composition of solid surfaces are now readily available. These include reflection-absorption infrared spectroscopy, ellipsometry, and contact angle measurements. The use of the various electron and ion spectroscopies, while requiring (in general) more complex (and expensive) equipment, allow additional dimensions to be added to an analysis.

This paper describes the application of four of these techniques to characterize thoroughly the surfaces of metals commonly encountered in adhesion problems, including steel, titanium, and aluminum. In particular, factors known to influence the success of adhesive bonding to these substrates have been investigated, including surface wettability, oxide composition and isoelectric point, and the nature of surface contaminants that result from exposure of clean surfaces to the laboratory atmosphere.

The particular techniques that we have used in the present study include isoelectric point measurements (IEPS) using an indicator dye method, contact angle measurements, X-ray photoelectron spectroscopy (XPS), and reflection-absorption infrared spectroscopy (RAIR). These techniques have proven to be very complementary to each other, overlapping enough in the types of information that they provide to allow an internal check on the validity of the results.

IEPS measurements were obtained through the use of the indicator dye method.[1] This is a simple technique that involves the visual observation of the color change that occurs in a small amount of indicator placed on the freshly prepared sample surface. The indicators used all initially exist in their acidic forms. The IEPS of the material being evaluated lies between the pK_a of the most basic indicator that exhibits a color change and the pK_a of next most basic indicator. This technique does not determine the exact IEPS, but rather gives a narrow range of pH values within which the IEPS lies. IEPS values obtained using this technique have been verified in at least one instance through the use of spectroscopic methods.[1]

Much information about the surface is contained in the IEPS value. Combined with a knowledge of the pK_a of polar adsorbate, Bolger and Michaels have shown[2,3] that the relative strength of interaction between a metal oxide surface and the adsorbate may be predicted. Boerio and Dillingham have shown[4] that this same information may be used to predict (in some cases) the relative stability of adsorption of an amine functional silane coupling agent during exposure to water of a known pH. This enabled predictions to be made of the pH of coupling agent deposition that resulted in the greatest improvement in adhesive joint durability during environmental exposure.

The wettability of metal surfaces has been recognized as a major factor in determining the strength of adhesive joints.[5,6] Wetting of the adherend surface by the adhesive must take place before intimate contact between the adhesive and adherend can occur. This results in the elimination of air pockets by allowing nearly complete penetration of the resin into surface asperities. This complete contact allows for maximum molecular interaction between the adhesive and adherend as well as maximum mechanical interlocking.

The wettability of the different surfaces was determined through the use of wettability envelopes. These are obtained by measuring the contact angle on the solid surfaces of liquids that have widely varying polar and dispersion force components of surface energy. The envelope defines, for a particular solid, the combinations of polar and dispersion force components which will allow a liquid to wet the solid surface.

The wettability envelopes were constructed using the methods of Smith and Kaelble.[7] To obtain the polar and dispersion components of the solid surface energy, the contact angles of several liquids with known polar and dispersion surface energy components were measured. The work of adhesion of these liquids to the solid surfaces was then calculated using the Young and Dupré equation:

$$W_a = \gamma_{lv}(1 + \cos\theta) \tag{1}$$

When these values are substituted into Eq. (2) along with the values of the polar and dispersion components of the liquid surface energies, a linear plot is produced with the slope and intercept giving the square roots of the dispersion and polar components of the solid surface energy.

$$\frac{W_a}{2(\gamma_{\mathrm{LV}}^{\mathrm{D}})^{1/2}} = (\gamma_S^{\mathrm{D}})^{1/2} + \left[\frac{\gamma_{\mathrm{L}}^{\mathrm{P}}\gamma_S^{\mathrm{P}}}{\gamma_{\mathrm{L}}^{\mathrm{D}}}\right]^{1/2} \tag{2}$$

The spreading coefficient for a liquid on a solid surface is given by Eq (3):

$$S = W_a - 2\gamma_{\mathrm{LV}} \tag{3}$$

The condition for a liquid to spread spontaneously on a solid surface is that this coefficient must be greater than or equal to zero. Hence, for spreading just to occur,

$$W_a = 2(\gamma^{\mathrm{P}}_{\mathrm{LV}} + \gamma^{\mathrm{D}}_{\mathrm{LV}}) \tag{4}$$

