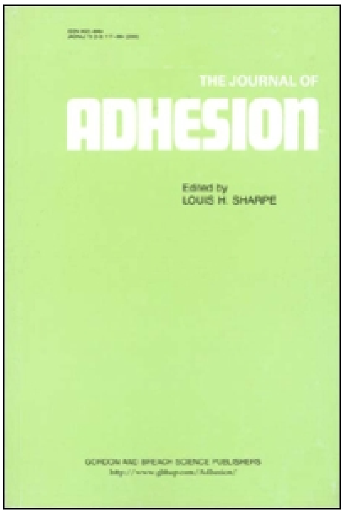

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# FT-IR Microscopy Studies of Water Ingress into Aluminum-Adhesive Joints

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# FT-IR Microscopy Studies of Water Ingress into Aluminum-Adhesive Joints

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FT-IR microscopy of the effect of humidity on epoxy thin films on anodized aluminum surfaces was performed in the absence of external stress. The oxide transformation was observed in the anodized samples. Moisture damage was greater in the untreated aluminum samples indicating that interfacial debonding occurs faster in these samples. Water damage was localized spatially. The only organic reaction seen was at the epoxy/air interface giving carboxylates at the surface.

KEY WORDS infrared; microscopy; aluminum; aluminum oxides, hydroxides, oxyhydroxides; epoxides; adhesive films; moisture; surfaces; surface treatment; chromic acid anodizing (CAA); sulfuric acid anodizing (SAA).

## INTRODUCTION

The loss of strength due to humidity exposure limits the lifetime of adhesive joints.[1,2] The mechanism by which water interacts with the adhesive joints is not known. However, several hypotheses have been proposed. Oxide dissolution by water was thought to be the primary reaction in environmental exposure.[1] Venables *et al.*[2] studied the hydration properties of anodized aluminum surfaces and concluded that the transformation to boehmite and consequently to bayerite was responsible for the formation of a weak boundary layer. Support for this hypothesis is found when inhibitors are used which prolong the lifetime of adhesive joints. It is not clear whether the improvement is due to suppression of the hydration reactions or interactions between the inhibitors and the epoxy resin. Belov[3] studied hydration properties of anodic films and found that the hydration of an anodic oxide depends on the coordinative ability of the corresponding anion to form bonds with the oxide surface. He also found that the chromic and sulfuric acid anodic films absorb relatively large amounts of anions. The activation energy for oxide hydration is large for anodic films formed in acidic solutions. Brockmann[4] argued that oxide dissolution is only possible in thin films but not on thicker films as obtained from anodizing conditions.

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Another degradation theory suggests the displacement of epoxy from the oxide surface by water. Kinloch *et al.*[5] used a thermodynamic approach to predict epoxy debonding from the oxide by water. His treatment does not consider forces other than polar forces to be involved in the adhesion phenomenon. Further, the theory can not predict lifetimes of joints.

Another theory suggests that the adhesive itself is the most susceptible component in an adhesive joint. Kerr *et al.*[6] studied the effect of water and ethanol on the cohesive and adhesive strength of joints. It was concluded that ethanol affected the cohesive strength while water affected the shear strength of the joint. Thus, water attacks the interface preferentially. On the contrary, others feel that the low water permeability of the adhesive is the rate determining step in the lifetime of the joint. Lefebvre *et al.*[7] studied humidity effects on adhesive joints and found a critical humidity level below which water does not affect the lifetime of the joints. This critical level is associated with: (1) a sudden increase of water solubility in the epoxy, (2) a corresponding increase in the adhesive volume, and (3) a large decrease in water mobility. Further, they found that water, irreversibly trapped by interchain hydroxyl groups, reacts with the uncured oxirane groups to form diols.

