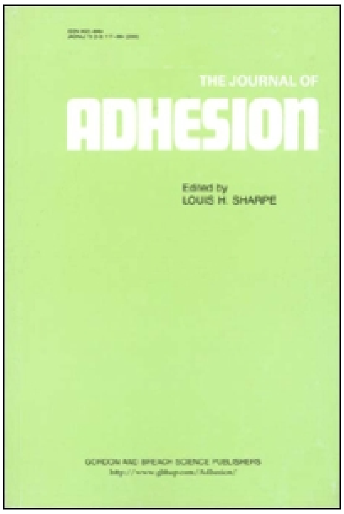

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FT-IR Characterization of the Surface of Aluminum as a Result of Chemical Treatment

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FT-IR was used to characterize the surfaces of Al after various chemical treatments. All of the oxide surfaces were composed of an anhydrous alumina, aluminum oxyhydroxide (pseudoboehmite) and aluminum hydroxide (close to Gibbsite). The major contaminants in the different oxides are chemisorbed CO_2, carbonates and bi-carbonates. The chromic acid anodized surfaces (CAA) contain more hydroxyls and water than the sulfuric acid anodized surfaces (SAA) while the latter contain more alumina (Al_2O_3). The CAA surfaces have a duplex structure mainly of hydrated and oxyhydroxylated layers over a hydrated alumina layer. The SAA surfaces have a triplex structure composed mainly of hydrated and hydroxylated layers over an oxyhydroxylated layer which is over a hydrated alumina layer. The surfaces chemically converted by the Iridite© process are composed of a duplex structure of a mixed organic-inorganic layer over a hydrated alumina. The organic portion of the layer was identified as a carbamate species.

KEY WORDS oxide; surfaces; aluminum; anodized; alumina; sectioning; contaminants.

INTRODUCTION

Anodic films of aluminum have attracted considerable attention because of their wide application in modern technology. Aluminum is usually anodized to protect the metal against corrosion, to improve its abrasive properties, to provide electrical insulation and to improve adsorption properties in adhesive joints. There are various ways of anodizing aluminum depending on whether acidic or basic solutions, AC or DC voltage, etc. are used, to give different structures.[1]

The structures of anodized Al layers have been studied previously.[2,3,4] Dorsey used FT-IR to study the structure of anodic aluminum[5,6,7] and concluded that the oxides are mainly composed of a barrier and porous layer; however, as noted by one of the reviewers of this paper, the barrier-porous structure used to describe anodic films is incorrect. The proper picture is a set of hollow cylinders with round

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bottoms composed of a passivating layer.[7a] He also found the porous layer to be mainly composed of alumina and the barrier layer of hydroxides. Maeland *et al.*[4] showed that the barrier layer was anhydrous and that the infrared band assigned to OH by Dorsey was an optical phonon due to aluminum alkoxides. Handke *et al.*[8,9] used various FT-IR techniques and improved the correlation between the spectra of the coatings and their structure. They showed that sulfuric acid anodized surfaces were composed mainly of aluminum oxide, oxy-hydroxide and hydroxides. Fin *et al.*[10] used various spectroscopic techniques to analyze anodized layers and concluded that anion incorporation as well as alloying elements were the differences between different anodic films. However, few studies have focused on the molecular structure of anodic films in the context of designing and developing new oxides for existing adhesive systems.

By combining FT-IR specular reflectance with chemical sectioning,[11] we have investigated the molecular composition and orientation of anodic Al films. These techniques, along with transmission spectra, were used to characterize anodic films. Chemical sectioning with sulfuric acid permitted in-depth spatial analysis of the formed films. This paper demonstrates the structural and spectral differences between anodic aluminum films formed in sulfuric acid as well as chromic acid and films formed in an etching solution (Iridite©).

EXPERIMENTAL

Materials

Aluminum coupons 1 × 1.5 inch (2.5 × 3.8 cm) 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 to a thickness of about 47 μm. Some coupons were anodized in chromic acid solutions according to Mil-A8625-E Type I specifications to a thickness of about 35 μm. The rest of the coupons were etched in a solution of cyanochromic acid complex (Iridite©). This treatment is widely used and little is known of the oxide structure it produces. Samples were kept in a desiccator under vacuum after treatment. Spectroscopic studies were done as soon as possible to avoid the build up of impurities and subsequent chemical modification.

Specular Reflectance Measurements

Specular reflectance measurements used an incidence angle of 74° with an aperture. All spectra were taken at a resolution of 4 cm^{-1} and coadded with 256 scans. Polarization was done with a KRS-5 wire grid polarizer to give s-polarized light (light with electric field tangential to the sample surface) and p-polarized (light with the electric field normal to the sample surface). It is widely known that s-polarized light gives no reflection spectra on metallic surfaces at grazing angles. However, for sufficiently thick organic or inorganic films on the metallic surfaces, reflection absorbance spectra are observed. In the case of amorphous solids, the vibrations of the molecular groups can occur near the phonon frequencies.

The reflection spectra were normalized to a standard thickness so that comparison could be made for the absorbance interactive.

Chemical Sectioning

Boiling 2M sulfuric acid solutions were used to dissolve the anodic oxides on the samples. Sulfuric acid was used because it only mildly attacks the aluminum below the anodic oxide.[11] Coupons were exposed for 2-minute time intervals, rinsed in distilled water and dried in a vacuum. The dissolution rate can be converted to penetration depth by weighing the coupons on a balance, using density values of 2.36 g/cm^3 for SAA samples,[1] 2.07 g/cm^3 for CAA samples and 1.89 g/cm^3 for the etched samples (Iridite©). The density value for the Iridite© sample was supplied by the plating company. A constant exposure area was used for all the samples. This was accomplished by clamping the coupons against a socket joint containing the boiling solution. The exposure area was 5.17 cm^2. Infrared reflectance spectra of these samples was carried out in an Irus© microscope at incidence angles ranging from 60–30° with no polarizer.

EXPERIMENTAL RESULTS AND DISCUSSION

The FT-IR transmission spectra from a sample obtained by scraping the oxide off the surfaces with a stainless steel knife are shown in the range from 4000 to 500 cm^{-1} in Figure 1a and the expanded region from 2200 to 600 cm^{-1} in Figure 1b for the four different Al samples (except for the untreated Al sample in which the specular reflectance spectrum is shown). The bands observed and their chemical assignments are shown in Table I.

The IR spectra reflect the well-known differences in the functionality of the treated surfaces.[9] The untreated Al surfaces show the simplest spectra, as expected. Bands due to bulk Al structure are observed: Al-O-Al stretching vibrations of amorphous Al_2O_3 at 968 and 760 cm^{-1}. The intensities of these peaks in the untreated sample compared with the chemically-treated samples reflect the greater contribution of the bulk components in the untreated samples. The remainder of the spectra of the untreated sample shows weak lines due to surface contamination and oxidation (these bands will be discussed in more detail later). The bands are weak and diffuse in the untreated sample relative to the treated samples.