Next, on a plot of $\gamma^{\mathrm{D}}_{\mathrm{LV}}$ versus $\gamma^{\mathrm{P}}_{\mathrm{LV}}$, we define the polar coordinates

$$T = [(\gamma^{\mathrm{D}}_{\mathrm{LV}})^2 + \gamma^{\mathrm{P}}_{\mathrm{LV}})^2]^{1/2} \tag{5}$$

$$\tan\theta = \frac{\gamma^{\mathrm{D}}_{\mathrm{LV}}}{\gamma^{\mathrm{P}}_{\mathrm{LV}}}$$

so that from (4), we get

$$W_a = 2(T\sin\theta - T\cos\theta) \tag{6}$$

which, when combined with

$$W_a = 2[(\gamma^{\mathrm{D}}_{\mathrm{L}}\gamma^{\mathrm{P}}_{S})^{1/2} + (\gamma^{\mathrm{P}}_{\mathrm{L}}\gamma^{\mathrm{P}}_{S})^{1/2}]$$

may be rearranged to obtain

$$T = \frac{(\gamma^{\mathrm{P}}_{S}\cos\theta)^{1/2} + (\gamma^{\mathrm{D}}_{S}\sin\theta)^{1/2}}{\cos\theta + \sin\theta} \tag{7}$$

which defines the wettability envelope.

If the surface in question has a large polar component to its surface energy, the envelope is elongated far along the abscissa. If the surface has a large non-polar component, then the envelope tends to extend along the ordinate. Exposure of an extremely clean metal surface to atmospheric contamination tends to pull the envelope in along the abscissa by reducing the polar nature of the surface (see, for example, Ref. 7). Etching a surface by oxidizing acids or caustic cleaners tends to dilate the envelope along the abscissa.

The envelope is determined exclusively by the surface energy of the solid. Points within the envelope represent liquids which will spontaneously spread and wet the surface while points outside the envelope represent non-spreading liquids, *i.e.* ones with a negative spreading coefficient.

XPS is a non-destructive, highly surface-sensitive technique for determining the composition of the uppermost atomic layers of a sample. When the surface of a solid is irradiated with high energy photons (*i.e.*, X-rays), core level electrons can be ejected from elements near the surface if the photon energy is greater than the binding energy of the electron plus the spectrometer work function. Conservation of energy dictates that the kinetic energy of the ejected photoelectrons will be given by

$$\text{K.E.} = h\nu - \text{B.E.} - \phi \tag{8}$$

where

K.E. = kinetic energy of electron

$h\nu$ = incident photon energy

B.E. = binding energy of electron

ϕ = spectrometer work function

The binding energies of the photoelectrons may be correlated to the element from which the element originated. Alteration of the chemical state of the parent atom through the formation of chemical bonds results in a shift of the binding energy of the electrons and allows (in some cases) compound identification.

Because of the limited mean free path of electrons in solids, some depth profiling is possible through varying the angle between the electron energy analyzer and the sample surface. When this angle is large (*i.e.*, grazing the surface) the effective electron path is long and only electrons near the surface will be detected. Conversely, small, near normal exit angles result in the detection of electrons that originate from deeper within the sample. The mean free path for photoelectrons in metals, oxides and polymers is about 5–20 Å, 15–40 Å, and 40–100 Å, respectively.[8]

RAIR is a technique for obtaining the infrared spectra of extremely thin films on reflecting substrates. The method involves reflecting infrared radiation that is polarized parallel to the plane of incidence off the surface at large, grazing angles of incidence. Under these conditions, the incident and reflected waves combine to form a standing wave that has considerable amplitude at the surface. On fairly good specular reflectors such as polished metals, evaporated metal films, or silicon wafers, the technique allows reasonable spectra to be obtained from absorbing films of approximately monomolecular coverage.

Because the desired signal in a typical RAIR experiment is only a small percentage of the total reflected energy, the advent of FTIR instruments has greatly facilitated the use of this technique. FTIR instruments typically provide improved signal-to-noise ratios (allowing large scale expansions) and greatly reduced scan time (thereby increasing the throughput) when compared to typical dispersive instruments. Spectra of monomolecular layers of organic compounds on good reflectors may now be obtained in minutes instead of hours.

EXPERIMENTAL

The materials that were investigated were interstitial-free steel, titanium-6Al–4V, and 2024-T3 aluminum. Small coupons were cut from 1.6 mm thick sheets of these materials to a size appropriate for the particular analytical technique being used.

The steel coupons were degreased in an aqueous solution of Parker 338, a proprietary alkaline cleaner, at 60 °C while the titanium and aluminum specimens were degreased by rinsing in 2-butanone.

The coupons were mechanically polished using standard metallographic techniques. This included rough polishing on dry SiC paper followed by fine polishing on wool broadcloth polishing cloths using successively finer grades of alumina dispersed in deionized, carbon-filtered water. The final polishing of the steel and titanium surfaces was accomplished using 0.05 μm alumina, while the final polishing of the aluminum samples was performed with MgO powder. The net result on all of the samples was a smooth, clear, highly reflective surface.

