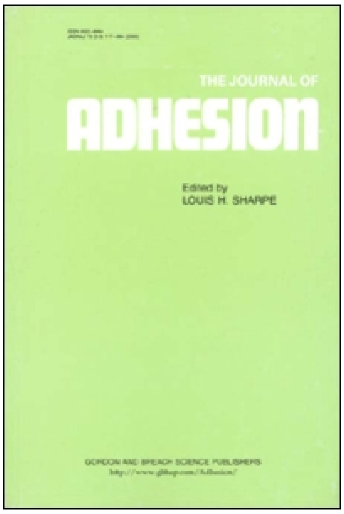

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Analysis of Thin Films on Metal Surfaces

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External reflection infrared spectroscopy was used in combination with other surface analysis techniques such as ellipsometry, Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) to determine the structure of organofunctional silanes adsorbed onto 2024 aluminum and titanium-6 Al, 4V mirrors. The results obtained indicated that the adsorption of γ-aminopropyltriethoxysilane (γ-APS) onto aluminum was a strong function of pH and adsorption time. Films formed by adsorption of γ-APS at pH = 8.5 were composed of polysiloxanes containing amine hydrochlorides. The structure of films formed by adsorption of γ-APS at pH = 10.4 depended on time. Films obtained after one minute were composed of polysiloxanes that did not interact strongly with the oxide but during 15 minutes adsorption the air-formed oxide was dissolved and copper accumulated near the surface of the mirrors. Films formed by the adsorption of γ-glycidoxypropyltrimethoxysilane (γ-GPS) onto aluminum were composed of polysiloxanes that did not interact strongly with the oxide. The structure of films formed by adsorption of γ-APS onto titanium did not depend on adsorption time. Films formed at pH = 10.4 were composed of low molecular weight oligomers that gradually polymerized to polysiloxanes during atmospheric exposure.

INTRODUCTION

Thin films formed by the adsorption of organic compounds onto the oxidized surfaces of metals are fundamentally important in adhesive bonding of metals. Accordingly, there has been considerable interest in developing techniques for determining the structure of such films. We have been particularly concerned with developing external reflection infrared spectroscopy.

Infrared spectroscopy has, of course, been widely used for investigating adsorption onto high surface area powders.[1,2] However, few applications to thin films on plane metal substrates have been reported because of the

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inherently weak infrared absorption by such films. When infrared radiation is reflected from the surface of a metal, the incident and reflected waves usually combine to form a standing wave having very small electric field amplitude at the metal surface and only minimal interaction between the infrared radiation and a surface film is obtained. However, when radiation polarized parallel to the plane of incidence is reflected from the substrate at large, nearly grazing angles of incidence, the electric field amplitude at the surface and the intensity of the infrared absorption by a surface film can be maximized.[3] Infrared spectra of very thin films can be obtained under these conditions and spectra of monolayers of fatty acids,[4] alcohols,[4] and amides[5] have in fact been reported.

In external reflection infrared spectroscopy, an absorption band for a surface film is observed as a band of reduced reflectivity for the substrate. Greenler[3] has shown that the depth of such a band is in general a complex function of the wavelength of the radiation, the angle of incidence, the thickness and optical constants of the film, and the optical constants of the substrate. However, Francis and Ellison[6] have shown that for angles of incidence less than about 80° and for good reflectors, the depth (ΔR) can be approximated as

$$\Delta R = \frac{\varepsilon c d_2}{n_2^3} \frac{9.212 \sin^2 \theta}{\cos \theta}$$

where ε, c, d_2, and n_2 are, respectively, the absorptivity, density, thickness, and refractive index of the film.

In most cases, the depths of the absorption bands for nearly monomolecular films are very small and must be enhanced in order to obtain spectra of usable intensity. This may be done by averaging several scans of the same spectral region or by making multiple reflections between a pair of sample mirrors. The number of reflections that can be made is, of course, a function of the reflectivity of the substrate. As a result, the sensitivity of external reflection infrared spectroscopy is greatest for good reflectors such as copper, gold, silver, and aluminum.

The purpose of this paper is to describe results obtained using external reflection infrared spectroscopy to determine the structure of films formed by the adsorption of organofunctional silanes onto the oxidized surfaces of aluminum and titanium alloys. Complementary results obtained from ellipsometry, Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) are also described.

EXPERIMENTAL

Aluminum sample mirrors were prepared by mechanically polishing 2024 alloy (Alcoa) with magnesium oxide polishing compound on kitten ear cloth.

After polishing, the mirrors were rinsed several times in distilled water at room temperature and then blown dry in a stream of nitrogen. Titanium sample mirrors were prepared by mechanically polishing 6Al, 4V alloy using γ-alumina polishing compound on billiard cloth. Immediately after polishing, these mirrors were also rinsed repeatedly in distilled water at room temperature and then blown dry in a stream of nitrogen. In all cases mirrors prepared as described above were initially hydrophilic but became hydrophobic during a few hours exposure to the laboratory atmosphere. Therefore, only freshly polished, hydrophilic sample mirrors were used for adsorption experiments.

Films of organic compounds were formed on the sample mirrors using the techniques described below. The mirrors were then mounted in a reflection accessory (Harrick Scientific Co.) in the sample beam of the infrared spectrophotometer (Perkin-Elmer Model 180). Polished but unfilmed mirrors were mounted in a second reflection accessory in the reference beam, enabling all spectra to be recorded differentially. A wire grid polarizer was used to isolate the parallel polarized component of the radiation entering the monochromator.

The reflection accessory was actually configured in two different ways, depending on the desired number of reflections. For titanium substrates, the configuration shown in Figure 1A, providing a single reflection at any angle of incidence, was used. For aluminum, the configuration shown in Figure 1B, providing any number of reflections at a fixed angle of incidence (78°) was used.

In some cases the sample mirrors were examined immediately before and after adsorption of the organic compounds using an ellipsometer (Rudolph Research Model 436). This procedure enabled the thicknesses of the oxides and the adsorbed films to be determined.

XPS and AES spectra were obtained using Physical Electronics X-ray photoelectron and Auger electron spectrometers at Bell Laboratories in Columbus, Ohio. Samples for XPS and AES were prepared in the same way as samples for infrared spectroscopy.