A. Chromic Acid Anodized Al

The most intense lines in the chromic acid anodized (CAA) samples arise from the hydroxyl absorption in the 3600 to 3400 cm^{-1} region reflecting the complex distribution of hydroxyl groups on the surface of the Al. Inorganic hydroxyl groups are expected to absorb in the 3510 and 3230 cm^{-1} region in addition to absorbed water. The result of this multifunctionality and their interaction through hydrogen bonding yields the broad band observed in this region.[12] Adsorbed water is also observed at 1658 cm^{-1} and at 1625 cm^{-1}, suggesting that there are several types of

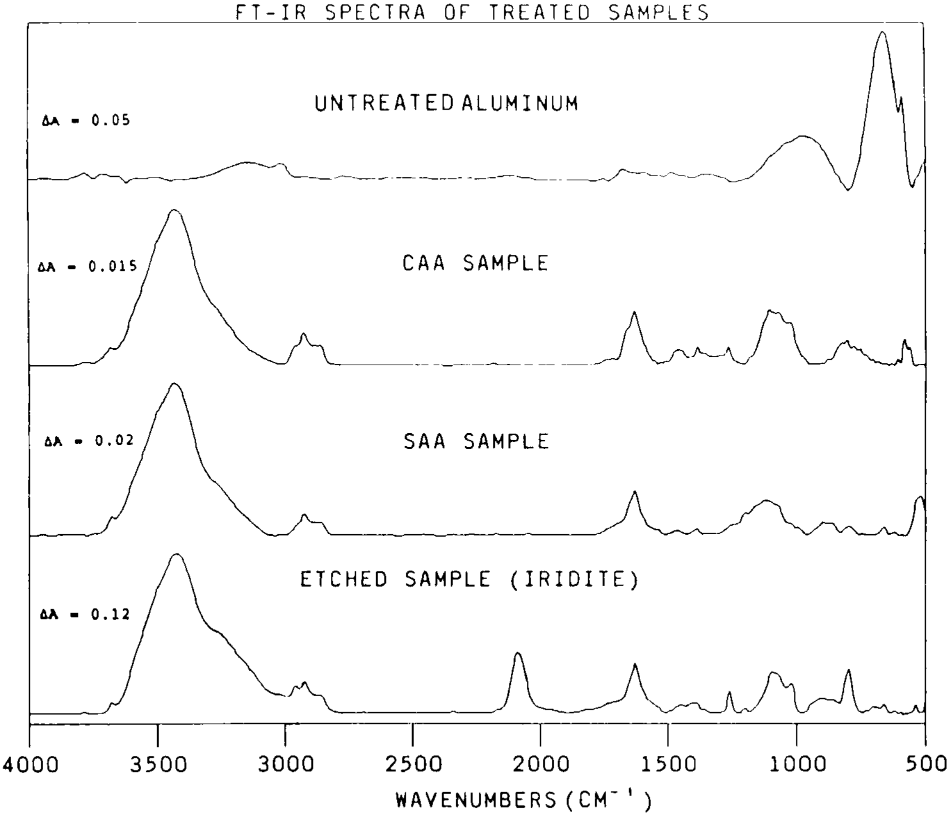


FIGURE 1a Transmission spectra of the treated and untreated aluminum samples.

adsorption sites for water in the CAA-treated samples. The bands due to the bulk Al structures are weak in the CAA spectra indicating that the spectra are primarily from the treated surface. Another set of intense lines are seen between 1200 and 950 cm^{-1} reflecting the structure of the oxide on the treated surface. The bands are indicative of aluminum oxyhydroxides and hydroxides species. The broadness of the bands reflects the presence of different species. The oxyhydroxides absorb strongly near 1072 cm^{-1} and weakly near 1175 cm^{-1}. This is consistent with a pseudoboehmite structure. Aluminum hydroxides absorb at 1020 cm^{-1} and 806 cm^{-1} with a band structure similar to Gibbsite. We assigned the hydrated oxide structure in the spectra to a structure close to Gibbsite. This was based on IR correlations with previously published spectra of aluminum hydroxides. We do not rule out Bayerite as a possibility. We did not perform x-ray analysis on these samples. The intense line near 1103 cm^{-1} is still unassigned but it is either due to boehmite or to chemisorbed water species of the form $Al\text{-}OH_2$.[13] Additional bands are observed related to the reactions and adsorption of CO_2 with the CAA surface. These bands are in the 1660 and 1200 cm^{-1} region. There are chemisorbed CO_2

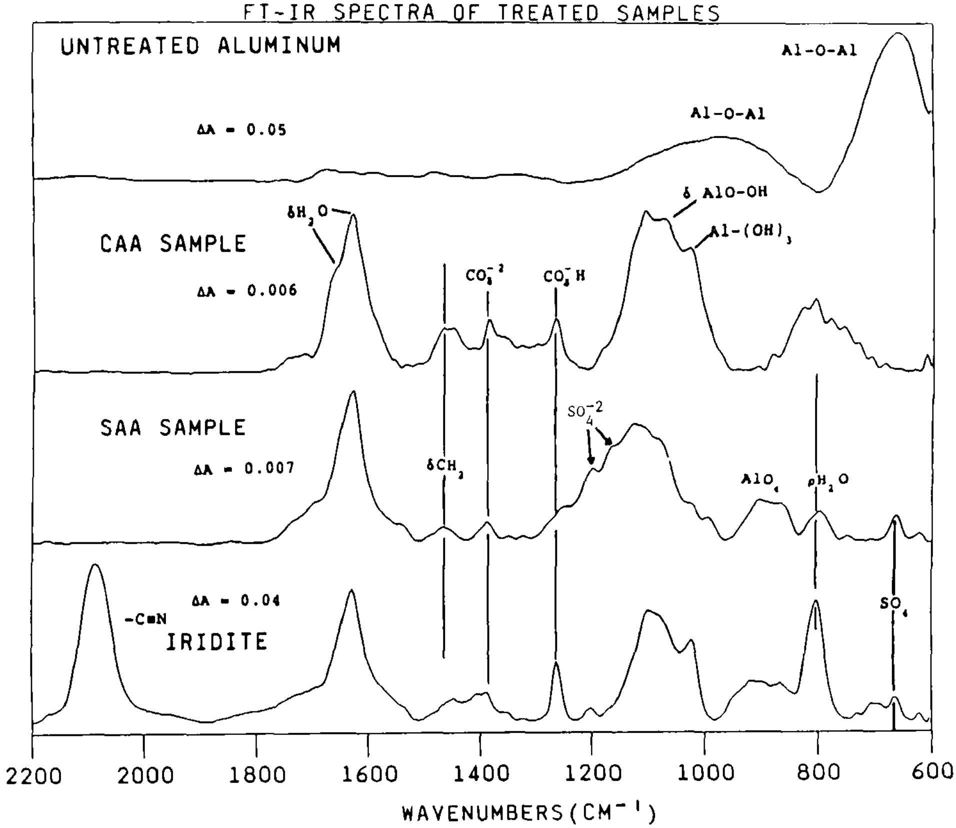


FIGURE 1b Transmission spectra of the treated and untreated samples for the region 1800–1600 cm^{-1}.

