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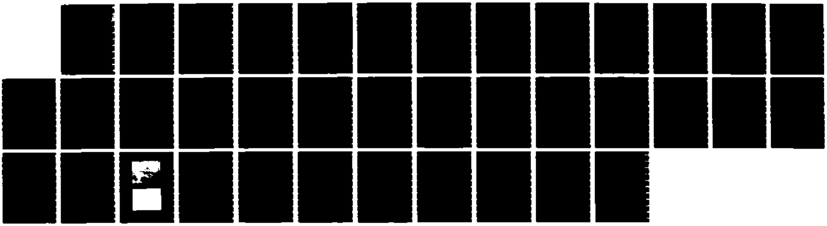

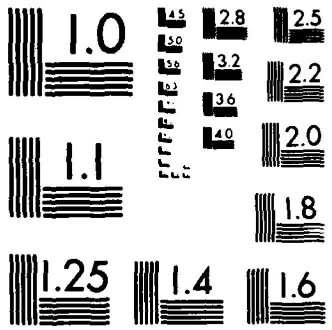
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VIRGINIA TECH
CENTER FOR ADHESION SCIENCE

SEMI-ANNUAL REPORT

AN INTERDISCIPLINARY APPROACH TO PREDICTIVE MODELING OF STRUCTURAL ADHESIVE BONDING

CHARACTERIZATION OF TI-6AL-4V OXIDES AND THE ADHESIVE/OXIDE INTERPHASE

BY

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FROM

CENTER FOR ADHESION SCIENCE
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*This report covers research done during the period September, 1985 through March, 1986.

I. INTRODUCTION

Ti-6Al-4V, a high strength, light weight corrosion resistant alloy, possesses many applications for structural adhesive bonding. This report covers the interaction of pretreated surfaces with heat, alkoxide primers, thin polymer films, structural epoxy, and hostile environments. The stability of the oxides at temperatures of 450°C is shown. Alkoxide primers enhance the durability of adhesively bonded aluminum ~~[2].~~ Characterization of alkoxide primers on Ti-6-4 has begun as well as evaluation of these primers in the wedge test. Thin polymer films on polished titanium are studied by grazing angle infrared spectroscopy. STEM, AES and XPS show the penetration of FM-300 into the porous oxide of CAA. Finally, the wedge test examines pretreatment stability in a variety of environments.

II. EXPERIMENTAL

A. Surface Pretreatments

The following pretreatments were used to create oxide layers on the Ti-6-4 surface: a 10 volt chromic acid anodization (CAA), a 10 volt sodium hydroxide anodization (SHA), a phosphate-fluoride acid etch (P/F), or a TURCO 5578 basic etch. PTURCO or PSHA designate that a pickling step preceded the TURCO or SHA pretreatments. Appendix I lists the pretreatment procedures and modifications for Ti-6-4 foil pretreatment.

B. Auger Electron Spectroscopy, AES

AES was done on a Perkin-Elmer PHI 610 scanning Auger microprobe at 3 to 5 kV electron beam voltage and 0.05 μa beam current. Samples were depth profiled by argon ion sputtering with a 4 kV ion beam voltage, a 25 ma emission current and a 0.2 μa ion beam current.

C. X-ray Photoelectron Spectroscopy, XPS

XPS analysis was obtained on both a KRATOS XSAM 800 spectrometer and a PHI 5300 ESCA system using a Mg anode. Samples were punched as 0.95 cm (0.38 in.) disks and scanned from 0 to 1000 ev. Narrow scans were made on any significant peaks observed in the wide scan spectra.

D. Scanning Transmission Electron Microscopy, STEM

STEM pictures were obtained on a Phillips EM-420T electron microscope. Pretreated Ti-6-4 foil was cut to 3 by 8 mm (0.12 - 0.31 inch) pieces. The magnifications ranged from 3200 to 100,000 times. Gold coating of the samples was not necessary.

E. Scanning Electron Microscopy, SEM

SEM photomicrographs were taken on a JEOL JSM-35-c electron microscope. Pretreated samples were punched as 0.95 cm (0.38 inch) disks and sputter coated with 20 nm of gold. Stereophotomicrographs were taken by the following procedure: At 200 x and at the tilt of interest, the sample was focussed. A spot on the sample was aligned with a center point marked on the screen. The z-axis was adjusted so that the spot chosen on the sample remained in line with the center point on the screen when the tilt axis was rotated ± a few degrees. The sample was photographed at the magnification desired. The sample was then tilted ± 7 degrees while keeping the spot on the sample aligned with the center spot of the screen using the x- and y axis controls. A second picture was taken. The pictures were aligned next to one another, placing the higher angle photograph on the left side.