Extreme care was taken during all phases of the sample preparation process to maintain very clean conditions. This included wearing rubber gloves during the polishing process and handling the specimens exclusively with hemostats. If these procedures were not adhered to, the resulting specimen would be partially hydrophobic due to adsorbed contamination.

Advancing contact angles were measured in the laboratory

TABLE I
pK_a's of indicator dyes used in IEPS determinations along with color changes observed on polished metal surfaces

		Color Change					
INDICATOR	pK_a	Ti-6Al-4V		I.F.steel		2024-T3 Al	
Bromophenol blue	4.0	RV	RV	RV	V	RV	RV
Bromocresol green	4.5	Y	Y	Y	B	Y	B
Bromothymol blue	7.0	Y	Y	Y	YB	Y	Y
Thymol blue	7.4	Y	Y	Y	Y	Y	Y
Alizarin yellow	10.5	Y	Y	Y	Y	Y	Y

R =red, V =violet, Y =yellow, B =blue

atmosphere using a Ramé–Hart sessile drop goniometer. The pK_a's of the indicators that were used were determined through titration using a pH meter and are listed in Table I. RAIR spectra were obtained using Harrick Scientific reflection accessories in a Perkin–Elmer 1800 FTIR spectrophotometer. XPS spectra were obtained with a Physical Electronics 5300 ESCA system using Mg K-alpha radiation. Spectra were referenced to a C1s binding energy of 284.6 eV correct for the effects of sample charging.

RESULTS AND DISCUSSION

1 IEPS Measurements

The pK_a's of the various indicator dyes used are listed in Table I along with the color changes noted on the various surfaces. The IEPS measurement on the steel surface suggests a value of about 7.0 for the isoelectric point. This correlates well with those values tabulated by Parks.[9] The 2024 Al results indicate that the IEPS lies between 4.5 and 7.0, again a reasonable value when compared to those for hydrated aluminum oxides in the review by Parks.[9] The IEPS measurements on the Ti–6AL–4V sample were indeterminate, however, as none of the indicators used exhibited a color change. This suggests that the IEPS is above about 10. The values reported by Parks that were obtained by other investigators, however, were consistently about 4.5 for freshly calcined samples and about 6.0 for hydrated samples.

The indicator dye technique is the most common one used to measure the IEPS of high surface area powders. It has also been used in the past with apparent success to measure the IEPS of low surface area samples such as metal coupons.[1] However, there is some doubt as to whether or not there is a high enough concentration of ionizable groups (*e.g.*, hydroxyls) on a planar metal surface to cause an observable color change in an indicator dye solution.

Color changes noted in dye solutions placed on metal surfaces could possibly be influenced by the dissolution of ionizable compounds from the sample surface. This phenomenon has been found to cause hysteresis in the measurement of the IEPS of other materials, as well as result in the measured IEPS being a function of the time required to record color changes in the indicator.[10] The measured IEPS would then be a function of both the IEPS of this altered surface and the pK_a of the dissolved species. Previous studies using RAIR have indicated that the oxides present on the polished surfaces of 2024-T3 aluminum[11] and interstitial-free steel[12] are soluble, depending upon the pH, while the oxide present on the polished surface of Ti–6Al–4V is insoluble over a fairly wide range of pH values.[11] Therefore, the lack of color change noted in the dyes placed on the titanium sample may merely reflect the insolubility of the oxide and bear little relation to its actual IEPS. The color changes noted on the other oxide surfaces may be due (at least in part) to a partial dissolution of those oxides.

In addition, the measured IEPS of a material may be greatly affected by the purity, cleanliness and history of the particular sample being investigated. The oxidation state and degree of hydration of the surface layers as well as the presence of defects and impurities (both adsorbed and structural) can cause a shift in the measured IEPS of more than one or two points. In view of the importance of the IEPS as a surface parameter as well as the sensitivity of this parameter to experimental conditions and sample preparation, published values should be used only after careful consideration of the individual experimental details.