species as noted by the bands at 1560 and 1410 cm^{-1} and unidentate carbonate species at 1384, 1360 and 830 cm^{-1}.[3] The nature of the band at 1260 cm^{-1} is still uncertain but it could be due to CH_3 groups. A difference spectrum of the CAA and SAA oxides between 1800 cm^{-1} and 600 cm^{-1} is shown in Figure 1c. The difference spectrum shows a broad negative peak between 1170–1060 cm^{-1}, a broad positive peak between 1230–1180 cm^{-1} and a small broad positive peak between 935 cm^{-1} and 790 cm^{-1}. The peak around 1100 cm^{-1} (associated with hydroxides) indicates the CAA oxide surface contains relatively more water and hydroxides than the SAA oxides. This is more clearly shown in Figure 1d which shows the difference spectrum of the OH region between SAA and CAA oxides. The negative peak around 900 cm^{-1} associated with Al-O vibrations indicates the greater amount of backbone oxide (alumina) on the SAA oxide. The negative peak near 1180 cm^{-1} is associated with the sulfate groups trapped in this oxide. Thus, CAA oxides contain more hydroxyls and water than the SAA oxides while the latter contains more alumina (Al-O-Al).[14]

TABLE I
Bands assignment of anodized aluminum surfaces

Assignment	Al	CAA	SAA	Iridite©
ν O-H free	—	3679w, sp	same	same
ν O-H H-bonded	—	3569s, bd	same	same
ν O-H water	3258m, bd	3428s, bd	same	same
ν O-H H-bonded	3258m, bd	3272m, bd	same	same
1072 + 1103	—	2170w	same	—
1072 + 700	—	1820–1700w	same	same
δ H-O-H	1625	1658m, bd	same	same
		1627s, bd		
δ CH_2	—	1465s	same	same
CO_3 asy ν_3	—	1450m, bd	same	same
		1384s, sp		
anh. CO_3 ν_3	—	1411w	same	same
asym. CO_2	—	1570m	same	same
		1360m		
HCO_3 asym. ν_3	—	1260s	same	same
		1240w		
Boehmite	—	1103s	same	same
Pseudoboehmite	—	1176m	same	same
		1072s		
Gibbsite	—	1029s	same	same
		975m		
		925w, 825m		806s
		806m		
alumina	960s	same	same	same
	760s			
Sulfate ν_3	—	—	1160m	—
			1200m	
Metal Carbonyl	—	—	—	2070s, bd

anh. = anhydrous	w = weak	s = strong	bd = broad
asym. = asymmetry	m = medium	sp = sharp	

B. Sulfuric Acid Anodized Al

The most intense bands in the sulfuric acid anodized (SAA) samples are due to water and hydroxyl groups (3600–3400 and 1620 cm^{-1} regions). From the position, shape and intensity of these bands, structures are present in SAA which are similar to those in the CAA-treated samples. This oxide surface also contains intense bands between 1200 and 1160 cm^{-1} that are characteristic of sulfates.[15] The bands at 1200, 1160, 995 and 663 cm^{-1} are due to the ν_3, ν_1, ν_4 vibrations of the sulfate groups.[15] Sulfate groups are also observed by other spectroscopic techniques for SAA-treated samples.[9,16] Two intense bands are seen in the lower wavenumber region (532 cm^{-1} and 516 cm^{-1}), due to water. The SAA surface also contains bands in the region between 1130 to 950 cm^{-1} similar to those in the CAA sample. Thus, the SAA samples contain oxyhydroxides and hydroxides of the type seen in the CAA samples. The set of bands between 1600 cm^{-1} and 1200 cm^{-1} are due to contamination of the kind noted for the CAA samples. This is consistent with previous studies of these systems.[9,10]

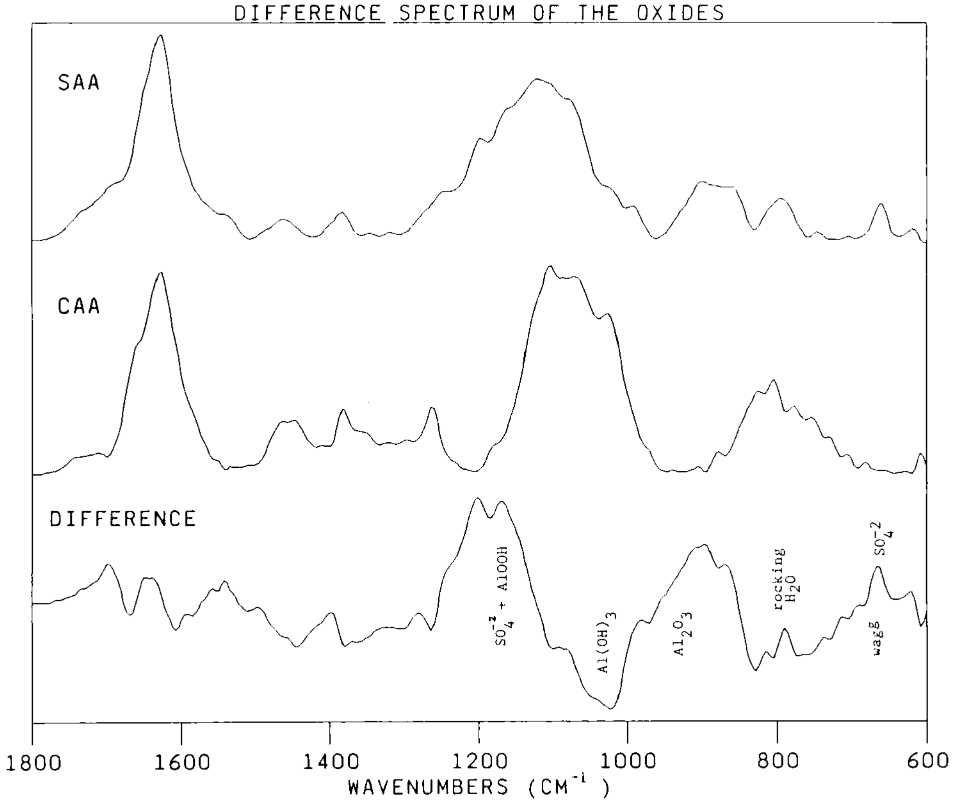


FIGURE 1c Difference spectra of the SAA and CAA oxides.

C. Chemically Treated (Iridite©) Al

The chemically-treated sample (Iridite©) spectrum is also shown in Figure 1. Bands associated with water and OH groups are the most intense bands in the spectrum for this sample treatment.[18] The shape, intensity and location of these bands are similar to those found in the anodized samples, indicating that similar water and OH structures exist in all three samples. The second most intense band is seen near 2070 cm^{-1}, due to metal-cyano groups. XPS work done on a similar sample showed high content of nitrogen atoms,[19] suggesting assignment of this band to the cyano group. Another intense band is seen at 802 cm^{-1}. This band is the overlapped combination of the rocking motion of water and oxyhydroxides. The set of bands between 700 cm^{-1} and 600 cm^{-1} are due to the libration modes of lattice water (water inside the oxide). Finally, the band at 540 cm^{-1} is assigned to the wagging mode of water.[15] Thus, this chemical treatment produces nearly the same water and hydroxyl structure as the anodized layers.