F. Sample Preparation for IR and Ellipsometry

Polished Ti-6-4 samples were prepared from lap shear coupons. 2.54 cm (1 inch) disks were cut and placed in brass holders. A series of polishing wheels were used, stepping to the next finer grit only when the titanium disk was covered with uniform scratches. The final wheel grit size was 0.05 microns. In the last step, the polished disks were placed in a vibrating bath containing Buehler Mastermet colloidal silica, allowing the samples to vibrate overnight.

Two alkoxide primers from Stauffer Chemical Company, E-8385 - an aluminum alkoxide and TNBT - tetra-n-butyl titanate were used as 1.0 wt% solutions in dry toluene. These solutions were spun coated on ferrotype plates or polished Ti-6-4. The plates were placed in a vacuum oven at ambient temperature overnight.

Poly-2-ethylhexylmethacrylate (PEHMA) was solution cast by spin coating from various weight percent solutions. PEHMA spun coat films were placed in the vacuum oven overnight at ambient temperature.

G. Infrared Spectroscopy

A Nicolet 5DX FTIR spectrometer was used with a grazing angle specular reflectance attachment shown in Figure 1. The chamber was purged with nitrogen gas for 30 minutes before a spectrum was obtained.

H. Ellipsometry

Substrate constants and film thicknesses were measured using a Gaertner L116A dual mode automatic ellipsometer. A nonabsorbing film and substrate program was used to calculate the refractive index, absorptivity and thickness values. A 1 mW helium-neon laser (632.8 nm) was the incident light source with a spot size of 1 mm on the sample. Both linear and circular polarization were used with a continuous rotating analyzer which automatically sampled 72 data points for each state of polarization.

I. Bonding

Wedge samples were pretreated and bonded at 175 C°(350 F), 1.72 MPa (250 psi), for 1.5 hours from a room temperature start. Two layers of epoxy were used with three layers of teflon film used as spacers, yielding a bond thickness of 0.0381 cm (0.015 in.). After bonding, a Ti-6-4 wedge was driven into one end of the sample, propagating an initial crack. The sample was then placed in an environment. Periodically, the position of the crack was measured. One of three alkoxide primers was coated on samples before bonding. P/F pretreated samples were dipped in a 1 wt% solution of LICA 38 (Ken-Rich) in isopropanol. Toluene solutions of E-8385 and TNBT (1 wt%) were brush coated onto P/F pretreated samples with either one or five coats.

III. RESULTS AND DISCUSSION

A. Effects of Heating on Ti-6-4 Oxides

The study of effects of heat on Ti-6-4 oxides continued from a previous report [1] at a higher temperature of 450°C. Ti-6-4 foil was pretreated by CAA, P/F, TURCO, or PSHA; placed in the KRATOS spectrometer; spectra obtained before heating; heated to 450°C and held at that temperature for 10 minutes; cooled and spectra obtained. Table I lists the elements detected on each pretreated surface, the binding energy and atomic percent before and after heating.

The CAA surface showed slight variations in the atomic percent of the elements detected before and after heating. The oxygen concentration increased while the titanium concentration decreased after heating. The high binding energy side of the carbon peak attenuated after heating - a phenomenon seen for all of the pretreated surfaces. The titanium peak shape did not change. The fluorine spectrum showed the appearance of a high binding energy peak at 689 ev.

The PSHA surface showed less variation in the atomic percent of the elements detected before and after heating than the CAA surface. The titanium peak shape did not change after heating.

The P/F surface showed a slight decrease in the carbon atomic percent between the before and after spectra obtained. After heating, the titanium $2p^3$ peak showed a broadening to the lower binding energy side.

The TURCO surface showed a marked increase in the iron concentration after heating. As with the P/F pretreated surface, the titanium $2p^3$ peak showed a broadening to the lower binding energy side after heating. The broadening of the Ti $2p^3$ peaks is caused by a reduction of the titanium oxide. Such an observation may bear directly on the stability of Ti 6-4 surface oxide layers on long term thermal aging.

B. Characterization of Alkoxide Primers

Alkoxide primers, such as aluminum alkoxides, enhance the durability of adhesively bonded aluminum [2]. A study has begun to characterize three alkoxide primers (E-8385, TNBT and LICA 38) and to investigate the effects of these alkoxide primers on adhesively bonded titanium. The characterization will be discussed here and the adhesive bonding will be discussed in the "Wedge Testing" section below.

XPS spectra were obtained for an aluminum alkoxide (E-8385) and tetra-n-butyltitanate (TNBT). The primers were spin coated from a 1 wt% toluene solution onto ferrotype plates. Table II lists the elements detected, the binding energies and the atomic percents. Chromium on the surface indicates the films are either less than 5 nm or are discontinuous. Less chromium was detected on the TNBT surface indicating either a thicker or less discontinuous

TNBT film than the E-8385 film. The E-8385 film showed the presence of aluminum, from the alkoxide, and the binding energy of the oxygen was indicative of aluminum oxide. The TNBT film showed the presence of titanium from the titanate and the binding energy of the oxygen was indicative of titanium oxide.