RESULTS AND DISCUSSION

Aluminum substrates

There has been considerable discussion regarding the nature of the oxides formed on aluminum adherends during various hydrothermal, etching, and anodization treatments. Therefore, the first phase of this research was concerned with determining the structure of the oxides on 2024 aluminum mirrors. When the surfaces of freshly polished mirrors were characterized using AES (see Figure 2), the only elements detected in significant concen-

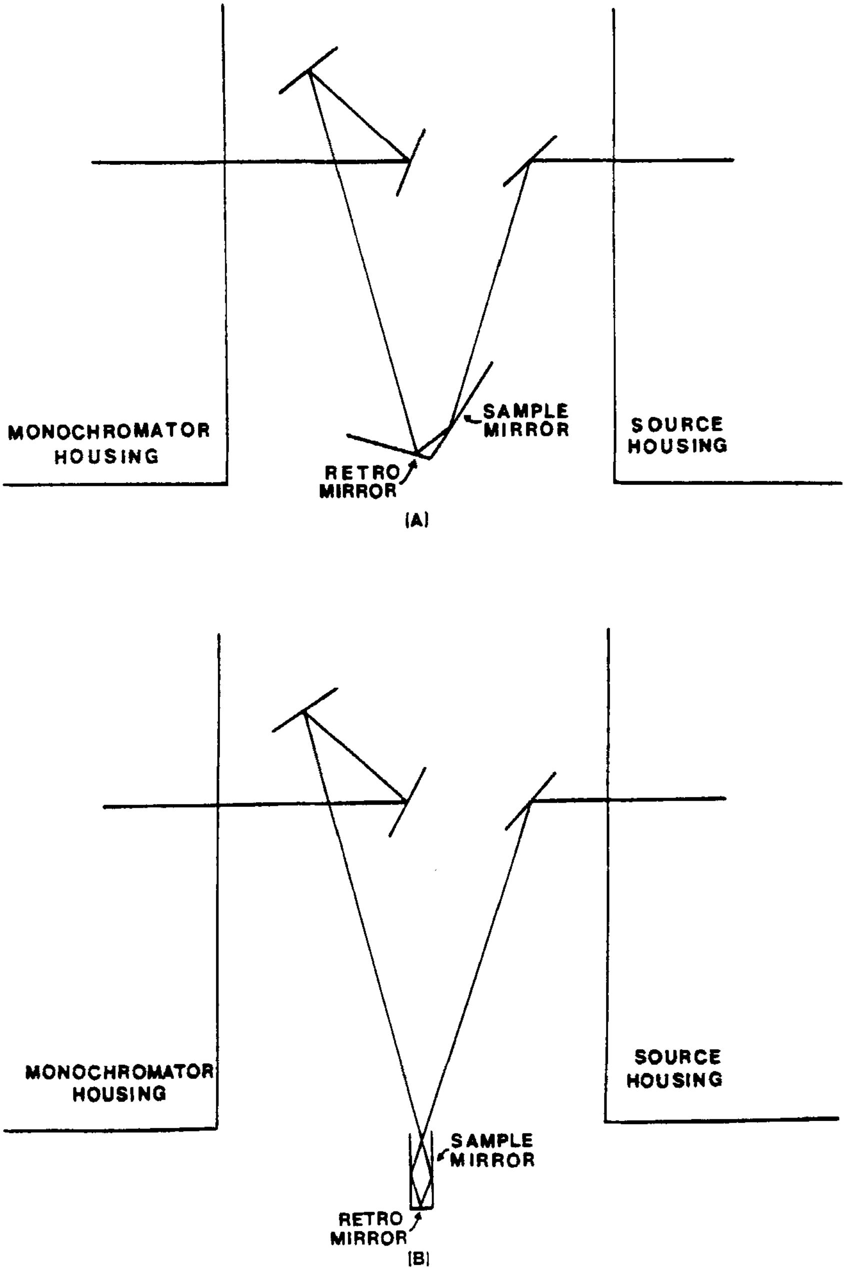


FIGURE 1 Sampling arrangement for external reflection infrared spectroscopy using (A) 1 reflection at any angle of incidence or (B) any number of reflections at 78° angle of incidence.

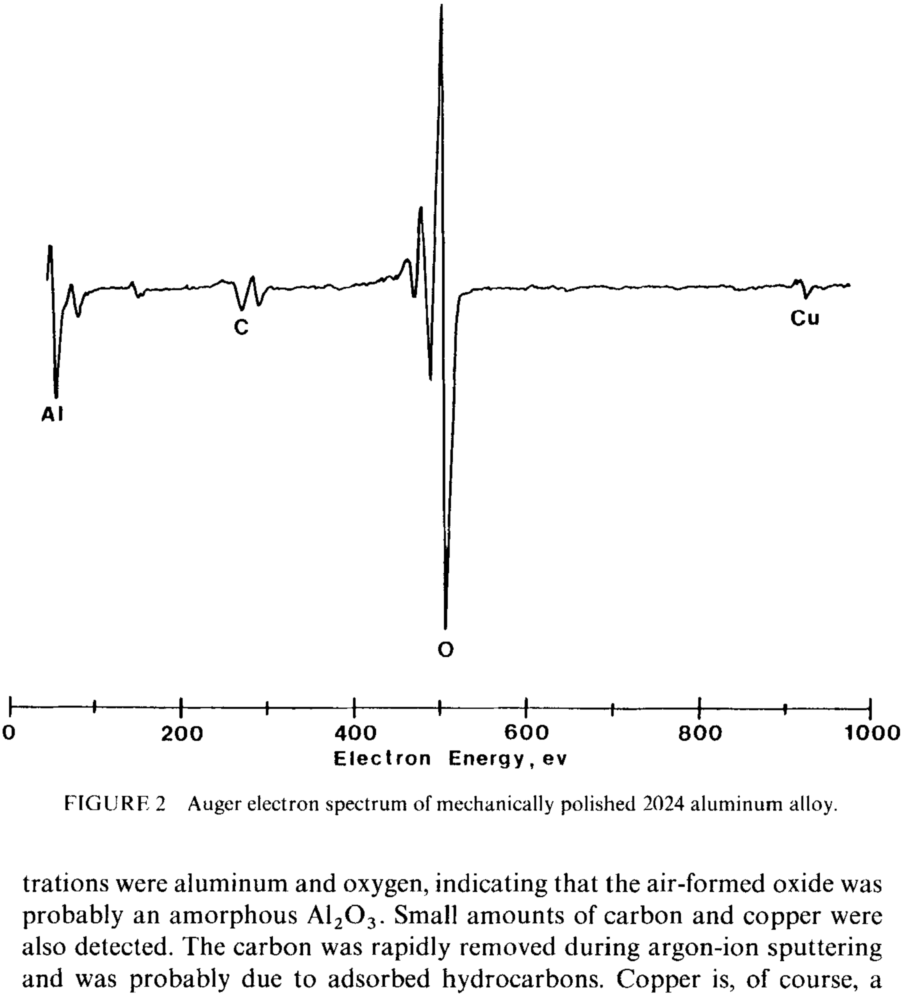


FIGURE 2 Auger electron spectrum of mechanically polished 2024 aluminum alloy.