2 Wettability Envelopes

The wettability envelopes for the steel, titanium, and aluminum surfaces prepared as described above are shown in Figure 1. The

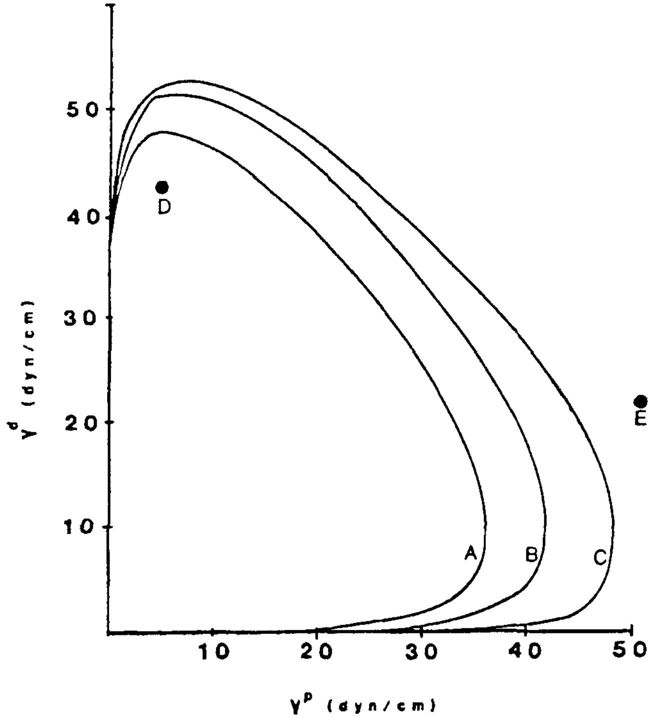

FIGURE 1 Wettability envelopes for (A) polished interstitial-free steel; (B) polished Ti–6Al–4V; (C) polished 2024-T3 aluminum; showing their relationship to (D) Epon 828/9.4 wt.% Shell curing agent D; and (E) deionized, carbon-filtered water.

surface preparation technique used is quite gentle when compared to grit blasting or many types of chemical etching and appears to result in surfaces which are of a less polar nature.[7] This may be due in part to the presence of the minute amounts of hydrocarbons which are an unavoidable consequence of polishing samples in laboratory air.

The envelopes for the three metals show a greater difference between the polar components of surface energy than the dispersion components. The polar component of oxide surface energy is due primarily to the presence of hydroxyls. The concentration of hydroxyls is determined by both the geometry of the oxide and the ability of the oxide to cleave water molecules and would be expected to differ from metal to metal. The dispersion component, on the other hand, may be largely a function of trace amounts of adsorbed hydrocarbons, which would be about the same for these three metals.

As indicated in Figure 1, water falls outside of the envelopes and is not expected to spread spontaneously on these surfaces. Typical epoxy adhesives would be expected to spread spontaneously on these surfaces, however. Figure 1 includes the point representing Epon 828 mixed with a tertiary amine salt curing agent. Gledhill *et al.* have shown[5] that exposure of relatively clean metal surfaces such as these to high relative humidities, however, can cause a change in the envelopes that result in non-wetting behaviour by such an adhesive.

3 XPS Data

The survey spectrum of mechanically polished interstitial free steel, obtained at a 45-degree exit angle, is shown in Figure 2 and demonstrates the presence of iron, oxygen, carbon, and copper. The C(1s) peak is located near 284.6 eV which indicates a thin layer of organic contamination on the surface, but not enough to act as an insulator and result in charging. The Fe(2p3/2) peak near 711.1 eV

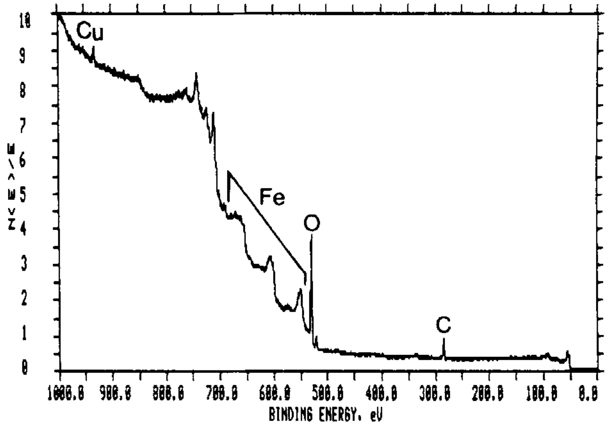

FIGURE 2 Photoelectron survey spectrum obtained from polished interstitial free steel at a 45-exit angle.

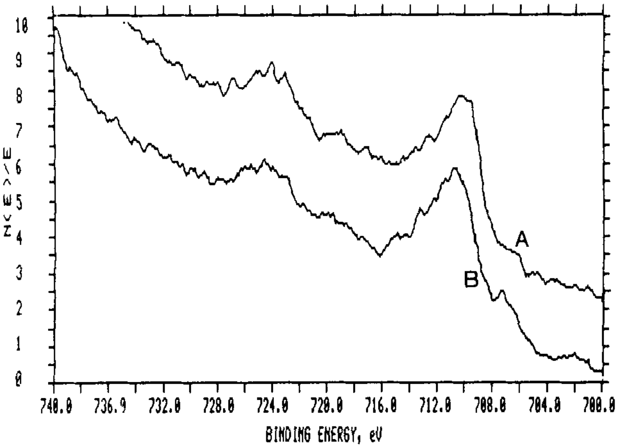

FIGURE 3 Fe(2p3/2) photoelectron spectra obtained from interstitial free steel using exit angles of (A) 45 and (B) 15 degrees.