Infrared spectra were obtained for neat E-8385 and as a film on a ferrotype plate. Figure 2 shows a comparison of the two spectra. The dotted peaks are those agreeing with peaks in the Sadtler Index for sec-butyl aluminum alkoxide [3]. The O-H stretching region indicated adsorbed water and hydroxyl groups are on the alkoxide film surface. These preliminary results are part of a focussed effort to carefully define the surface layer resulting from the application of alkoxide primers.

C. Characterization of PEHMA Films

A study has begun to determine the orientation of poly(2-ethylhexylmethacrylate) on the surface of polished Ti-6-4 using FTIR at a grazing angle. Spectra of PEHMA films obtained at grazing angle are compared to a solution spectrum. Figure 3 shows two grazing angle spectra. The top spectrum is for a 73 nm thick film spun coat from a 1 wt.% solution in toluene. The bottom spectrum is a 25 nm thick film spun coat from a 0.4 wt.% solution in toluene. Table III lists the major peaks and their assignments. The solution spectrum in Figure 4 is a subtraction spectrum of PEHMA so the solvent is not seen. Table IV lists the major peaks and their assignments. The peak positions of the films matched those of the solution spectrum well. The doublet occurring at 1177.6 and 1154.2 cm^{-1} in the solution spectrum showed the 1177.6 cm^{-1} peak with a greater intensity. The same trend is exhibited in the 73 nm film but reversed in the 25 nm film. This may be due to surface orientation. Further investigations are planned to address this reversal.

D. Penetration of Epoxy into the Porous Oxide

Questions have arisen as to whether the FM-300 epoxy penetrates the porous structure of an oxide such as CAA. This is a basic question in understanding the mechanism of adhesion. To answer this question, Ti 6-4 foil was pretreated with CAA, known to yield a porous oxide. FM-300 was pressure cured onto one side of the CAA foil. Because of foil flexibility, the adhesive could be peeled from the metal yielding an adhesive failure side (AFS) and a metal failure side (MFS). Both of these surfaces were studied by STEM, XPS, and AES with depth profiling. Figure 5 shows the STEM photomicrographs. The porous structure of the MFS is not as clear as for a freshly pretreated surface [1]. The porosity is faintly visible. The AFS looks as if the adhesive was pulled from the pores.

To reinforce this hypothesis, XPS was performed on both surfaces. Table V lists the elements detected, the binding energies and the atomic percentages. The AFS surface did not show epoxy, but rather titanium oxide with a high percentage of fluorine. The titanium peak on the MFS showed the presence of titanium metal and oxide. These XPS results showed that the failure was occurring within the CAA oxide at the base of the pores. However, the question of epoxy penetration was not answered. The oxygen and carbon peaks were curve fit. Table VI lists the curve fit data for oxygen. The oxygen peaks of the MFS and the AFS are similar. The primary peak was indicative of titanium oxide. The AFS showed a higher percentage of the higher binding energy component. This can be due to the epoxy, if the epoxy penetrated the pores. The AFS was then depth profiled with AES, monitoring the carbon, oxygen, fluorine and titanium signals. Figure 6 shows the profile. The carbon signal was present throughout the profile indicating that the epoxy had indeed penetrated the porous structure.

E. Wedge Testing

To accelerate the environmental effects on the wedge configuration, wedge samples were immersed in a variety of environments: 80° and 95°C water, 80°C acidic (pH = 2.0) buffer. Table VII lists results for the durable oxides produced by various pretreatments. Both CAA and SHA showed complete durability for two weeks; however, crack growth was observed for longer times in 95°C water. The TURCO surface, while remaining durable in 80°C water, showed crack propagation in 16 days in 95°C water. P/F, on the other hand, showed poor durability with cracks usually propagating to failure within 24 hours.

CAA, TURCO, and P/F pretreated samples were placed in 80°C acidic buffer at a pH of 2.0. Figure 7 shows the test results. All of the pretreatments showed crack propagation. The acidic buffer dissolved part of the titanium, thus the buffer was not a fair test of bond durability.

Alkoxide primers were used on the worst case, P/F pretreated surfaces, to enhance bond durability in water immersion environments. Figure 8 compares the P/F pretreated samples immersed in 80°C and 95°C water and P/F pretreated sample primed with LICA 38 and immersed in 80°C water. The LICA 38 primed samples showed a marked increase in durability. Figure 9 compares one coat and five coats of E-8385 and TNBT on P/F surface. Five coats of the primer on the P/F surface were more durable than one coat, consistent with results reported by Pike [2] for aluminum bonded with epoxy. Figure 10 compares five coats of E-8385 and TNBT. The aluminum alkoxide, E-8385, showed better durability than the titanate, TNBT. Rate of crack growth was determined from the slope of a line fit to the data. Figure 11 shows rate of crack growth versus time. At 95°C, an increase in rate of crack propagation follows an initial decrease in rate. This result implies the joint design dominates the initial crack growth. The environment then dominates causing an increase in the rate of crack propagation. Figure 12 shows the rate of crack growth versus G_1 in J/m^2.