trations were aluminum and oxygen, indicating that the air-formed oxide was probably an amorphous Al_2O_3. Small amounts of carbon and copper were also detected. The carbon was rapidly removed during argon-ion sputtering and was probably due to adsorbed hydrocarbons. Copper is, of course, a major alloying constituent in 2024 aluminum and the concentration of copper increased slightly during sputtering. Results obtained from ellipsometry indicated that the oxide on freshly polished mirrors was between 30 and 50Å in thickness. Infrared spectra of these oxides were characterized by an extremely strong absorption band near 960 cm^{-1} that was assigned to an Al—O—Al stretching vibration of amorphous Al_2O_3 (see Figure 3A).

Freshly polished aluminum mirrors were then given various hydrothermal treatments. When mirrors were immersed in boiling distilled water for five minutes, spectra similar to that in Figure 3B were obtained. These spectra were characterized by absorption bands near 3399, 3099, 1640, 1375, 1080, 847, and 650 cm^{-1} and the oxide was readily identified as pseudoboehmite

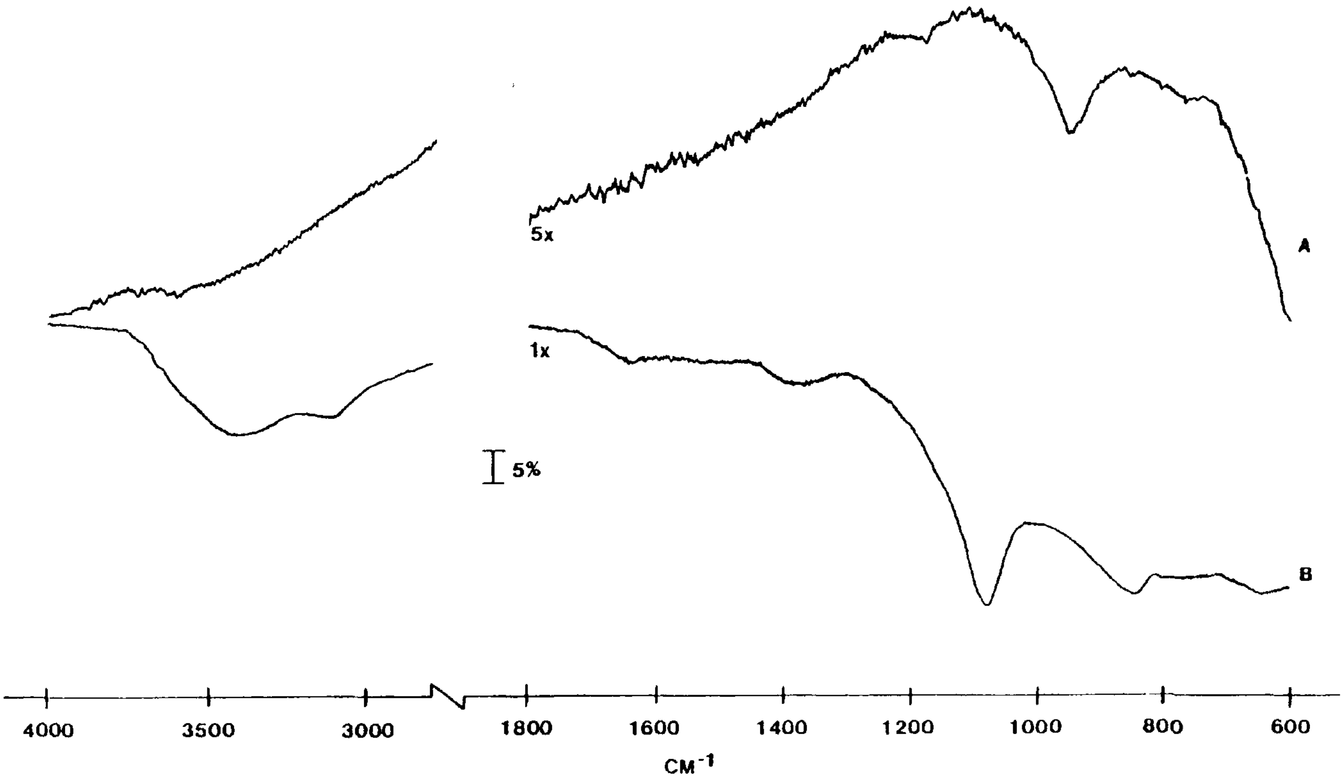


FIGURE 3 Infrared spectra of oxides formed on mechanically polished 2024 aluminum alloy: (A)—natural oxide; (B)—oxide obtained after immersion in boiling water for five minutes.

($Al_2O_3 \cdot XH_2O$, $X \approx 2$). When the temperature of the water treatment was lowered, the rate at which the natural oxide transformed to pseudoboehmite was also reduced. For example, only the natural oxide was observed after five minutes at 63°C but only pseudoboehmite was observed after sixty minutes. When the temperature was lowered to 40°C, only the natural oxide was observed after one hour (see Figure 4A). Pseudoboehmite began to appear after sixteen hours (Figure 4B) and only pseudoboehmite was observed after 24 hours (Figure 4C). At room temperature, the natural oxide was the only oxide present after 22 hours.