(Figure 3A) and the O(1s) peak near 529.8 eV (Figure 4A) are both part of a thin layer of Fe_2O_3 located directly beneath the contamination. A higher binding energy shoulder is also present in the O(1s) spectrum and this peak is probably due to either an iron hydroxide or oxidized carbon species. The copper evident in the

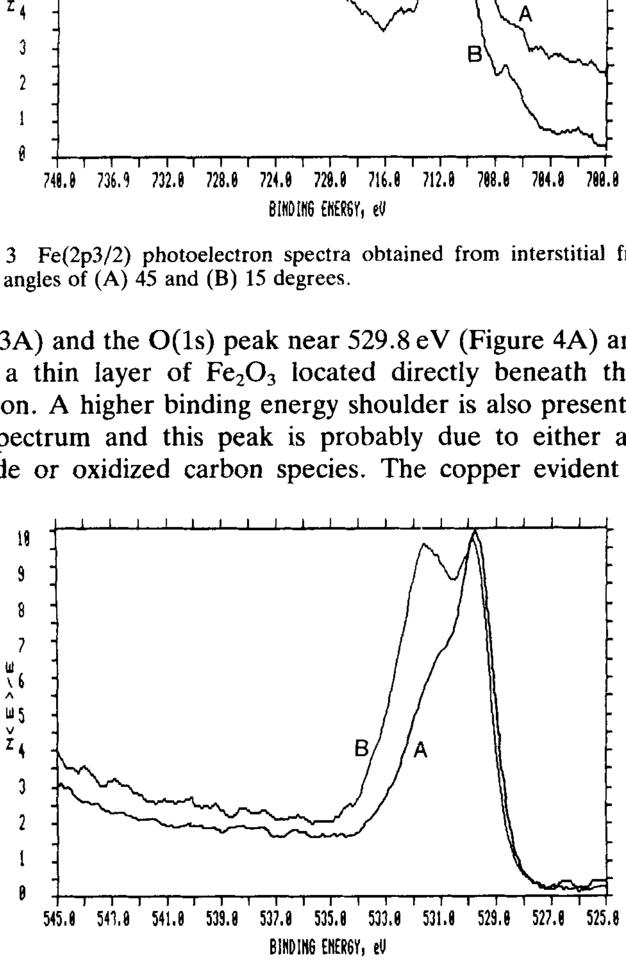

FIGURE 4 O(1s) photoelectron spectra obtained from interstitial-free steel using (A) 45- and (B) 15-degree exit angles.

survey spectrum has an unknown origin. Most likely it is present as a residual element in the metal, as interstitial free steel is derived partly from recycled metal.

Next, the sample was rotated so that the surface was normal to the electron energy analyzer. This allows detection of electrons originating from deeper within the sample. The Fe(2p) spectrum (Figure 3B) shows an additional peak near 707 eV which is characteristic of elemental iron. This indicates that the oxide is approximately 40 Angstroms thick.

The O(1s) peak also showed a change as a function of exit angle (Figure 4B). At grazing exit angles, the component near 531.6 eV, characteristic of either hydroxide or possibly a carboxylate species, has greatly increased in intensity relative to the oxide peak near 529.8 eV. This suggests that the material containing this oxygen is located within the first few Angstroms of the surface.

The survey spectrum of the polished Ti–6aL-4V specimen, obtained at a 15-degree exit angle, demonstrates the presence of titanium, oxygen, carbon, and trace amounts of aluminum. A closer look at the Ti(2p) peak near 458.0 eV (Figure 5A) and the O(1s) peak near 529.8 eV (Figure 6A) indicates the presence of a thin film of TiO_2, the native oxide on mechanically polished Ti–6Al–4V.[11] The grazing angle O(1s) spectrum (Figure 6B) shows the same higher binding energy peak near 531.6 eV present on the steel surface.

The Ti(2p) spectrum obtained at normal incidence angles (Figure 5B) shows an additional weak peak near 454 eV that is characteristic of elemental titanium. This implies again an oxide on the order of about 40 Angstroms thick.