Su *et al.*[8] performed fatigue tests of adhesive joints as a function of ageing and concluded that fatigue life improved with humidity. Further, the durability performance showed a close relation with the adhesive water uptake. Bowditch *et al.*[9] studied the effect of the equilibrium water content on the mechanical properties of finely dispersed oxides in epoxy adhesives. They did not observe a critical humidity level below which water does not affect the adhesive joint. Thus, water affected the mechanical properties of the sample irrespective of the water content. It does appear that, in adhesive joints at low humidity, water is mostly situated in the bulk adhesive away from the interface and, with increasing water content, that water penetrates to the interface. Thus, plasticization is thought to be a major effect at low water content. However, recent work now suggests hardening of the epoxy with humidity. Raveh *et al.*[10] performed shear stress tests and hardness studies of epoxy/alumina joints as a function of ageing. They concluded that the durability of adhesive joints depends on a competition between epoxy hardening and weakening of the epoxy/oxide interface.

Another mode of environmental degradation of adhesive joints is corrosion. Brockmann *et al.*[4] argued that, for thick anodic films on aluminum, durability of adhesive joints was determined by corrosion processes. His arguments were based on the observation that it takes a long time to dissolve thick oxide films and that cathodic delamination of the adhesive is a possible reaction. Watts[11] argued that cathodic delamination by water leads to oxide reduction, polymer saponification and interfacial debonding. He also concluded that these degradation mechanisms could be occurring simultaneously and, in the case of fusion-bonded epoxy on steel, oxide reduction occurs first followed by interfacial delamination due to water. Oxide reduction is thought to dominate under high cathodic potentials while interfacial delamination dominates in the unpolarized case. Dickie *et al.*[12] used ESCA to investigate the failure mechanisms in epoxy/dicyandiamide adhesives on cold-rolled and galvanized steels. They concluded that oxide dissolution was the dominant mechanism in the absence of any applied potential. Thus, the resulting pH in the adhesive plays a role in the stability of the oxide. Aluminum oxides are unstable under basic conditions and in epoxy/dicyandiamide adhesives on anodized aluminum joints. Interfacial delamination is thought to be insignificant in epoxy adhesives on anodic aluminum due to the large surface areas associated with anodic surfaces. Thus, oxide reduction and polymer degradation are the major degradation mechanisms in epoxy adhesive/anodic aluminum joints.

Recent developments in FT-IR microscopy allow this problem to be re-examined, particularly as it concerns the nature of the moisture-induced chemical reactions in the epoxide and oxide layers.

## EXPERIMENTAL

### Materials

Aluminum (2024-T3) coupons (1×1.5 inch; 25.4×38.1 mm) were mechanically polished to 3 μm roughness and then degreased with 2-butanone. The coupons were then sent to a plating company to be anodized in sulfuric acid solutions according to Mil-A8625-E type II specifications with the anodizing conditions as shown in Table I.

Thickness measurements were made on a Permascope EWP9 (Fischer Instrument) with ±12 μm uncertainty.

The adhesive used was Epon 828® (Shell), with dicyandiamide as the curing agent and Durion® (Dow Chemical) as an accelerator. A dilute epoxy adhesive solution, $3.7\times10^{-3}$ g/ml in DMF, was prepared for thin film studies. The proper amount of solution was added to the 1×1.5 inch (25.4×38.1 mm) coupons and the samples were spin coated at 2000 rpm (30 seconds) and then 4000 rpm (1 minute). The samples were then placed in a vacuum oven at 35°C for 12 hours to drive off residual solvent. The film thickness ranged from 1.0 to 1.2 μm as determined by the eddy current method. (The deposition of the epoxy system was accomplished by spin-casting on the anodized and untreated portions of the same Al sample (see Fig. 1)). The square coupons of anodized and untreated aluminum samples were pressed with a clamp against a socket (with a 1.5 mm diameter hole) which was joined to a 125 ml flask containing a saturated solution of KBr (72% humidity at 35°C). The

TABLE I

| Type II | | Type I | |
|---|---|---|---|
| Conc. Sulfuric Acid (85%) | 20 wt% | Chromic Acid | 5 wt% |
| Water | 80 wt% | | 95 wt% |
| volts | 18 volts | | 40 volts |
| current | 23 Amps/ft$^2$<br>(0.025 Amp/cm$^2$) | | 1.5 Amps/ft$^2$<br>(0.0016 Amp/cm$^2$) |
| temperature | 20°C | | 40°C |
| time | 60 Min. | | 30 Min. |
| thickness | 34 μm | | 19 μm |