Although the alkoxide primers show many-fold increases in the durability of the P/F pretreated surface, the improved durability is not equal to that of the more durable oxides previously listed in Table VII.

The locus of failure in the P/F, and P/F primed with E-8385 or TNBT was investigated using XPS. Table VIII lists the XPS results. The XPS spectra of the unprimed P/F metal failure (MFS) and adhesive failure (AFS) surfaces indicate the locus of failure to be at the epoxy/oxide interface - adhesive failure. No bromine found in the epoxy was detected on the MFS and no titanium was detected on the AFS. The spectra from the primed failure surfaces indicated the locus of failure occured between the primer and the epoxy and not between the primer and the oxide. The primer was on the MFS, but no bromine was detected. Bromine was observed on the AFS, but conclusive evidence of the presence of primer was not available.

IV. SUMMARY AND FUTURE WORK

Alkoxide primers on Ti-6-4 enhanced bond durability with the P/F pretreatment. The locus of failure was found to be at the primer/epoxy interphase rather than at the metal oxide interphase. More wedge tests are planned using alkoxide primers on more durable oxides such as CAA, SHA, and TURCO. The locus of failure in the wedge test will be compared to those of stress-durability tests now in progress. From the STEM, XPS, and AES results, FM-300 is believed to penetrate the porous structure of a CAA surface. Microtomy with STEM may also yield supporting evidence. Quality FTIR reflectance spectra can be obtained for thin films of PEHMA on polished Ti 6-4. The next step is to determine the orientation of these films using a method suggested by Debe [4]. Oxide thermal stability was the same at 450°C as 350°C, namely a broadening of the titanium oxide peak to the lower binding energy side with the TURCO and P/F pretreated surfaces. The effect this has on bond durability is still not known.

V. REFERENCES

1. J. A. Filbey and J. P. Wightman, ONR report, 1985.
2. R. A. Pike, Int. J. Adhesion and Adhesives, 5, 3, 1985.
3. The Sadtler Standard Spectra, Sadtler Research Laboratories, 1984.
4. M. K. Debe, Appl. Surface Sci., 14, 1, 1982-83.

APPENDIX I

Chromic Acid Anodization (CAA)

1. Gritblast with an Econoline gritblaster at approximately 100 psi and held approximately 5 cm from the coupon.
2. Wipe with methyl ethyl ketone (MEK).
3. Soak in sodium hydroxide solution (13g/250ml) at 70 C for 5 minutes.
4. Rinse three times in deionized water.
5. Pickling step: Immerse in pickle solution (15ml conc. HNO_3, 3ml 49%w/w HF, 82ml H_2O)

   at room temperature for 5 minutes.
6. Rinse three times in deionized water.
7. Anodize at room temperature for 20 minutes at 10 volts, 26.9amp/sq.m (2.5amp/sq.ft.) in a chromic acid solution (50g. CrO_3/1000ml) with a Ti 6-4 coupon as the cathode. 49% w/w HF is added to attain the desired current density.
8. Rinse three times in deionized water.
9. Blow dry with prepurified N_2 gas until visibly dry.

Phosphate/Fluoride Acidic Etch (P/F)

1. Gritblast as above.
2. Wipe with MEK.
3. Soak to Sprex AN-9 solution (30g/1000ml) at 80°C for 15 minutes.
4. Rinse three times in deionized water.
5. Immerse in pickle solution (31ml 49%w/w HF, 213ml conc. HNO_3/1000ml) at room temperature for 2 minutes.

9\. Rinse three times in deionized water.

7\. Soak in phosphate/fluoride solution (50.5g Na_3PO_4, 20.5g KF, 29.1ml 49%w/w HF/1000ml) at room temperature for 2 minutes.

8. Rinse three times in deionized water.
9. Soak in deionized water at 65°C for 15 minutes.
10. Blow dry in prepurified N_2 until visibly dry.

TURCO Basic Etch

1. Gritblast as above.
2. Wipe with MEX.
3. Soak in TURCO 5578 solution (37.6g/1000ml) at 70-80°C for 5 minutes.
4. Rinse three times in deionized water.
5. Soak in TURCO 5578 solution (360g/1000ml) at 80-100°C for 10 minutes.
6. Rinse three times in deionized water.
7. Soak in deionized water at 60-70°C for 2 minutes.
8. Blow dry in prepurified N_2 until visibly dry.