The survey spectrum of mechanically polished 2024-T3 aluminum, obtained at a 15-degree exit angle, demonstrates the presence of aluminum, copper, oxygen and carbon (4% copper is present in 2024 Al as an alloying element). The C(1s) peak appeared near 286.2 eV, indicating about 1.6 V of charging. This peak also has a higher binding energy component characteristic of either a hydroxide or an oxidized hydrocarbon, such as a carbonate or bicarbonate species. Spectra obtained at a 90 degree exit angle show the presence of a peak due to metallic aluminum near 72.6 eV (Figure 7), again suggesting an oxide that is only a few tens of Angstroms thick.

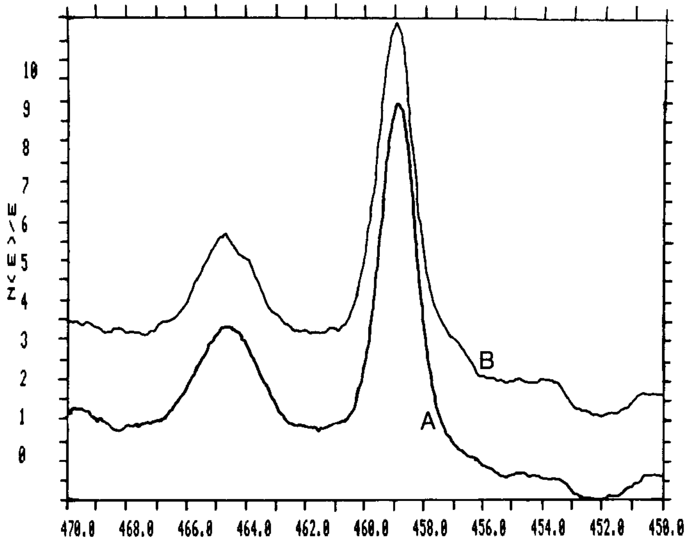

FIGURE 5 Ti(2p) photoelectron spectra obtained from Ti–6Al–4V using exit angles of (A) 15 and (B) 45 degrees.

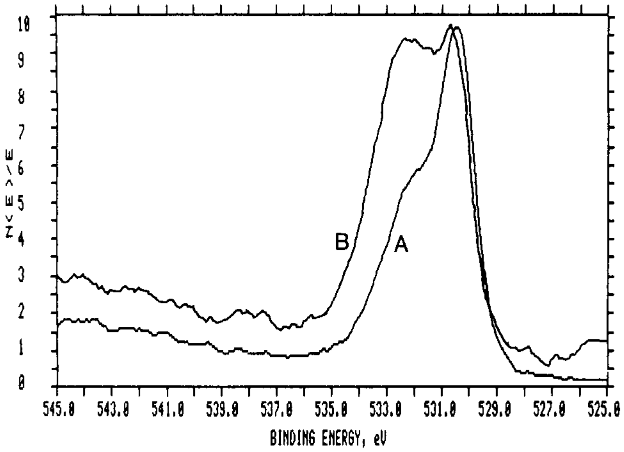

FIGURE 6 O(1s) photoelectron spectra obtained from Ti–6Al–4V using exit angles of (A) 45 and (B) 15 degrees.

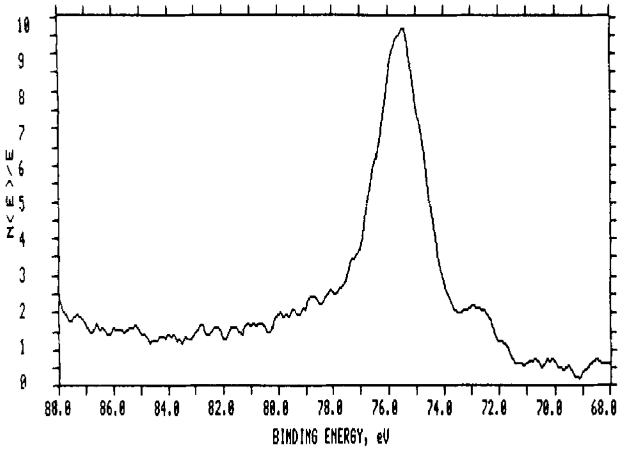

FIGURE 7 Al(2p) photoelectron spectrum obtained from 2024-T3 aluminum using a 15-degree exit angle.

The polishing procedure appears to produce similar surfaces on all three meatals—a thin oxide film underneath a layer of carbon-containing compounds. The stable adsorption of this carbonaceous material, even under UHV and X-ray bombardment, suggests that at least some of this material may be chemisorbed rather than physisorbed.