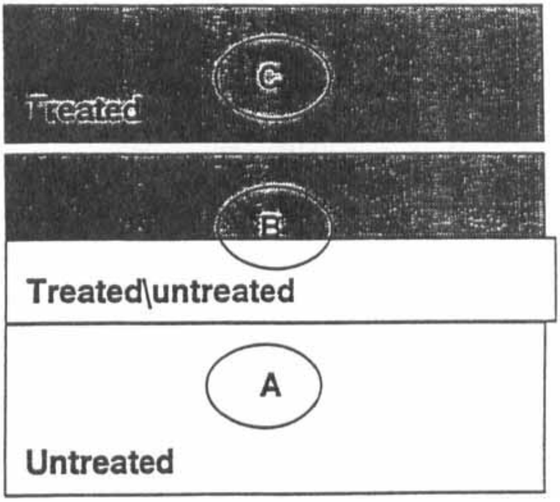

FIGURE 1 Spatial IR sampling A: untreated; B: untreated/treated; C: treated.

flask was kept at 35°C with a water bath. The samples were then removed from the humidity chamber after appropriate exposure times for FT-IR specular reflectance studies.

### Instrumentation

All of the FTIR spectra were obtained with a rapid scanning infrared microprobe (Irus©) with a liquid nitrogen cooled MCT detector. Spectra were obtained with a resolution of 4 $cm^{-1}$ and 512 scans. Triangular apodization was applied and interferograms were transformed with 8192 points with no zero filling. Specular reflectance at grazing angle was performed. An area $500 \times 500$ $\mu m$ in size was imaged by rastering with a round 100 $\mu m$ diameter aperture across the sample (see Fig. 2). Further, the images shows the speckle effect, which is a mosaic-like picture when the image is a collection of pixels. The images show the intensity of a given species (vibration of a molecular group) as a function of spatial position. The intensities were normalized for constant thickness. The spectra collected were a sum of the spectra of the oxide and the adhesive. The adhesive spectrum was subtracted, using a non-linear least squares fitting program, until the 1510 $cm^{-1}$ band disppeared. The signal-to-noise ratio (S/N) and band width of the oxyhydroxide band were 117 and 85 $cm^{-1}$, respectively, while those of the C—O—C band were 46 and 39 $cm^{-1}$, respectively. Thus, the oxyhydroxide band was the stronger and broader of the two bands, and it showed clearly below the C—O—C band around the 1100 $cm^{-1}$ area. The interfaces between the treated and untreated areas of the sample were sharp. The roughness of the oxide is smaller than the imaging window used in this experiment. The samples were imaged before and after two weeks and after three months of exposure to 72% relative humidity at 35°C.

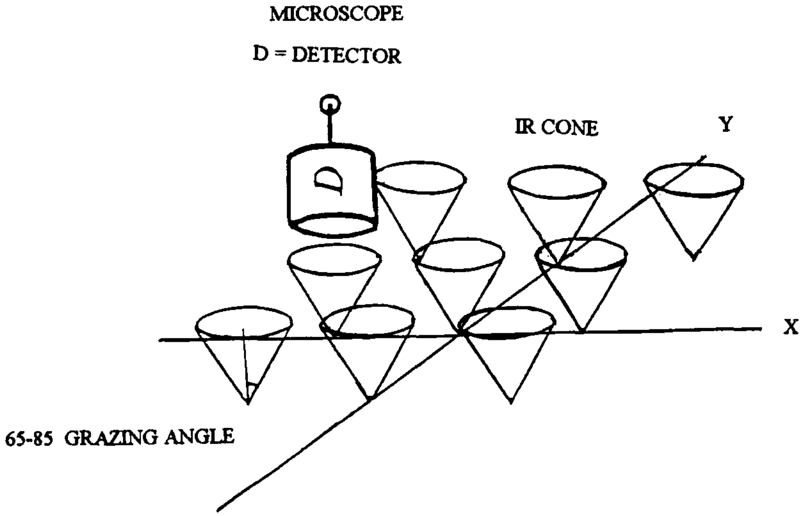

FIGURE 2 Diagram of infrared microscopic experiment using a 100 μm diameter aperature rastered across the sample.