Sodium Hydroxide Procedure

1. Rinse with MeOH, acetone, air dry
2. Immerse in Super Terj (30g/l) at 80°C for 15 minutes
3. Soak in water at 50 - 60°C for 15 minuites
4. Anodize in NaOH solution (5.0M)
   - Stainless steel mesh cathod
   - 20 C
   - 10 v
   - 30 minutes
   - Current: for 8 sq. in. immersed, the current was 1c amp initially and decreased to a constant 0.4 amp by 11 minutes.
5. Rinse in running tap water for 20 minutes
6. Dry in oven at 60°C for 10 minutes.

TABLE I

XPS RESULTS OF HEATING STUDY OF Ti 6-4

Treatment	Element	B.E.	A.P.
CAA before heating	Carbon	285.0	25.
	Oxygen	530.4	50.
	Titanium	459.0	17.
	Fluorine	685.0	5.2
	Aluminum	74.5	3.2
CAA after heating	Carbon	285.0	26.
	Oxygen	530.8	55.
	Titanium	459.3	13.
	Fluorine	685.4	3.3
	Aluminum	74.8	2.4
SHA before heating	Carbon	285.0	18.
	Oxygen	530.9	55.
	Titanium	459.3	12.
	Calcium	347.9	7.7
	Phosphorus	134.4	3.1
	Silicon	102.2	1.9
	Aluminum	74.5	1.8
SHA after heating	Carbon	285.0	19.
	Oxygen	531.0	51.
	Titanium	459.3	14.
	Calcium	348.0	8.3
	Phosphorus	133.9	3.5
	Silicon	102.8	3.0
	Aluminum	75.1	2.2

TABLE I, continued

Treatment	Element	B.E.	A.F.
TURCO before heating	Carbon	285.0	30.
	Oxygen	530.2	60.
	Titanium	458.7	6.4
	Iron	711.1	2.6
	Aluminum	73.5	1.7
TURCO after heating	Carbon	285.0	28.
	Oxygen	530.5	58.
	Titanium	458.9	6.5
	Iron	709.6	6.3
	Aluminum	74.4	1.7
P/F before heating	Carbon	285.0	24.
	Oxygen	530.4	55.
	Titanium	459.0	16.
	Phosphorus	133.6	2.4
	Aluminum	74.0	2.0
P/F after heating	Carbon	285.0	19.
	Oxygen	530.8	58.
	Titanium	459.2	17.
	Phosphorvus	133.9	3.1
	Aluminum	74.6	3.5

TABLE II

XPS RESULTS FOR INORGANIC PRIMERS

Treatment	Element	B.E.	A.P.
1% E-8385 on ferrotype	Carbon	285.0	18.
	Oxygen	531.7	69.
	Chromium	578.1	13.
	Aluminum	74.9	8.2
1% TNBT on ferrotype	Carbon	285.0	26.
	Oxygen	530.5	56.
	Chromium	577.3	4.3
	Titanium	459.0	13.

TABLE III

PEAK ASSIGNMENTS FOR FTIR SPECTRA OF PEHMA FILMS

25 nm Film	73 nm Film	Assignment
2964.8 cm^{-1}	2964.8 cm^{-1}	C-H asym. str., $-CH_3$
2935.9	2935.9	C-h asym. str., $-CH_2$, $-CH_2$-alkanes
2874.1	2872.0	C-H sym. str., $-CH_3$
1734.1	1734.1	C=O str.
1464.1	1466.0	$-CH_2-$ scissoring, alkanes CH_3 asym. bending def.
1394.6	1390.8	C-H sym. bending def., Ch_3
1267.3	1267.3	C-O-C asym. str., sat. aliphatic esters
1244.2	1244.2	
1182.4	1184.4	C-O-C sym. str., sat. aliphatic esters
1136.1	1155.4	
1078.0		C-C str. and CH_3 rocking
858.9	873.8	Ti-O

TABLE IV

PEAK ASSIGNMENTS FOR FTIR SPECTRA OF PEHMA IN SOLUTION

Peak	Assignment
2961.8 cm^{-1}	C-H asym. str., $-CH_3$
2932.5	C-H asym. str., $-CH_2$-alkanes
2873.0	C-H sym. str., $-CH_3$
2861.0	C-H sym. str., $-CH_2$-alkanes
1728.3	C=O
1464.1	$-CH_2$-scissoring, alkanes $-CH_3$ asym. bending def.
1267.3	C-O-C asym. str., sat. aliphatic esters
1240.5	
1177.6	C-O-C sym. str., sat. aliphatic esters
1154.2	