4 RAIR Data

The RAIR spectrum of freshly polished 2024-T3 aluminum is shown in Figure 8. It is characterized in part by a strong band near 960 cm^{-1} due to the Al–O–Al stretching vibrations of amorphous Al_2O_3. Well crystallized and anhydrous aluminum hydroxides (that is, hydroxides containing only compositional and not molecular water) tend to show distinct peaks due to O–H stretching vibrations between about 3400 and 3500 cm^{-1}.[13–15] The absence of well defined peaks in this region of Figure 8 and the presence of a broad, intense band centered near 3500 cm^{-1} suggests that the surface hydroxide has little structure and contains large amounts of water that is hydrogen bonded to the lattice hydroxyls.

Figure 8 has two other bands of interest near 1540 and 1380 cm^{-1}. Other workers have noted broad absorbances in this region[13–16] but

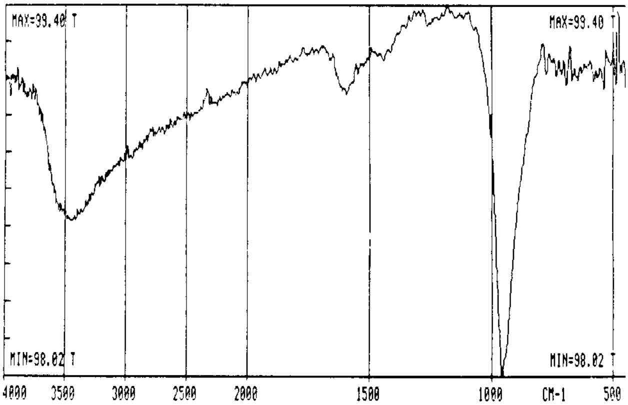

FIGURE 8 Reflection-absorption infrared spectrum obtained from polished 2024-T3 aluminum immediately after polishing.

the bands demonstrated little structure and were attributed to the O–H bending modes of molecular water in an unspecified state.

Aluminum oxides are very soluble in solutions of high pH. Etching aluminum coupons with solutions of concentrated NaOH has been shown to produce a surface with identical corrosion behaviour to evaporated aluminum films.[17] This process has also been shown to be quite effective as a pretreatment for adhesive bonding of aluminum, resulting in strong and durable adhesive joints with highly reproducible performance.[18] In the course of investigation of an NaOH etch as a pretreatment for the adhesive bonding of aluminum, it was found that the RAIR spectra of the etched aluminum surfaces demonstrated most of the same features as the spectra of the polished surfaces but with more intense and hence more easily analyzed bands.

Etched surfaces were prepared for RAIR spectroscopy by immersing freshly polished 2024-T3 coupons into 10 wt.% NaOH for about 15 seconds, followed by a thorough rinse in deionized, carbon-filtered water. The samples were then dried with compressed N_2 and immediately placed into the spectrophotometer.

Figure 9A shows the spectrum of a freshly etched 2024-T3 aluminum mirror. The most obvious difference between this spectrum and the spectrum of the polished surface is the absence of the strong band near 950 cm^{-1} and the presence of a strong band

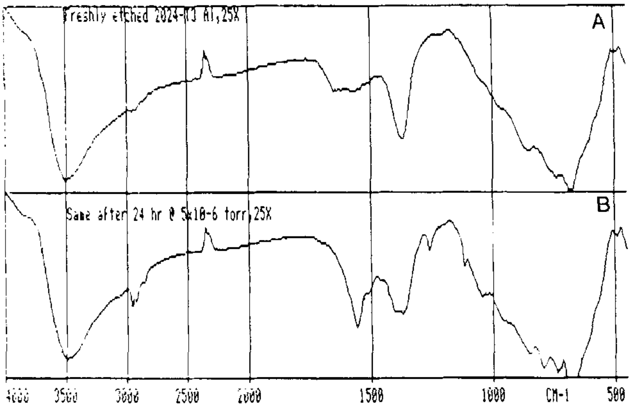

FIGURE 9 Reflection-absorption infrared spectrum obtained from 2024-T3 aluminum after etching for 10 seconds in 10% NaOH. Spectrum (A) was obtained immediately after etching while spectrum (B) was obtained after 24 hours in vacuum at approximately 10^{-6} torr.

near 670 cm^{-1} in its place. The 670 cm^{-1} mode has been shown to be due to a TO phonon of Al_2O_3 while the 950 cm^{-1} mode is due to a LO phonon.[14,20]

The optics of specular reflection at high angles of incidence dictate that for extremely thin films (where the film thickness is much less than the wavelength of the incident light), normally inactive LO phonons become capable of interacting with the electric field component of the incident radiation.[19] This explains the band due to the LO phonon near 950 cm^{-1}. The band near 670 cm^{-1}, representing a TO phonon, is visible in the spectrum of the etched surface. This is expected in films whose thickness approaches that of the wavelength of the incident radiation and suggests that the etching process produces an oxide film of considerably greater thickness than the polishing procedure.