## RESULTS AND DISCUSSION

Aluminum has a high reactivity toward water and oxygen, but it is protected by a thin oxide layer. Aluminum has a range of oxides, oxyhydroxides, and hydroxides, the principal ones being α- and $\gamma$-$Al_2O_3$. The oxyhydroxides are α- (diaspore) $\gamma$-ALOOH (boehmite), and the hydroxides are (Al $(OH)_3$) gibbsite, bayerite, and nordstrandite. Our results show the nature of the chemical transformations of these oxides, oxyhydroxides, and hydroxides of aluminum as a result of exposure to water through an epoxy overlayer.

The reflectance spectra obtained are a composite of the absorbances of the epoxy and the aluminum oxides. The results will be presented for selected absorbances indicative of specific structural forms.

The initial spatial distribution of the oxyhydroxide (Al-OOH) species on the CAA and untreated aluminum sample after exposure to humidity for two weeks is shown in Figure 3. The figure shows a smooth rise in the oxyhydroxide band at 1104 $cm^{-1}$ due to the CAA treatment. However, when the sample is exposed to humidity for over three months, changes occur on the oxide surface (see Fig. 4). The figure also shows a rough image with new peaks. These peaks are not associated with surface roughness in the original sample before exposure. Thus, they are consequences of water interaction and they are assigned to formation of new boehmite. This is further supported by the fact that when the intensity of the band at 934 $cm^{-1}$, associated with the oxide group Al—O—Al, is plotted with respect to position on the sample surface there is a corresponding depression in the area where there was an increase in the oxyhydroxides (see Fig. 5) and a relatively large intensity in the hydroxyl image (3420 $cm^{-1}$) of the same area (see Fig. 6). Thus, the effect of water on the anodic aluminum/epoxy joints is to transform the oxides of the anodic film

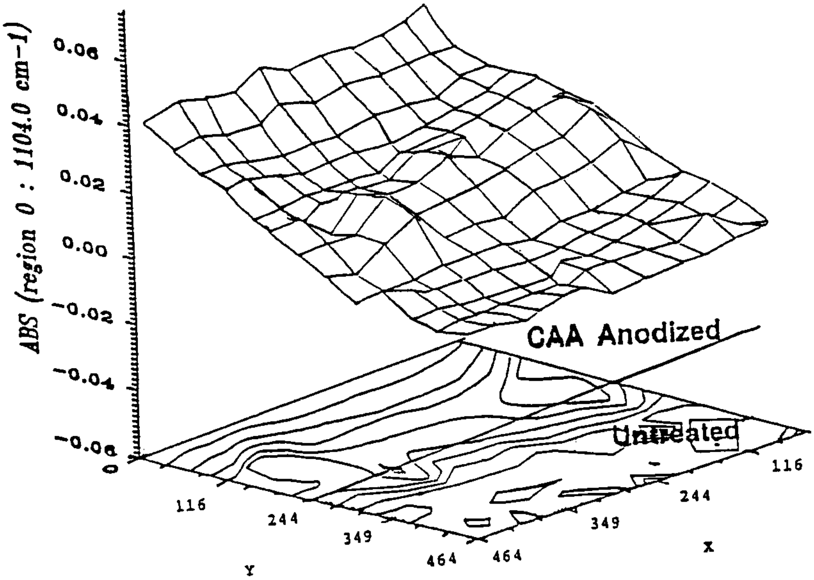

FIGURE 3 Three-dimensional plot of the oxyhydroxide vibrational band at 1104 cm$^{-1}$ as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over two weeks. The absorbance values are scale expanded arbitrarily in order to get a good view of the surface.