D. Thermal Studies

In order to clarify some of the spectral assignments of the treated samples, thermal studies were conducted. FT-IR transmission difference spectra of the CAA-treated

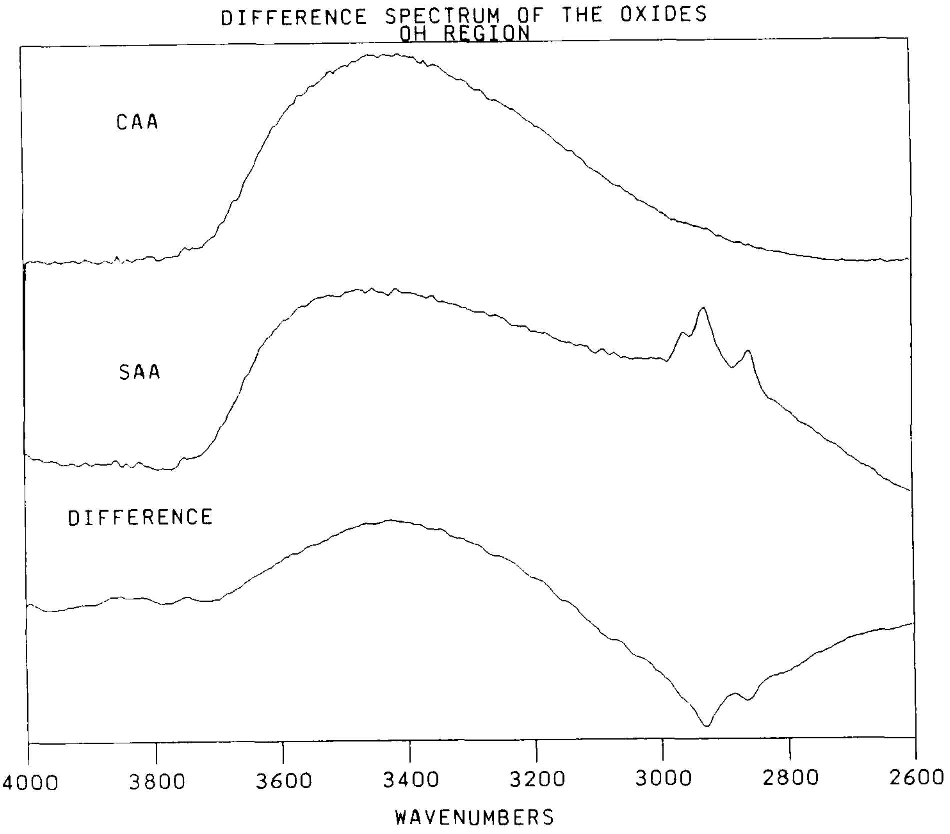


FIGURE 1d OH region of the difference spectra of the anodized oxides.

samples heated to 180°C for 0.5 hours and evacuated are shown in Figure 2. Heating should remove water bands from the spectra, making identification of bands associated with water easy (assuming little change occurs in the oxide structure during dehydration).

The difference spectrum reflect the bands associated with water lost during dehydration (1620, 1120–1100, 800 and 700–500 cm^{-1}). There is a broadening and an increase in the bands centered around 920 cm^{-1}. This suggests the formation of Al-O-Al and hydrogen bonded OH species during heating. This result illustrates the well-known relation between dehydration and oxide formation as follows:

$$\text{Al-OH} + \text{Al-OH} \rightarrow H_2O + \text{Al-O-Al} \quad (1)$$

$$2\ \text{Al-OH--OH}_2 \rightarrow \text{Al-OH--OH-Al} + 2\ H_2O \quad (2)$$

This has the consequence of lowering the Bronsted acidity and basicity of the treated surface.[17] The bands at 1260 cm^{-1} and 1246 cm^{-1} decreased during dehydration, indicative that these bands are associated with water and CO_2. The same results were obtained for the etched samples (Iridite©) as seen in Figure 3. Previous work on the interaction of water and CO_2 on oxides[13] assigned the 1246 cm^{-1} band

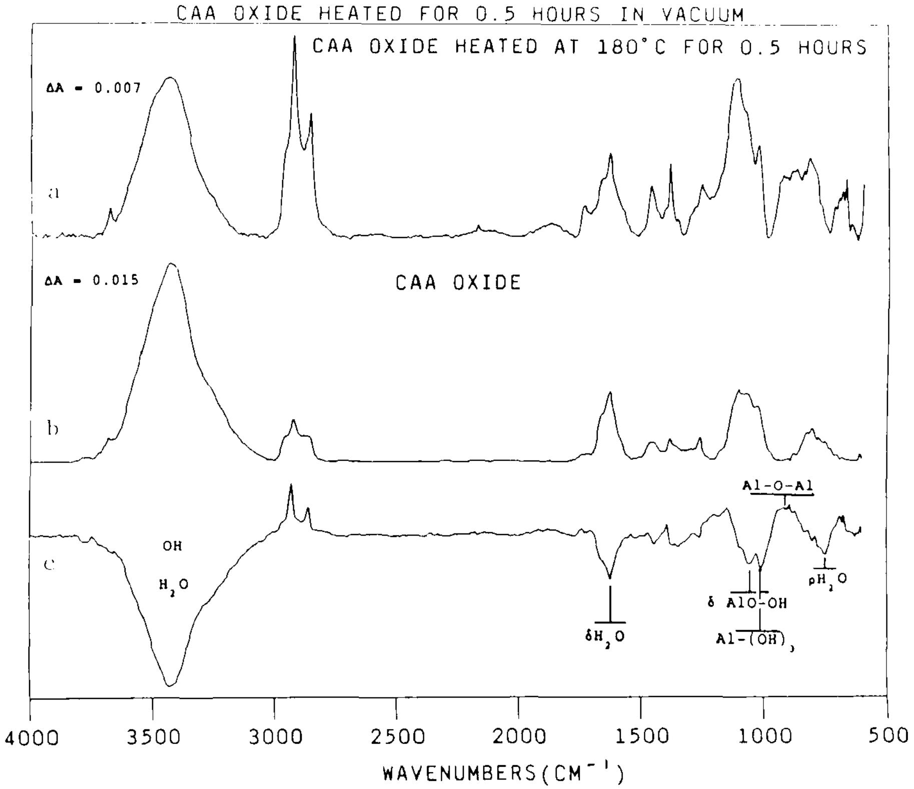


FIGURE 2 Transmission spectrum of the CAA a) heated sample, b) room temperature sample and c) difference of a) − b).

to bicarbonates. Thus, it is possible that such bands in our samples are also due to bicarbonates.

We carried out tests where the anodic films were heated up and *in situ* IR spectroscopy (specular reflectance) was done. The results were that the CAA-anodized Al samples contained more hydroxides and water (area under the peak) than the SAA-anodized Al samples, even though the SAA film is much thicker than the CAA film. Thus, we proceeded to perform the same test by weighing the same amount of oxide to elucidate density difference effects and the results showed that the CAA film contained more hydroxides and water than the SAA film.

E. Chemical Sectioning

In order to study the spatial distribution through the thickness of the treated surfaces, a chemical sectioning technique[11] of the treated surfaces was done by immersing the treated samples as a function of time in a 2M solution of sulfuric acid. The specular reflectance spectra obtained at incidence angles ranging from 60 to 20° are shown in Figure 4a for the CAA-treated samples.