The bands seen in Figure 9A near 1540 and 1380 cm^{-1} are more intense and more well defined than in the spectrum of the polished sample. There is an additional band that appears as a shoulder in this spectrum near 1650 cm^{-1} that is not apparent in the spectrum of the polished surface.

The aluminum mirror whose RAIR spectrum is shown in Figure 9A was placed in a vacuum system and maintained at a pressure of about 5×10^{-6} torr. After about 24 hours, the mirror was removed from the vacuum system and another RAIR spectrum obtained from its surface.

The spectrum shown in Figure 9B was obtained after the vacuum exposure and several interesting changes may be observed. The shoulder near 1650 cm^{-1} has disappeared completely and was probably due to the O–H bending vibrations of loosely bound molecular water remaining in the oxide from the etching process.[15,19] The band originally near 1380 cm^{-1} has decreased in intensity and another band has developed near 1400 cm^{-1}. The broad band near 3500 cm^{-1} has also undergone a slight decrease in intensity. The band near 1380 cm^{-1} present in the spectrum of the as-etched surface may be due to the C–O stretching vibrations of a carbonate species formed during the etching process. The same band is noted in the bulk spectrum of sodium carbonate.[20] Initially hydrogen bonded to excess water in the hydroxide layer, the removal of some of this water through exposure to vacuum would reduce the amount of hydrogen bonding in this carbonate, thus accounting for the appearance of a band at a slightly higher frequency near 1400 cm^{-1}. The broad band near 3500 cm^{-1} is due to the O–H stretching vibrations of lattice hydroxyls that are strongly hydrogen bonded.[15] The vacuum exposure at room temperature was not a vigorous enough treatment to remove much of this water, hence only a slight decrease in the intensity of this band occurs.

The weak bands in Figure 9B near 1070 and 1120 cm^{-1} are probably due to the Al–OH bending vibrations of pseudoboehmite, a partially crystalline oxyhydroxide of aluminum. This indicates that removal of some of the excess water from this etched surface has resulted in the conversion of a portion of the initially amorphous hydroxide to a more highly ordered form. The increase in intensity of the band near 1540 cm^{-1} accompanies this formation of pseudoboehmite and the band is probably due to the O–H bending of hydroxyls present as part of the pseudoboehmite structure.

The oxide film present on mechanically polished 2024-T3 aluminum appears to consist primarily of an amorphous, hydrated Al_2O_3. On the basis of the spectra obtained from etched aluminum surfaces, the O–H bending region of the RAIR spectrum appears to show evidence of both hydroxyls that are part of the hydroxide structure (1540 cm^{-1}) and a small amount of what appears to be a bicarbonate species (1380 cm^{-1}), probably originating from atmospheric CO_2 incorporated into the oxide film during the polishing process.

SUMMARY

The techniques discussed in this paper are all relatively straightforward and may be applied directly towards the solution of the types of problems encountered in adhesion science. They allow detailed characterization of adherend surfaces and the effects of various surface preparation techniques and treatments. They can provide much information about the specific interactions between coatings, adhesives and substrates. They also permit precise determination of the locus of failure of an adhesive joint as well as the determination of the nature of any chemical changes that may have accompanied that failure.

The techniques employed here all provide complementary information. Contact angle measurements allow the prediction of the interaction between specific liquids and solid surfaces. XPS is excellent at determining the atomic constituents of the surface regions of a material and provides some information regarding chemical composition, while RAIR provides a detailed picture of the nature of the chemical bonds present in these same regions. The extremely high signal-to-noise ratios provided by FTIR instrumentation has decreased the required scanning time to the point where it is now practical to study films that are on the order of a few tens of Angstroms thick on a fairly routine basis.

The IEPS of a particular material appears to be an important parameter related to corrosion, adhesive bond strength and durability. Obtaining meaningful values of this parameter using an indicator dye technique seems to be difficult, however, and more methods need to be evaluated.

The surfaces of 2024-T3 aluminum, Ti–6AL–4V, and interstitial-free steel show quite a few similarities in the as- polished state. The surfaces are covered with oxides of comparable thicknesses which are initially quite clean. The surface energy, as demonstrated by wettability envelopes, does not vary widely from one to the other. This may be due in part to the presence of similar amounts of adsorbed water[5] as well as similar amounts of adventitious hydrocarbons. Both RAIR and XPS suggest the possibility that some of this carbonaceous material exists as a carbonate or a bicarbonate species. These surfaces behave quite differently as adherends during long term environmental exposure,[4,12] however, and factors such as the susceptibility of the surface to corrosion appear to have considerable influence here.

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