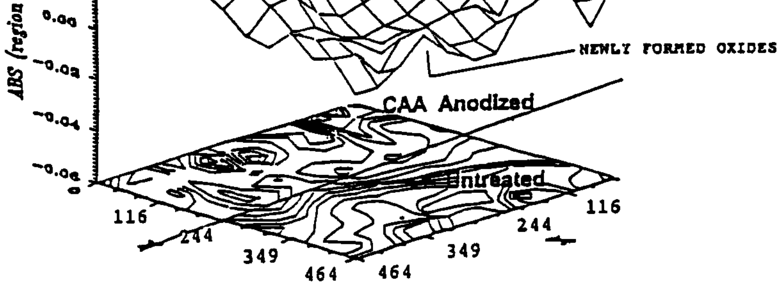

FIGURE 4 Three-dimensional plot of the Al—O—Al vibrational band at 1104 cm$^{-1}$ as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months. The absorbance values are scale expanded arbitrarily in order to get a good view of the surface.

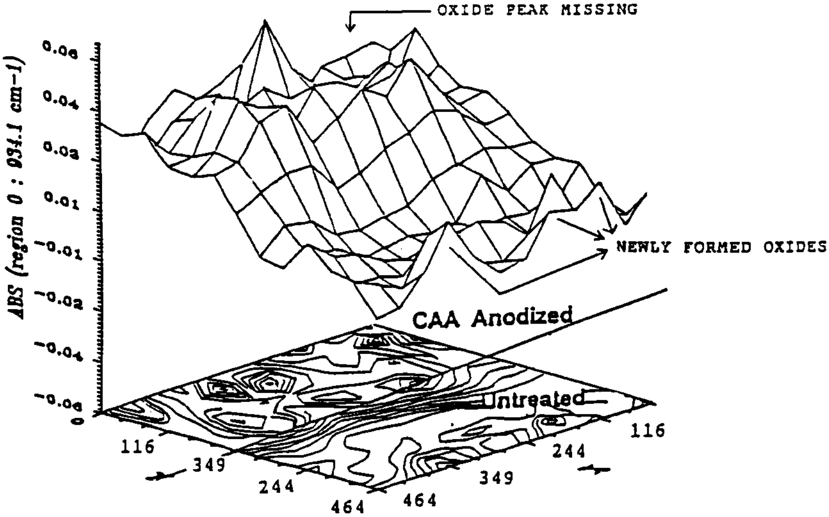

FIGURE 5 Three-dimensional plot of the Al—OH vibrational band at 934 $cm^{-1}$ as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months. The absorbance values are scale expanded arbitrarily in order to get a good view of the surface.

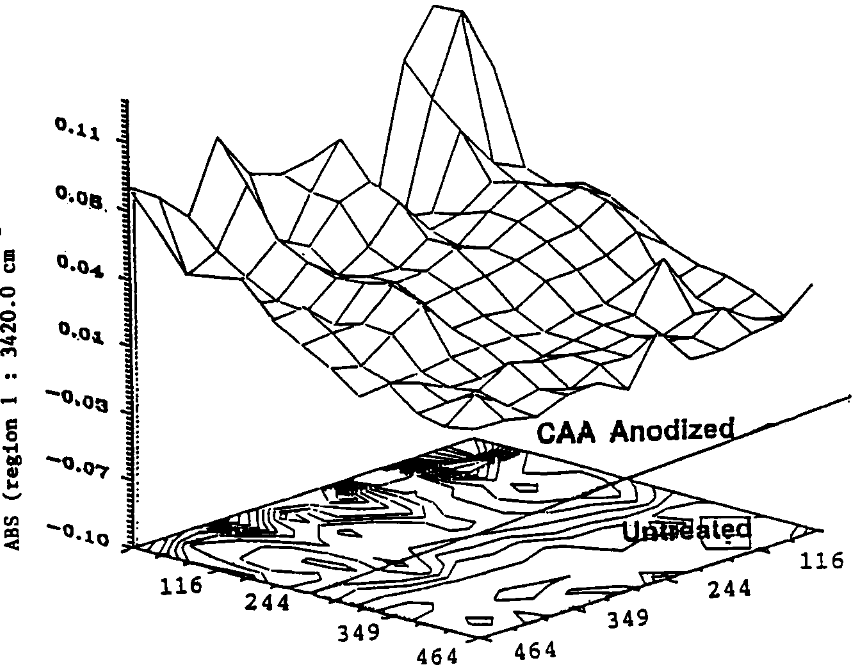

FIGURE 6 Three-dimensional plot of the oxyhydroxide vibrational band at 3420 $cm^{-1}$ as a function of spatial coordinates on the sampled area of the CAA/untreated aluminum sample. The area was exposed to humidity for over three months. The absorbance values are scale expanded arbitrarily in order to get a good view of the surface.