These results differ somewhat from those previously reported[7] relating the strength of epoxy/aluminum adhesive joints to the hydrothermal treatment given to the adherends prior to adhesive bonding. The strength of joints prepared from adherends immersed in distilled water at 10°C reached a maximum after about 30 minutes immersion time and then slowly decreased as immersion time was increased. It was suggested that this behavior was related to the formation after 30 minutes of a thin layer of bayerite (β-$Al_2O_3 \cdot 3H_2O$) that strongly adsorbed the epoxy resin. It was also suggested that increased immersion time resulted in thicker films of bayerite that were mechanically weak, resulting in the decreased joint strengths observed for long immersion times. However, the results obtained here indicate that bayerite is not formed by a simple hydrothermal treatment of mechanically polished 2024 alloy. What is observed is the transformation of amorphous Al_2O_3 to pseudoboehmite at a rate that increases with temperature.

γ-Aminopropyltriethoxysilane (γ-APS) films on aluminum

Films of γ-APS were formed on freshly polished aluminum mirrors by immersing the mirrors in 1% aqueous solutions of γ-APS for appropriate times, withdrawing the mirrors, and blowing the excess solution off the mirrors using a strong stream of nitrogen. The structure of such films was determined as a function of pH and immersion time. As shown in Figure 5A, films formed by adsorption from solutions acidified to pH = 8.5 by addition of HCl were characterized by infrared absorption bands near 3300, 3000, 1600, 1500, and 1080 cm^{-1}. The bands near 1600 and 1500 cm^{-1} may be assigned to deformation vibrations of protonated amino (NH_3^+) groups while the broad band near 3000 cm^{-1} may be assigned to the stretching modes of the same groups, indicating that γ-APS is probably adsorbed onto aluminum from solutions acidified with HCl as the hydrochloride. The band near 3300 cm^{-1} is undoubtedly due to the stretching vibrations of SiOH groups, indicating that the adsorbed γ-APS is highly hydrolyzed. The strong band near 1080 cm^{-1} is undoubtedly due to an SiO asymmetric stretching mode, indicating that some of the hydrolyzed γ-APS condensed on the surface to form siloxane polymers.

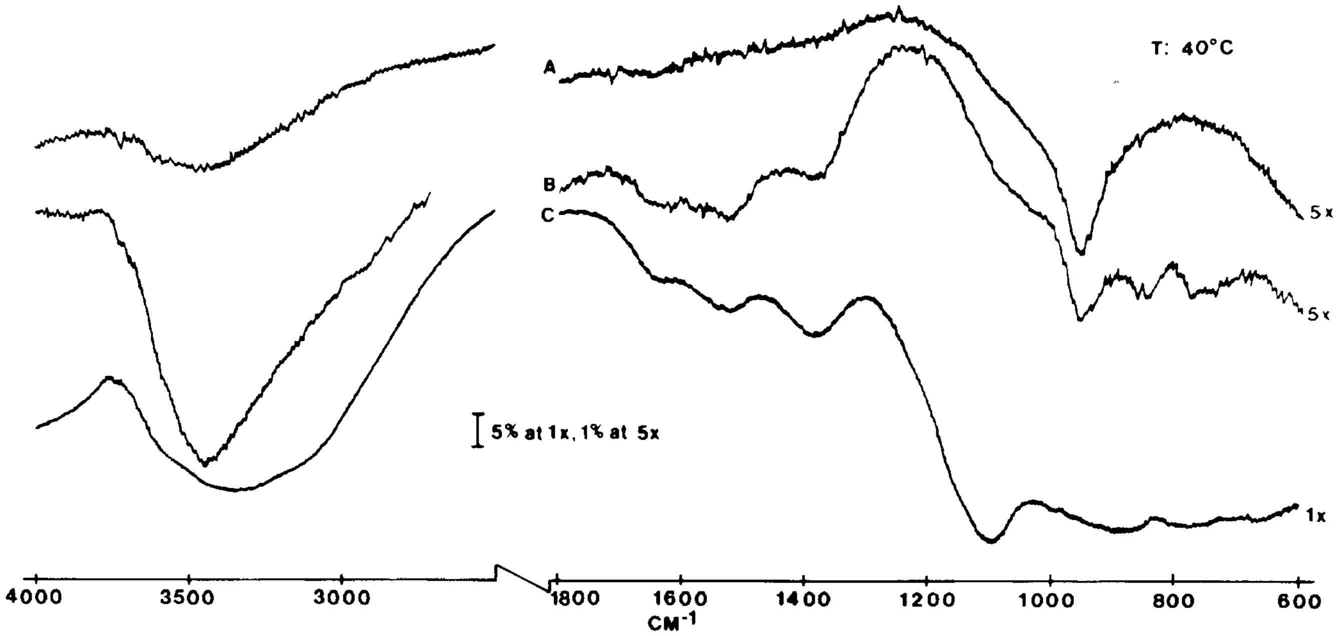


FIGURE 4 Infrared spectra of oxides formed on mechanically polished 2024 aluminum alloy during immersion in water at 40°C for (A)—one hour, (B)—16 hours, and (C)—24 hours.