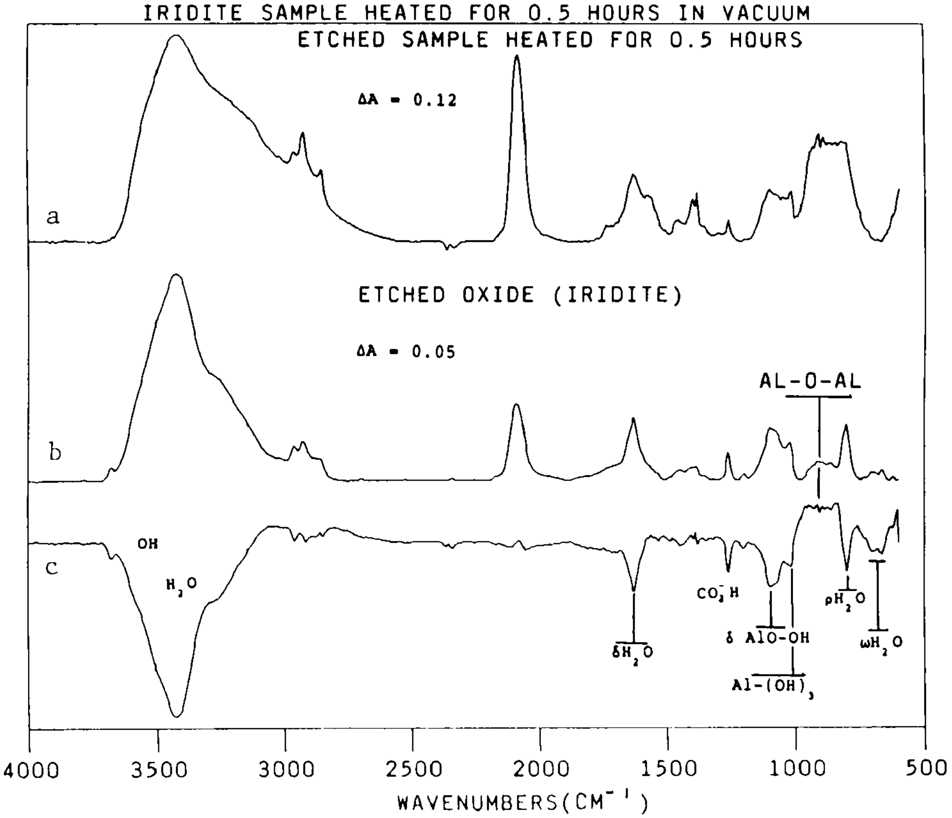


FIGURE 3 Transmission spectrum of the chemically treated (Iridite©) a) heated sample, b) room temperature and c) difference a) − b).

The spectra reflect the chemical structure of anodized surfaces.[8] The broad band at 1150 cm^{-1} decreases while the broad band at 950 cm^{-1} is relatively unaffected as the thicknesses of the films decrease. The broad band at 1150 cm^{-1} is associated with the longitudinal optical phonons of the hydroxides.[8] The band at 950 cm^{-1} is associated with the Al-O-Al species.[8] Thus, as shown in Figure 4b, the hydroxides and water are preferentially concentrated near the surface of the treated samples while the alumina (of the kind seen in the untreated sample) is concentrated near the metal substrate. The bands associated with the contaminating species are concentrated near the surface as they are not observed after a short period of dissolution. However, the bands associated with carbonates remain after some periods of dissolution. They are either incorporated in the oxide network or they are within the pores which penetrate into the barrier layer.[1] It is possible that the carbonates are formed during sample exposure in air during the dissolution testing. If this is the case then carbonate formation is uniquely associated with lattice water since no carbonates are seen when the barrier oxide is at the surface. Similar results were obtained for the SAA-treated samples as seen in Figure 5a. However, these samples

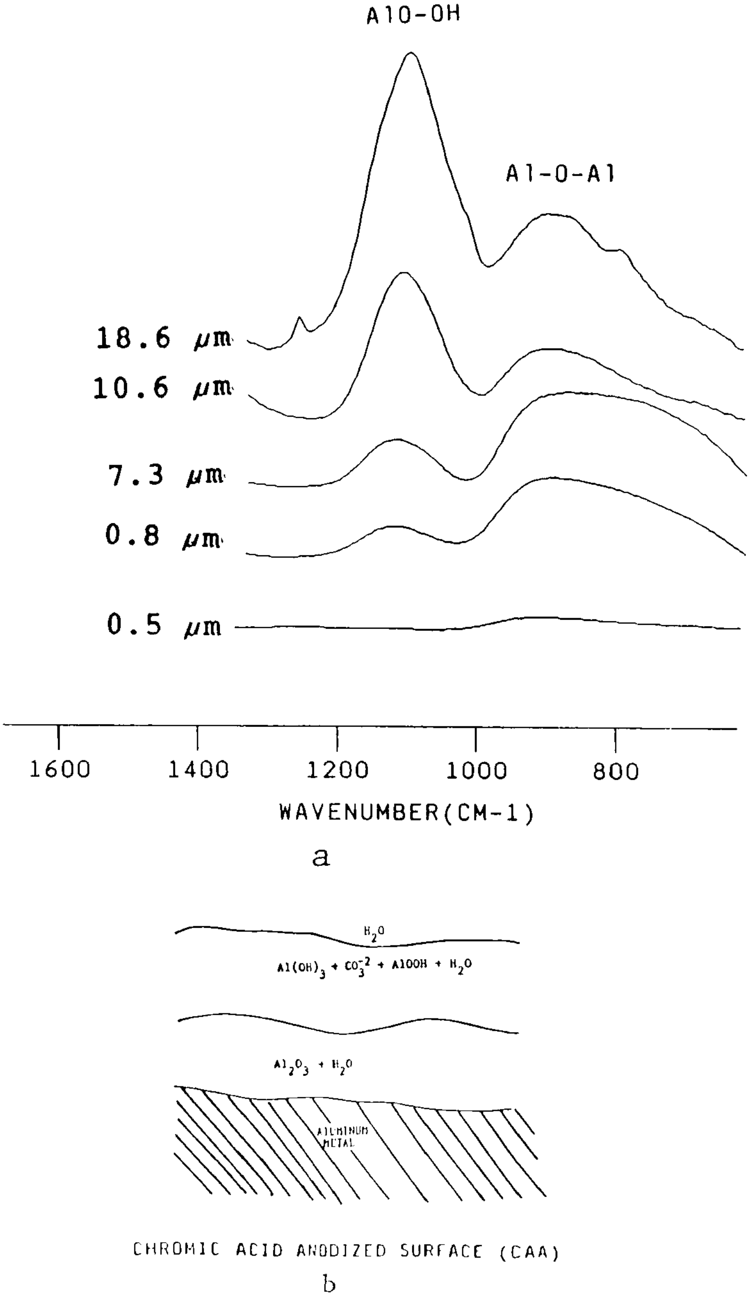
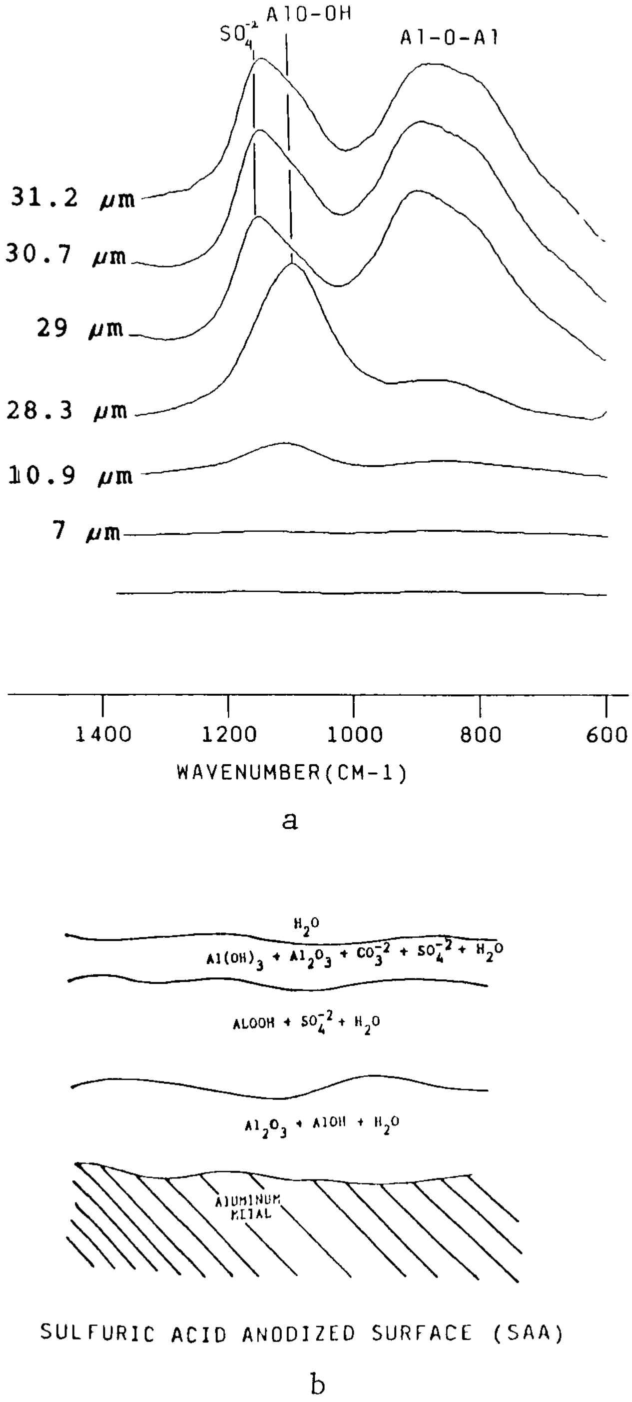