TABLE V

XPS RESULTS FROM MFS AND AFS SURFACES PRODUCED BY PEELING CURED FM-300 FROM CAA TI-6-4 FOIL

Surface	Element	B.E.	A.P.
MFS	Carbon	285.0	21.
	Oxygen	530.4	48.
	Titanium	459.1	20.
	Fluorine	685.4	11.
AFS	Carbon	285.0	22.
	Oxygen	530.6	26.
	Titanium	459.4	7.2
	Fluorine	685.5	43.
	Nitrogen	402.2	1.3

TABLE VI

XPS CURVE FIT RESULTS OF OXYGEN 1S PHOTOPEAK FROM MFS AND AFS SURFACES PRODUCED BY PEELING CURED FM-300 FROM CAA TI 6-4 FOIL

Surface	B.E.	A.P.
MFS from CAA/ FM-300	530.4	35.
	531.6	9.4
	532.5	3.7
AFS from CAA/ FM-300	530.5	18.
	531.6	4.6
	532.4	3.6

TABLE VII

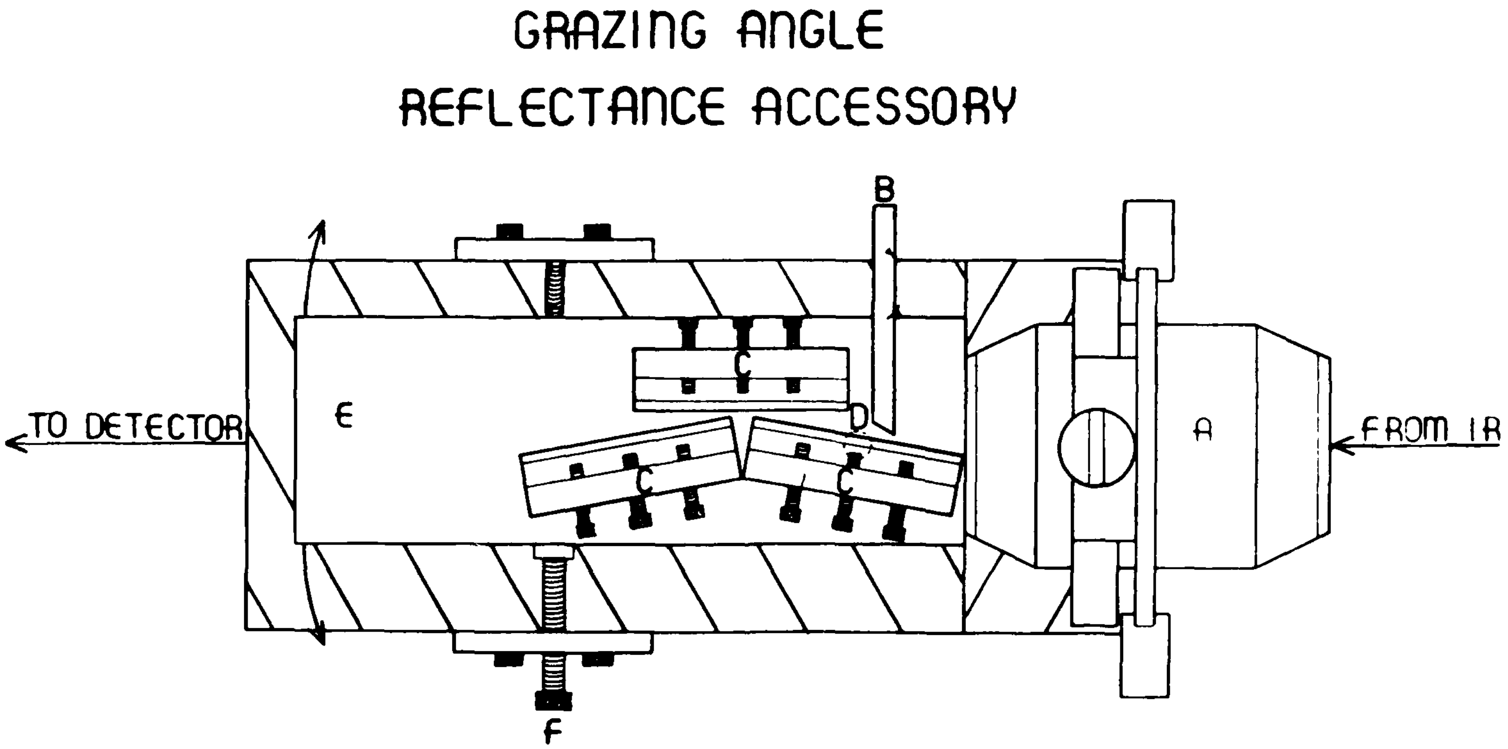
WEDGE TEST RESULTS OF THE "DURABLE OXIDES"