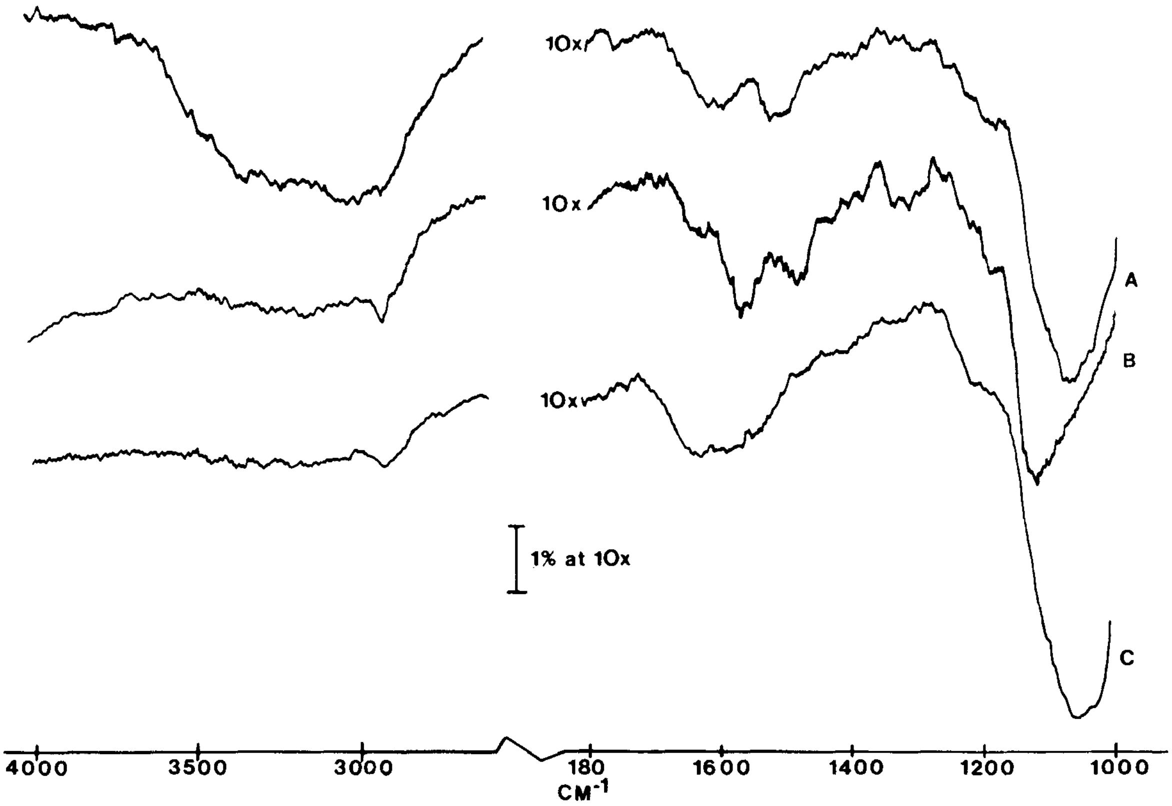
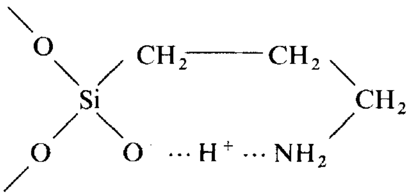


FIGURE 5 Infrared spectra of films formed by adsorption of γ-APS onto aluminum mirrors: (A)—15 minutes adsorption at pH = 8.5; (B)—1 minute adsorption at pH = 10.4; (C)—15 minutes adsorption at pH = 10.4.

However, it is interesting to note that the corresponding band is observed near 1130 cm^{-1} for γ-APS films adsorbed onto iron from aqueous solutions at similar pH values.[8] The low frequency observed for γ-APS on aluminum may indicate that γ-APS is adsorbed onto aluminum as rather low molecular weight oligomers or that there is a strong interaction between γ-APS and the oxidized surface of aluminum.

When films were formed by adsorption of γ-APS onto aluminum mirrors from 1% aqueous solutions at the natural pH (10.4), the structure of the films depended on the adsorption time. Films formed during a one minute adsorption time were characterized by infrared bands near 2920, 1630, 1570, 1470, 1330, and 1100 cm^{-1} (see Figure 5B). The weak band near 2920 cm^{-1} may easily be assigned to CH stretching modes in the propylamine groups. The strong band near 1100 cm^{-1} is again assigned to the SiO asymmetric stretching mode, indicating polymerization of γ-APS on the surface. The higher frequency of this band for films formed during one minute adsorption at pH = 10.4 than for films formed during fifteen minutes adsorption at pH = 8.5 may indicate greater interaction between the silane and substrate in the latter case.

The origin of the bands near 1570 and 1470 cm^{-1} is less certain. Similar bands have been observed for γ-APS adsorbed onto iron mirrors from 1% aqueous solutions at pH = 10.4.[8] These bands are near where deformation modes of NH_3^+ groups are expected and it has been suggested that such groups might be obtained by formation of strongly hydrogen bonded ring structures[8]



or by interaction of γ-APS with the oxide through the amino group.[8] However, we have recently determined that the infrared spectra of some aliphatic amines such as laurylamine are also characterized by infrared bands near 1570 and 1470 cm^{-1} if the amines are exposed to carbon dioxide in the atmosphere. Amine bicarbonates can apparently be formed during such exposure. The bands near 1570 and 1470 cm^{-1} in spectra of γ-APS films formed on aluminum during one minute adsorption at pH = 10.4 may be related to formation of bicarbonates or to strong hydrogen bonding of the amino groups that is similar to the bonding in bicarbonates.

Films formed during fifteen minutes adsorption time at pH = 10.4 were characterized by a strong absorption band near 1080 cm^{-1}, by a weak, broad band extending from about 1650 cm^{-1} to about 1500 cm^{-1}, and by a weak band near 2920 cm^{-1} (see Figure 5C). As before, the weak band near 2920 cm^{-1} may be assigned to the CH stretching mode in propylamine groups. The strong band near 1080 cm^{-1} indicates polysiloxane formation but the low frequency of this band may indicate substantial interaction between the silane and the oxide. In fact, it was observed that the absorption band near 960 cm^{-1}, which is characteristic of the air-formed oxide on the aluminum, decreased in intensity during adsorption of γ-APS at pH = 10.4 for fifteen minutes, indicating dissolution of the oxide and, perhaps, deposition of an aluminum/γ-APS complex on the surface. The broad, weak band extending between 1650 and 1500 cm^{-1} may be related to hydrogen bonding of the amino groups.

Preliminary results obtained from X-ray photoelectron spectroscopy were generally consistent with the conclusions based on the infrared spectra. However, in some cases the XPS spectra provided new insight into the interaction between γ-APS and the oxidized surface of aluminum. The XPS spectrum of γ-APS adsorbed onto aluminum at pH = 8.5 is shown in Figure 6A and several interesting features may be noted. The nitrogen 1*s* binding energy is at about 402.0 ev. This value is somewhat above that usually observed for free, primary amino groups ($\sim$399.5 ev), indicating that the amino groups in γ-APS adsorbed at pH = 8.5 are protonated, probably as hydrochlorides. The aluminum 2*p* band near 75.7 ev is substantially stronger than the silicon 2*p* band near 102.9, indicating that the γ-APS films were quite thin or, perhaps, indicating that aluminum was included in the films. The oxygen 1*s* binding energy is observed near 532.6 ev. This value is greater than that usually observed for metal oxides and is undoubtedly indicative of siloxane polymer formation.