FIGURE 4 a) Specular reflectance spectra of CAA samples of different surface thickness, b) Diagram of bi-layer structure of chromic acid anodized surface (CAA).


SO$_4^{-2}$
AlO-OH
Al-O-Al
31.2 μm
30.7 μm
29 μm
28.3 μm
10.9 μm
7 μm
1400
1200
1000
800
600
WAVENUMBER(CM-1)
a
H$_2$O
Al(OH)$_3$ + Al$_2$O$_3$ + CO$_3^{-2}$ + SO$_4^{-2}$ + H$_2$O
ALOOH + SO$_4^{-2}$ + H$_2$O
Al$_2$O$_3$ + AlOH + H$_2$O
ALUMINUM METAL
SULFURIC ACID ANODIZED SURFACE (SAA)
b

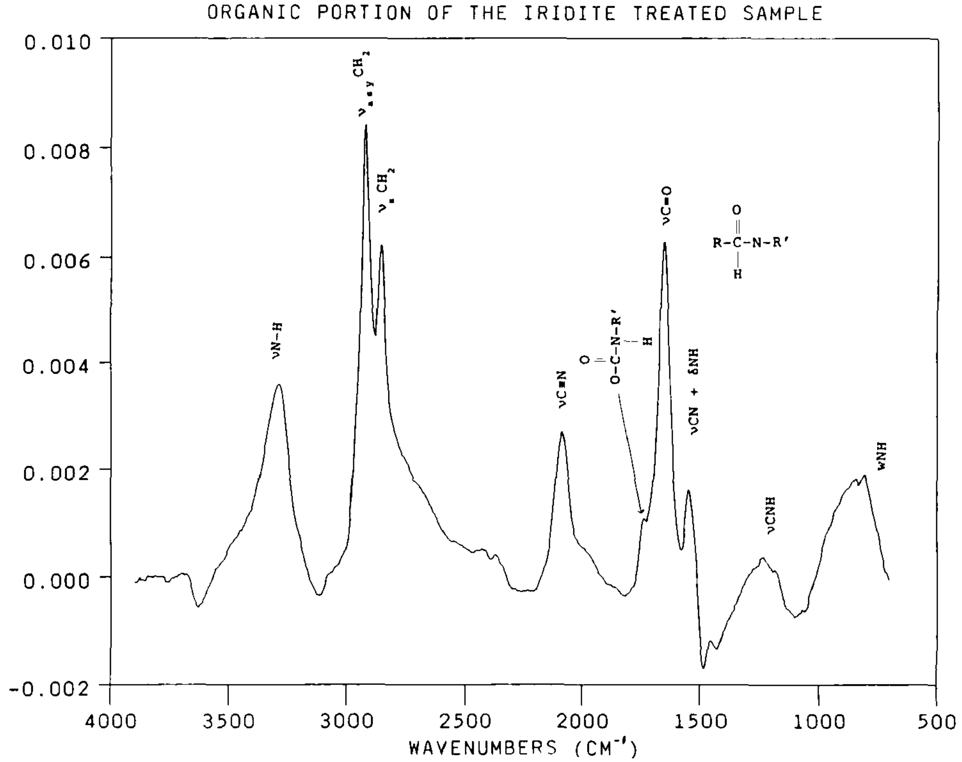


FIGURE 6 Difference spectrum of the organic layer from the inorganic layer of the Iridite© treated sample.

show strong hydroxyl absorption (band near 1100 cm^{-1}) resulting from the 6 to 8 minutes exposure to sulfuric acid. This is indicative of the gradients of structures existing in anodized samples. These results are consistent with the oxide structure developed by other workers for anodized samples.[8] Thus, as shown in Figure 5b, the SAA oxides appear to have a tri-layer structure by this anodizing process as follows: hydrated, oxyhydrated and alumina/oxyhydrated and hydrated/hydrated and alumina which is different from the CAA oxide which has a duplex structure.

The chemical sectioning of the chemically-treated sample was also studied. All of the bands decreased uniformly with time. This is a gradual transition from a mixed organic-inorganic structure to hydrated alumina. By subtracting one spectrum from the other, one can isolate the organic layer and this is shown in Figure 6. The figure shows organic bands at 3300 cm^{-1}, 1640 cm^{-1}, 1560 cm^{-1}, 1230 cm^{-1} (broad) and 800 cm^{-1} (broad). These bands are assigned to a carbamate. The bands at 2920 cm^{-1} and 2850 cm^{-1} are due to CH_2 groups while the band at 2079 cm^{-1} is due to nitrile groups covalently bonded to either chromium or iron atoms. Thus, alumi-

FIGURE 5 a) Specular reflectance spectra of SAA samples of different surface thickness, b) Diagram of tri-layer structure of sulfuric acid anodized surface (SAA).

num surfaces treated by the Iridite© process are duplex structures composed of a mixed organic-inorganic layer (carbamates + hydroxides) above a hydrated alumina (Al_2O_3).