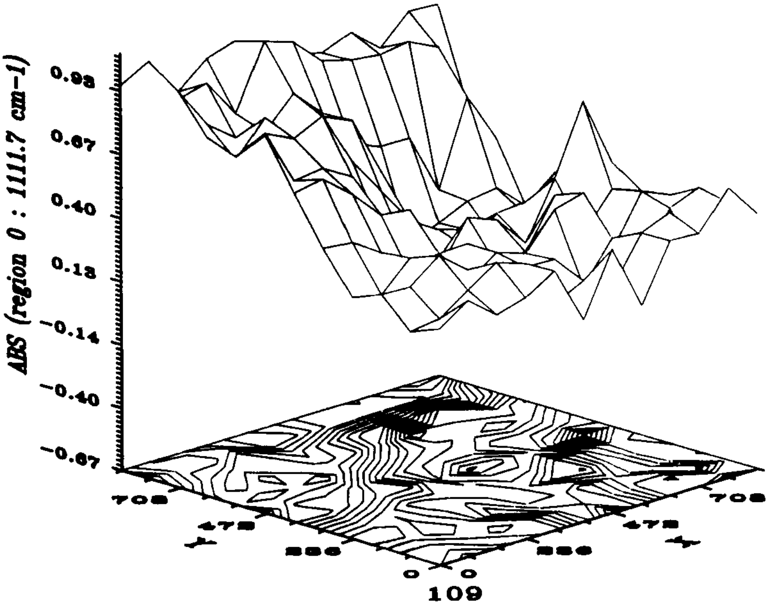

FIGURE 7 Three-dimensional plot of the oxyhydroxide vibrational band at 1111.7 cm$^{-1}$ as a function of spatial coordinates on the sampled area of the SAA/untreated aluminum sample. The area was exposed to humidity for over three months. The absorbance values are scale expanded arbitrarily in order to get a good view of the surface.

into boehmite. In the untreated Al portion of the sample, there appears to be both oxide and oxyhydroxide formation occurring simultaneously. The same effect, but to a lesser extent, is seen in the SAA/untreated aluminum sample as shown in the image of the oxyhydroxide species (see Fig. 7). Although, this technique is insensitive to interfacial delamination by water because of the lack of chemical reaction in this process, it is very sensitive to chemical changes in the oxide and the adhesive itself. The damage mechanism in the untreated aluminum seems to be different from the anodized sample; that is, there is oxide conversion in the anodic case, and oxide and hydroxide creation in the untreated aluminum case. The extent of this transformation is higher for the untreated aluminum portion of the sample. The oxide formation in the untreated aluminum/epoxy sample may indicate that interfacial delamination of the epoxy from the aluminum surface has occurred. It is not clear whether interfacial delamination occurred in the anodized aluminum/epoxy samples. The only organic damage observed was the production of carboxylate species which were found at the outer surface of the epoxy film (the epoxy-air interface). The carboxylate species were completely removed upon polishing with a 0.05 μm polishing cloth.

## CONCLUSIONS

FT-IR microscopy related to the effect of humidity on thin films of adhesive on anodized aluminum joints was performed in the absence of external stresses. With moisture uptake, boehmite formation was seen in anodized aluminum/adhesive joints. Newly-formed oxides were seen in the untreated aluminum/adhesive joints given similar exposure to humidity. The extent of moisture damage was greater in the untreated aluminum/adhesive joints. The only moisture damage to the adhesive was the formation of carboxylates which were at the air/epoxy interface away from the oxide. The anodized aluminum/adhesive joints are more resistant than untreated aluminum/adhesive joints to humidity effects.

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