The XPS spectrum of γ-APS adsorbed onto aluminum from 1% aqueous solutions at pH = 10.4 for one minute is shown in Figure 6B. In this case the nitrogen 1*s* binding energy is observed near 400.8 ev. This value is intermediate between those usually observed for free and protonated amino groups and may indicate hydrogen bonding of the amino groups. The aluminum and silicon bands near 75.7 and 102.9 ev, respectively, are more nearly equal in intensity than for the pH = 8.5 sample, probably indicating that the γ-APS films formed at pH = 10.4 were somewhat thicker than those obtained at pH = 8.5. It is interesting to note that a weak band characteristic of copper was observed near 933.5 ev for γ-APS adsorbed onto aluminum at pH = 10.4 for one minute. Copper is, of course, the major alloying element in 2024 aluminum and there may have been some tendency for copper to segregate near the surface during treatment of the substrate with aqueous solutions of γ-APS at high pH values. Such segregation of copper to the surface during FPL etching of 2024 aluminum has been reported.[9]

The XPS spectrum of γ-APS adsorbed onto aluminum from 1% aqueous

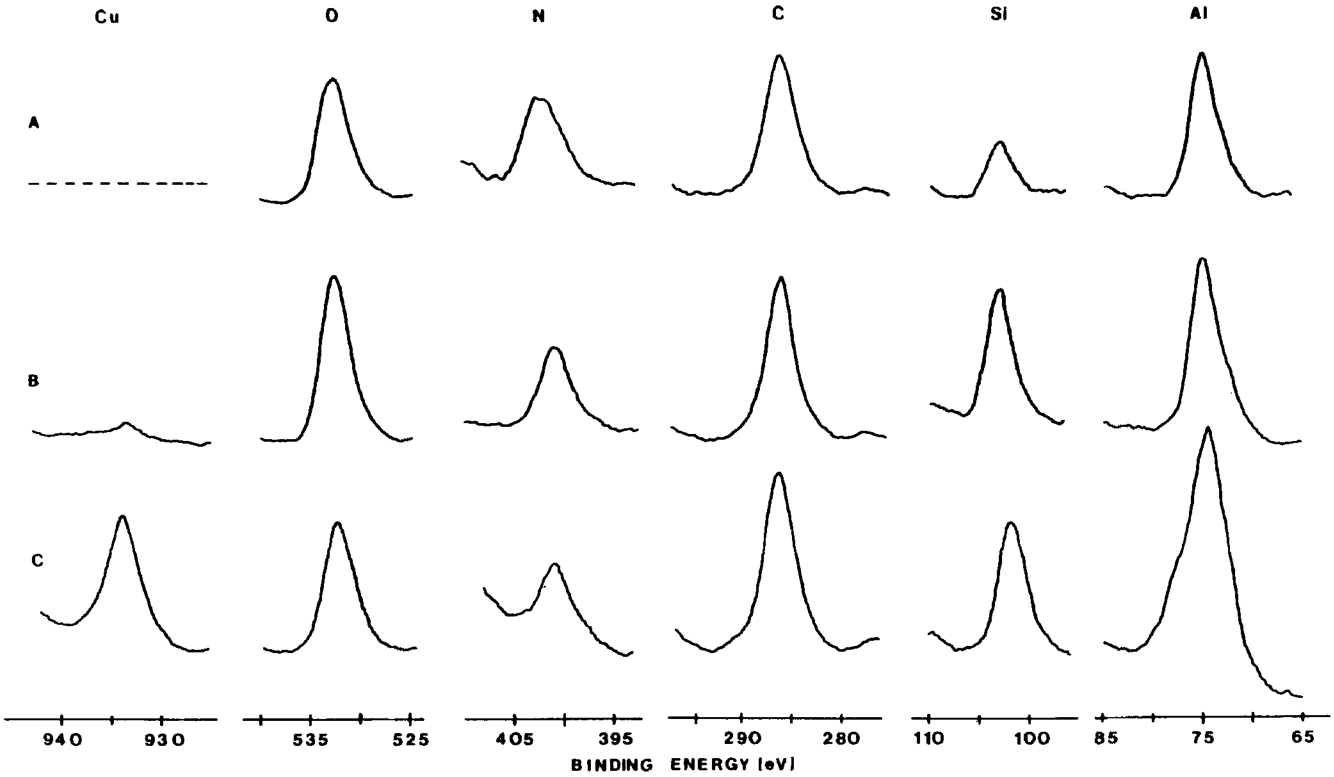


FIGURE 6 X-ray photoelectron spectra of films formed by adsorption of γ-APS onto aluminum mirrors: (A) 15 minute adsorption at pH = 8.5; (B) 1 minute adsorption at pH = 10.4; (C) 15 minute adsorption at pH = 10.4.

solutions at pH = 10.4 for 15 minutes is shown in Figure 6C. The nitrogen 1*s* binding energy was again observed near 400.8 ev. The Al/Si ratio was between the values observed at pH = 8.5 (Figure 6A) and at pH = 10.4 for 1 minute immersion (Figure 6B). Perhaps the most interesting aspect of Figure 6C is the large band characteristic of copper observed near 933.5 ev. This result implies a substantial accumulation of copper near the surface during lengthy treatment of 2024 alloy with aqueous solutions of γ-APS at pH = 10.4 and is especially significant considering that large concentrations of copper at the interface may be related to poor durability of adhesive bonds to aluminum.[9]

We have recently obtained preliminary results concerning the hydrothermal stability of epoxy/aluminum lap joints prepared from adherends primed with γ-APS.[10] Joints prepared from adherends primed with γ-APS at pH = 8.5 retained 93% of their original strength after 20 days immersion in water at 60°C. Joints prepared from adherends primed with γ-APS at pH = 10.4 for 15 minutes were in fact less durable, retaining only about 80% of their initial strength after such water immersion. The poor durability of the latter joints may be related to the accumulation of copper near the surface although other factors are undoubtedly also involved.

γ-Glycidoxypropyltrimethoxysilane (γ-GPS) on aluminum.