F. Polarization Results

The FT-IR specular reflectance of CAA-treated samples obtained at 75° with s and p-radiation is shown in Figure 7. The transmission spectrum is also shown in the figures for comparison. The p-polarized spectrum is shown in Figure 7b. The most intense bands are from the vibrations of the Al-O-Al species (1114 and 987 cm^{-1}). Thus, the Al-O-Al species are oriented normal to the surface. The rest of the bands in the p-spectrum are weak. The s-polarization reflectance spectrum is shown in Figure 7c. The most intense lines arise from the 3600 to 3400 cm^{-1} and 1620 to 1200 cm^{-1} regions. These bands are assigned to vibrations of the Al-OH, and the absorption of the H_2O and carbonate species.[9] Thus, water, OH and carbonate species are oriented tangential to the surface.

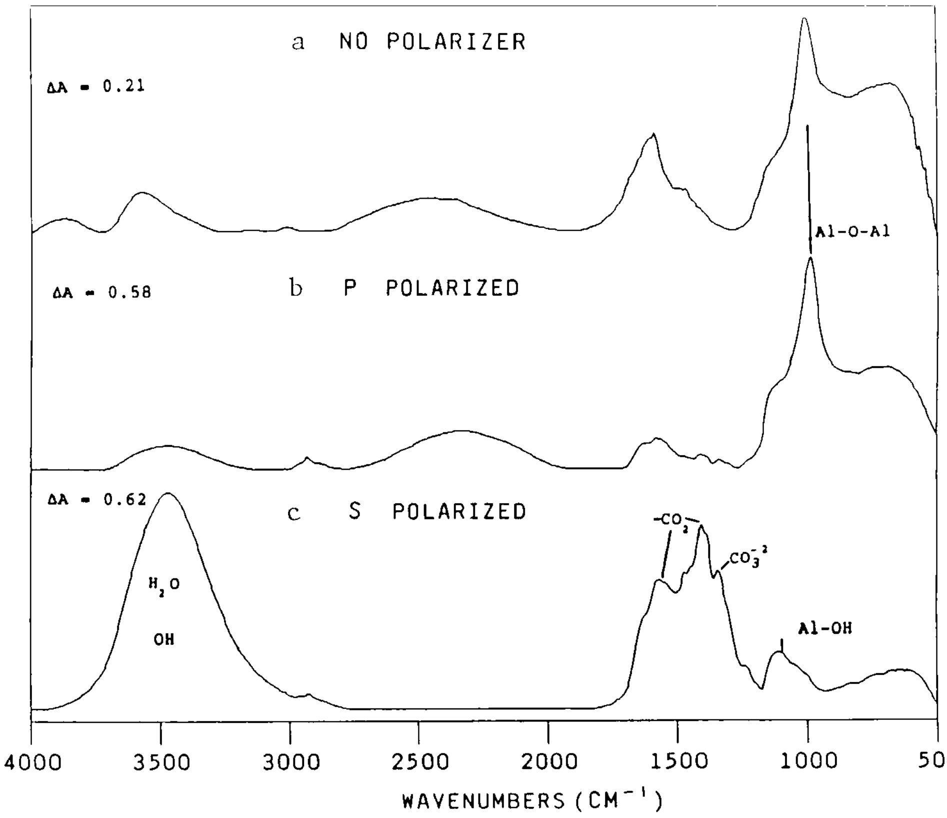


FIGURE 7 Grazing angle specular reflectance spectra of CAA samples with light polarized a) no polarizer, b) perpendicular to the sample surface and c) parallel to the sample surface.

The FT-IR reflectance spectra obtained by polarized radiation are shown in Figure 8 for the SAA sample. Band assignments are shown also in the figure.

The p-polarized spectrum is shown in Figure 8b. Since the SAA-treated surfaces are virtually transparent, the spectrum shows intense birefringences (2655 and 1530 cm^{-1}). However, there are bands due to absorbing species not associated with the interference phenomena. These are the weak bands at 1210 cm^{-1} and 1030 cm^{-1} due to SO^{-2} and Al-OH species. The s-polarized spectrum is shown in Figure 8c. Again, the appearance of birefringence is noted at 2000 cm^{-1} and 2800 cm^{-1}. However, there are two sharp bands at 1132 and 962 cm^{-1}.

The FT-IR reflectance spectra obtained by polarized radiation are shown in Figure 9 for the chemically-treated sample. Bands assignments are also shown in the figure. The p-polarized spectrum of this sample is shown in Figure 9b. As can be seen from the figure, all the bands are present with the most intense bands occurring at 2090, 948 and 937 cm^{-1}. These bands are assigned to metal-cyano, Al-OH and Al-O-Al, respectively. Other bands present are at 856, 601 and 567 cm^{-1}. They are assigned to the wagging, rocking and libration modes of water.

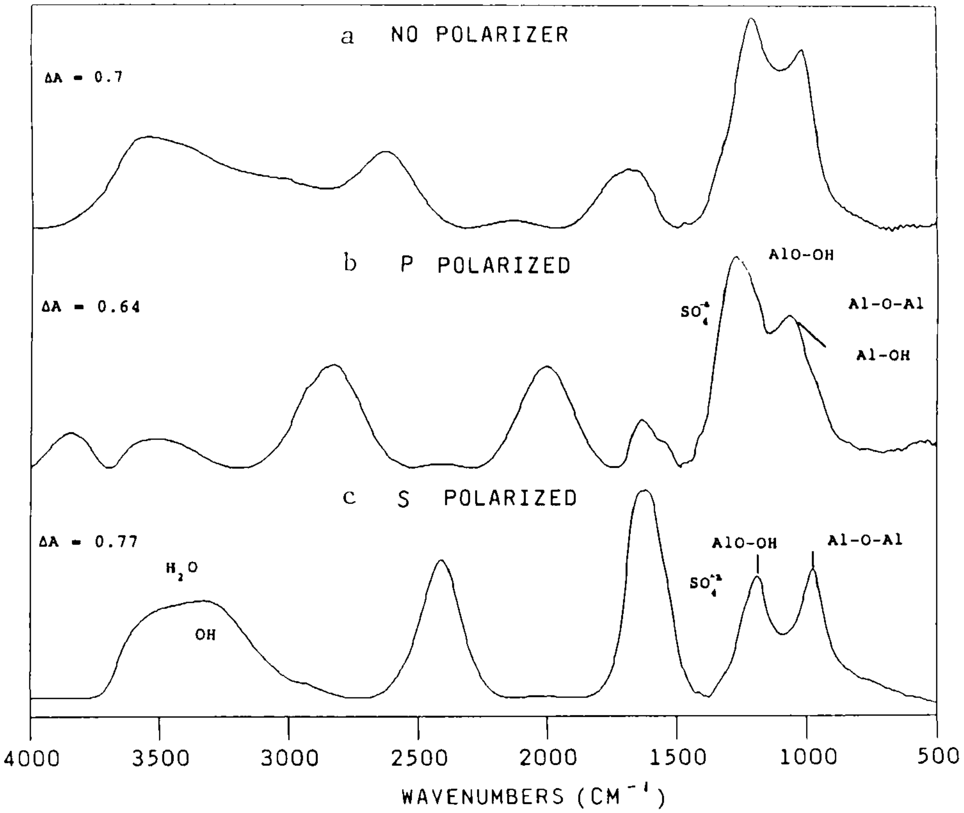


FIGURE 8 Grazing angle specular reflectance spectra of SAA samples with light polarized a) no polarizer, b) perpendicular to the sample surface and c) parallel to the sample surface.