The structure of films formed by the adsorption of γ-GPS onto aluminum mirrors from aqueous solutions has also been investigated using infrared spectroscopy. However, γ-GPS was found to be a rather poor film former and although several different techniques were tried, discontinuous films with poorly reproducible thicknesses were usually obtained. The best films were obtained by immersing freshly polished aluminum mirrors into 1% aqueous solutions of γ-GPS containing a few drops of acetic acid as a catalyst for hydrolysis and then withdrawing the mirrors at a constant rate (0.125 or 0.250 inches per minute) using a motorized device constructed for this purpose. The same technique was used for uncatalyzed solutions although the results were somewhat less satisfactory.

The spectrum shown in Figure 7 was typical of those obtained from mirrors immersed in catalyzed solutions as described above. A single strong absorption band was observed near 1105 cm^{-1} while a weaker band was observed near 1190 cm^{-1}. The transmission infrared spectrum of γ-GPS is dominated by three intense bands near 1200, 1085, and 820 cm^{-1} that are associated with the $SiOCH_3$ groups.[11] The virtual absence of the bands near 820 and 1085 cm^{-1} from the spectrum in Figure 7, along with the reduced intensity of the band near 1190 cm^{-1}, indicates that the films formed on aluminum are highly hydrolyzed. However, the appearance of the strong band near 1105 cm^{-1} in that spectrum indicates that the resulting silanols had polymerized on the

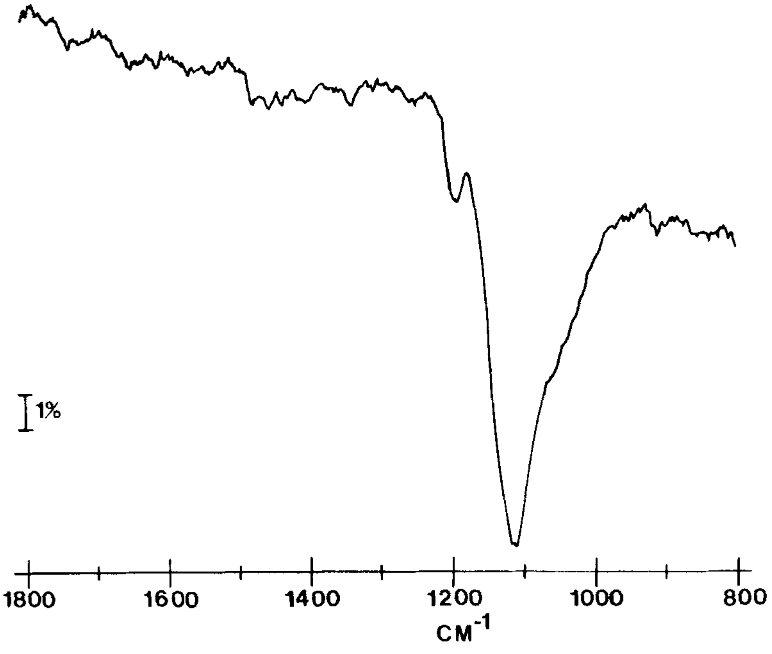


FIGURE 7 Infrared spectrum of γ-glycidoxypropyltrimethoxysilane adsorbed onto aluminum from catalyzed 1% aqueous solution.

surface. The spectra obtained from mirrors immersed in uncatalyzed solutions were similar to that shown in Figure 7 except that the band near 1190 cm^{-1} was usually more intense, indicating less extensive hydrolysis in such films. The spectra of γ-GPS films formed on aluminum substrates were always similar to those previously observed for γ-GPS on iron,[12] indicating that there is no strong interaction between γ-GPS and the air-formed oxide on aluminum. However, a more complete understanding of such interactions should be obtained from the results of infrared and XPS investigations presently underway utilizing much thinner films.

Titanium substrates

The surface of freshly polished titanium-6Al, 4V mirrors was characterized using AES (see Figure 8). Titanium and oxygen were the only elements detected in significant concentrations, indicating that such surfaces were probably composed of TiO_2. A considerable amount of carbon was also detected on the mirrors but was easily removed by argon–ion sputtering and was undoubtedly due to adsorbed hydrocarbons. Traces of silicon and zinc

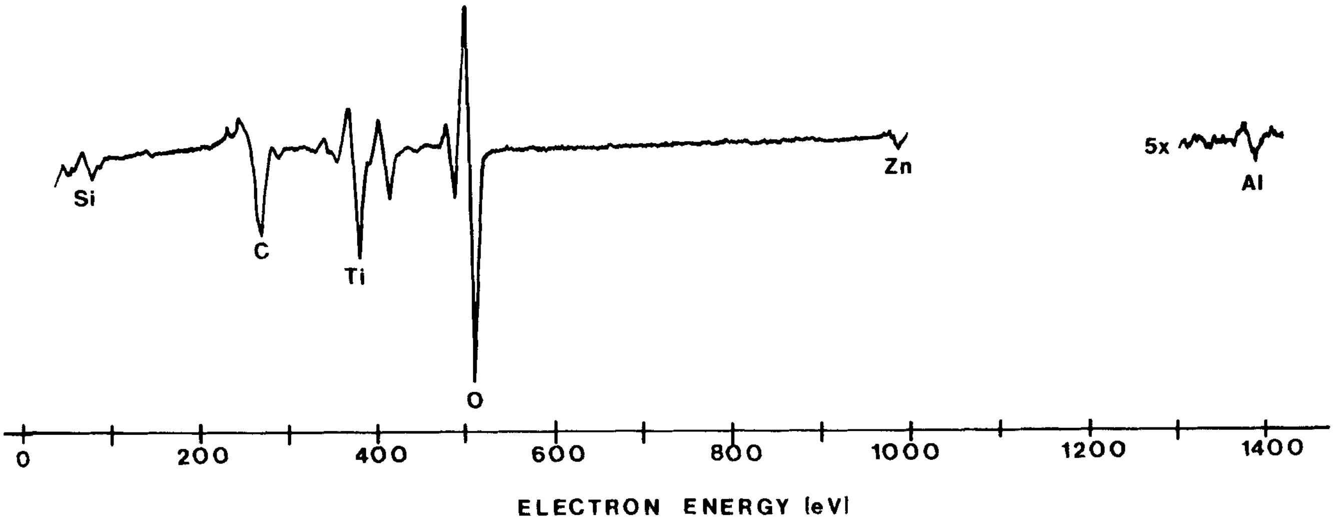


FIGURE 8 Auger electron spectrum of mechanically polished titanium-6Al-4V alloy.

were found on the surfaces but were also easily removed by sputtering. The amounts of aluminum and vanadium detected were extremely small.

γ-Aminopropyltriethoxysilane films on titanium

Films of γ-APS were formed on freshly polished titanium mirrors by immersing the mirrors in 1% aqueous solutions of γ-APS at the natural pH (~10.4) for appropriate times, withdrawing the mirrors, and blowing the excess solution off the mirrors using a strong stream of nitrogen. Results obtained from ellipsometry indicated that the films prepared in this way were typically about 100Å in thickness. The infrared spectra of such films were characterized by absorption bands near 1570, 1470, and 1070 cm^{-1} (see Figure 9A) and were similar to spectra of films formed on aluminum mirrors during one minute immersion in 1% aqueous solutions of γ-APS at the natural pH (see Figure 5B). Immersion times ranging from one minute to 60 minutes were considered but the infrared spectra of the adsorbed films were all similar. As indicated above, the structure of γ-APS films on aluminum did depend on immersion time.

Films formed by adsorption of γ-APS onto titanium mirrors from 1% aqueous solutions at pH = 10.4 were unstable during exposure to the laboratory atmosphere (see Figure 9). The band originally observed near 1070 cm^{-1} gradually split into components near 1140 and 1040 cm^{-1}. The band near 1070 cm^{-1} is probably characteristic of SiO stretching in low molecular weight oligomers while the bands near 1140 and 1040 cm^{-1} are probably characteristic of SiO stretching in polysiloxanes, indicating polymerization on the surface of the mirrors. Some tendency for the band near 1470 cm^{-1} to decrease in intensity and for the band near 1570 cm^{-1} to increase in frequency during atmospheric exposure was also observed (see Figure 9). Similar effects have been observed for γ-APS adsorbed onto iron substrates at the natural pH[13] but not for γ-APS adsorbed onto aluminum during 15 minutes immersion in solutions at pH = 10.4.

CONCLUSIONS

The results obtained here indicate that external reflection infrared spectroscopy is an effective surface analysis technique, especially when combined with other techniques such as ellipsometry, Auger electron spectroscopy, and X-ray photoelectron spectroscopy. The interaction of γ-aminopropyltriethoxysilane (γ-APS) with the oxidized surface of aluminum is a complex function of pH and immersion time. Under some conditions copper may accumulate near the surface of 2024 aluminum adherends immersed in aqueous solutions of γ-APS

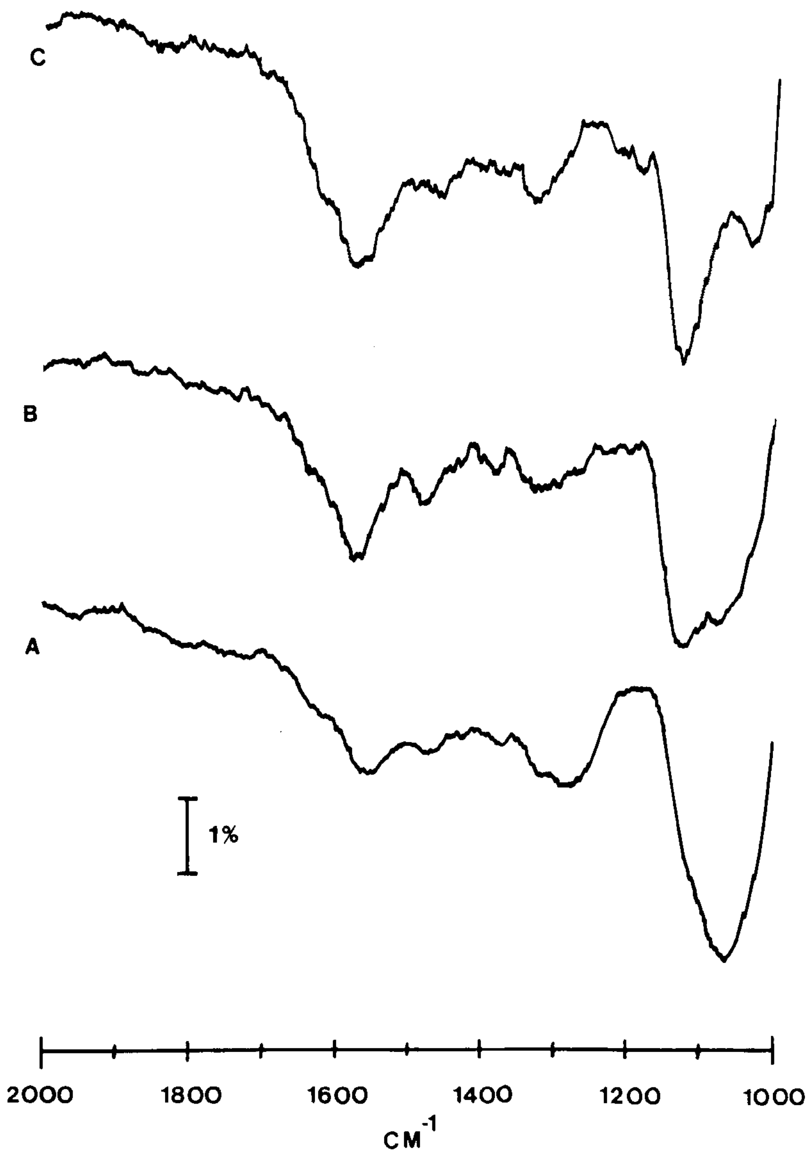


FIGURE 9 Infrared spectra of films formed by γ-APS adsorbed onto titanium mirrors from 1% aqueous solutions at pH = 10.4. (A) immediately after preparation, (B) after exposure to lab atmosphere for 5 hours, and (C) after exposure to lab atmosphere for 3 days.

and may limit the durability of adhesive joints prepared from such adherends. By comparison, γ-glycidoxypropyltrimethoxysilane (γ-GPS) does not interact strongly with the oxidized surface of aluminum when adsorbed from aqueous solutions. γ-APS is adsorbed onto titanium-6Al, 4V alloy from aqueous solutions at pH = 10.4 as low molecular weight oligomers that polymerize during atmospheric exposure to form polysiloxanes.

Acknowledgements

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