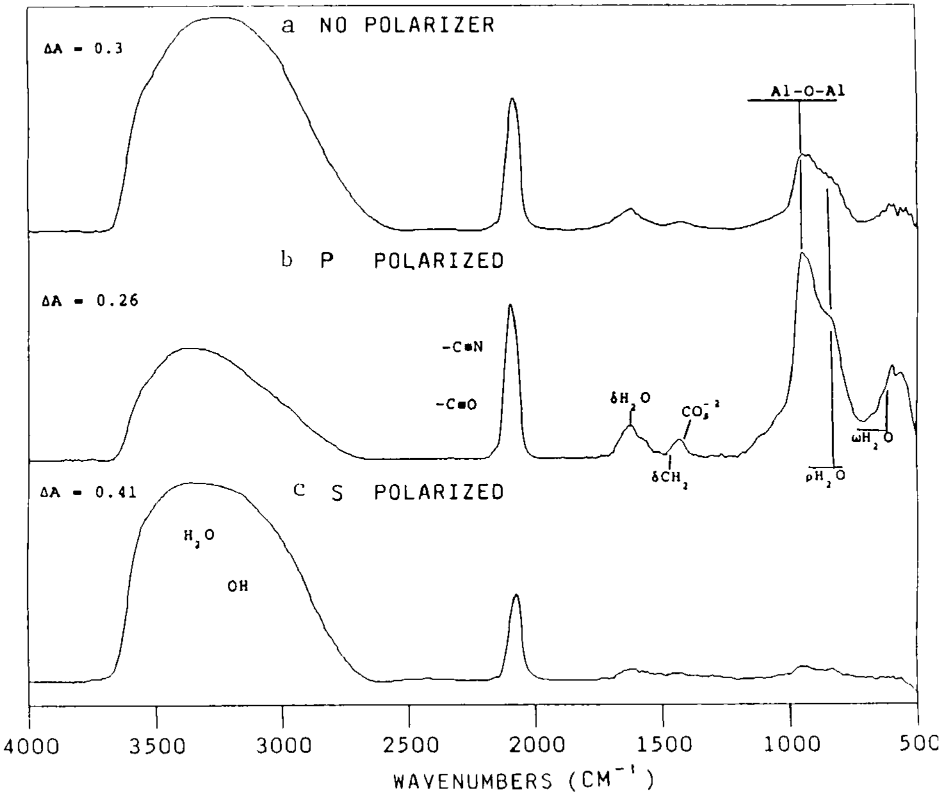


FIGURE 9 Grazing angle specular reflectance spectra of the etched samples (Iridite©) with light polarized a) no polarizer, b) perpendicular to the sample surface and c) parallel to the sample surface.

The s-polarized spectrum of this sample is shown in Figure 9c. The most intense bands arise at 2071 and in the region 3600 to 3200 cm^{-1}. They are due to metal-cyano, water and OH groups. Thus, water, metal-cyano and OH groups are isotropically oriented in these samples. Therefore, its structure is different from that of the anodized samples.

CONCLUSIONS

It is shown that FT-IR reflectance is a particularly powerful technique for characterizing anodic surfaces. Identification of molecular species and their orientation with respect to the surface is possible. It is shown that the major contaminants in the different oxides are chemisorbed CO_2, carbonates and bi-carbonates. All of the oxide treatments have contributions from anhydrous alumina, aluminum oxyhydroxide (pseudoboehmite) and aluminum hydroxide (Gibbsite). CAA oxides contain more hydroxides and water than the SAA oxides while the latter contain more alumina. CAA oxides are duplex structure of hydrated and hydroxylated layers above an oxyhydrated layer. The chemically-converted surface by the Iridite© process shows a duplex structure of a mixed organic-inorganic layer above a hydrated alumina. The organic portion of the layer is a carbamate species.

References

1. J. O'M. Bockris, Ralph E. White and B. E. Conway, *Modern Aspects of Electrochemistry,* vol. 20 (Plenum Press, New York, 1989).
2. V. P. Parkhytik, Ju. E. Makushok, V. A. Labunov and V. A. Sokal, *Zh. Prikl, Spektrosk.* **44,** 494 (1986).
3. V. T. Belov, *Zashch. Metal.* **4,** 597 (1986).
4. A. J. Maeland, R. Rittenhouse and K. Bird, *Plating* **63,** 56 (1976).
5. G. A. Dorsey, Jr., *J. Electrochem. Soc.* **113,** 169 (1966).
6. G. A. Dorsey, Jr., *J. Electrochem. Soc.* **115,** 1057 (1968).
7. G. A. Dorsey, Jr., *J. Electrochem. Soc.* **115,** 1053 (1968).

7a. K. Wefers, C. Misra, Alcoa Laboratories Report, "Oxides and Hydroxides of Aluminum" (1987).

8. M. Handke, C. Paluszkiewicz and W. Wyrwa, *Material Chemistry* **5,** 199 (1980).
9. M. Handke and C. Paluskiewicz, *Infrared Phys.* **24** (No. 2/3), 121 (1984).
10. N. Fin, H. Dodiuk, A. E. Yaniv and L. Drori, *Applied Surface Science* **28,** 11 (1987).
11. H. Takahashi, K. Jujimoto, H. Konno and M. Nagayama, *J. Electrochem. Soc.* **131,** 1856 (1984).
12. D. W. Berreman, *Physical Review* **130** (No. 6), 2193 (1963).
13. Kazuo Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Fourth Ed. (John Wiley & Sons, New York, 1986).
14. J. B. Benzinger, S. J. McGovern and B. S. H. Royce, "IR Photoacoustic Spectroscopy of Silica and Aluminum Oxide," *ACS Symposium Series* **288,** Martin L. Deviney and John L. Gland, Eds. (Am. Chem. Socy, Washington, DC, 1984), pp. 449–463.
15. L. H. Little, *Infrared Spectra of Adsorbed Species* (Academic Press, New York, 1966).
16. Y. Fukuda and T. Fukushima, *Bull. Chem. Soc. Jpn.* **53,** 3125 (1980).
17. R. J. Chester and J. D. Roberts, *Int. J. Adhesion & Adhesives* **9** (No. 3), 129 (1989).
18. A. Lehmann, *Phys. Stat. Sol.* **148,** 401 (1988).
19. E. A. Podoba, S. P. Kodali, R. C. Curley, D. McNamara and J. D. Venables, "Adhesive Bond Durability with Conversion Coatings," *Appl. of Surf. Sci.* **9,** 359–376 (1981).