Pretreatment	Time (days)	Environment	Crack Length (cm)
CAA	49	80°C H_2O	0
CAA	14	95°C H_2O	0
CAA	41	95°C H_2O	0.9
SHA	16	95°C H_2O	0
SHA	25	95°C H_2O	0.3
TURCO	26	80°C H_2O	0
TURCO	16	95°C H_2O	0.1

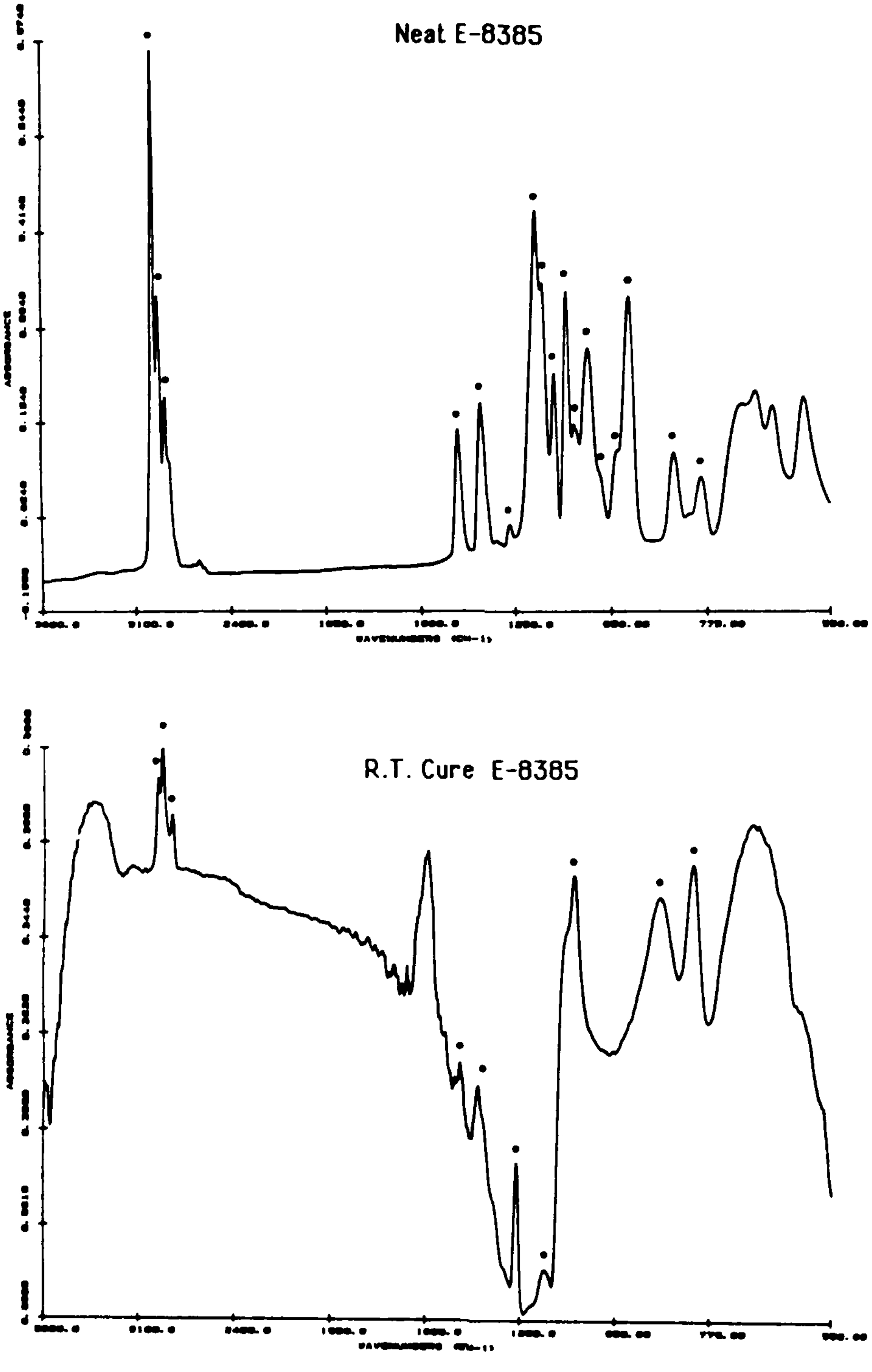
TABLE VIII

XPS RESULTS FROM WEDGE TEST
LOCUS OF FAILURE

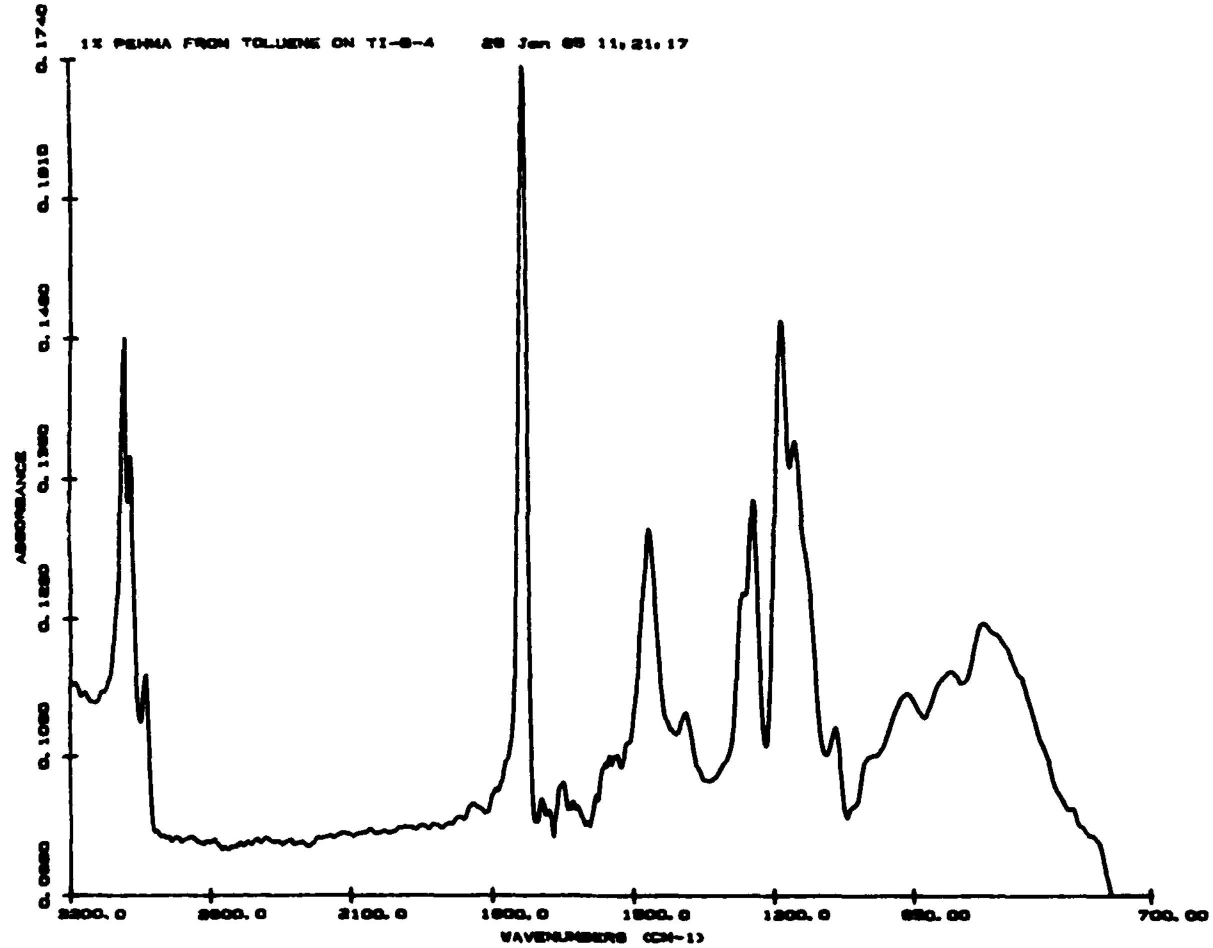
Treatment	Element	B.E.	A.P
MFS from P/F	Carbon	285.0	45.
	Oxygen	532.5,531.9	45.
	Titanium	459.0	4.7
	Silicon	103.0	4.8
	Aluminum	trace	trace
AFS from P/F	Carbon	285.0	63.
	Oxygen	532.9	32.
	Bromine	183.8	0.4
	Silicon	102.5	0.9
	Nitrogen	400.1	2.2
	Aluminum	70.6	1.9
MFS from E-8385 on P/F	Carbon	285.0	20.
	Oxygen	532.2,530.6	64.
	Titanium	458.8	2.5
	Silicon	102.7	3.9
	Nitrogen	400.1	2.3
	Aluminum	74.4	7.8
AFS from E-8385 on P/F	Carbon	285.0	35.
	Oxygen	532.6	54.
	Bromine	70.7	0.2
	Silicon	103.2	3.7
	Nitrogen	400.2	2.5
	Aluminum	74.7	4.6
MFS from TNBT on P/F	Carbon	285.0	32.
	Oxygen	532.2,530.6	55.
	Titanium	459.0	5.7
	Silicon	102.8	5.4
	Calcium	348.0	1.2
	Aluminum	trace	
AFS from TNBT on P/F	Carbon	285.0	61.
	Oxygen	533.1	32.
	Bromine	183.9	0.6
	Silicon	trace	
	Nitrogen	400.0	3.6
	Aluminum	70.8	3.1



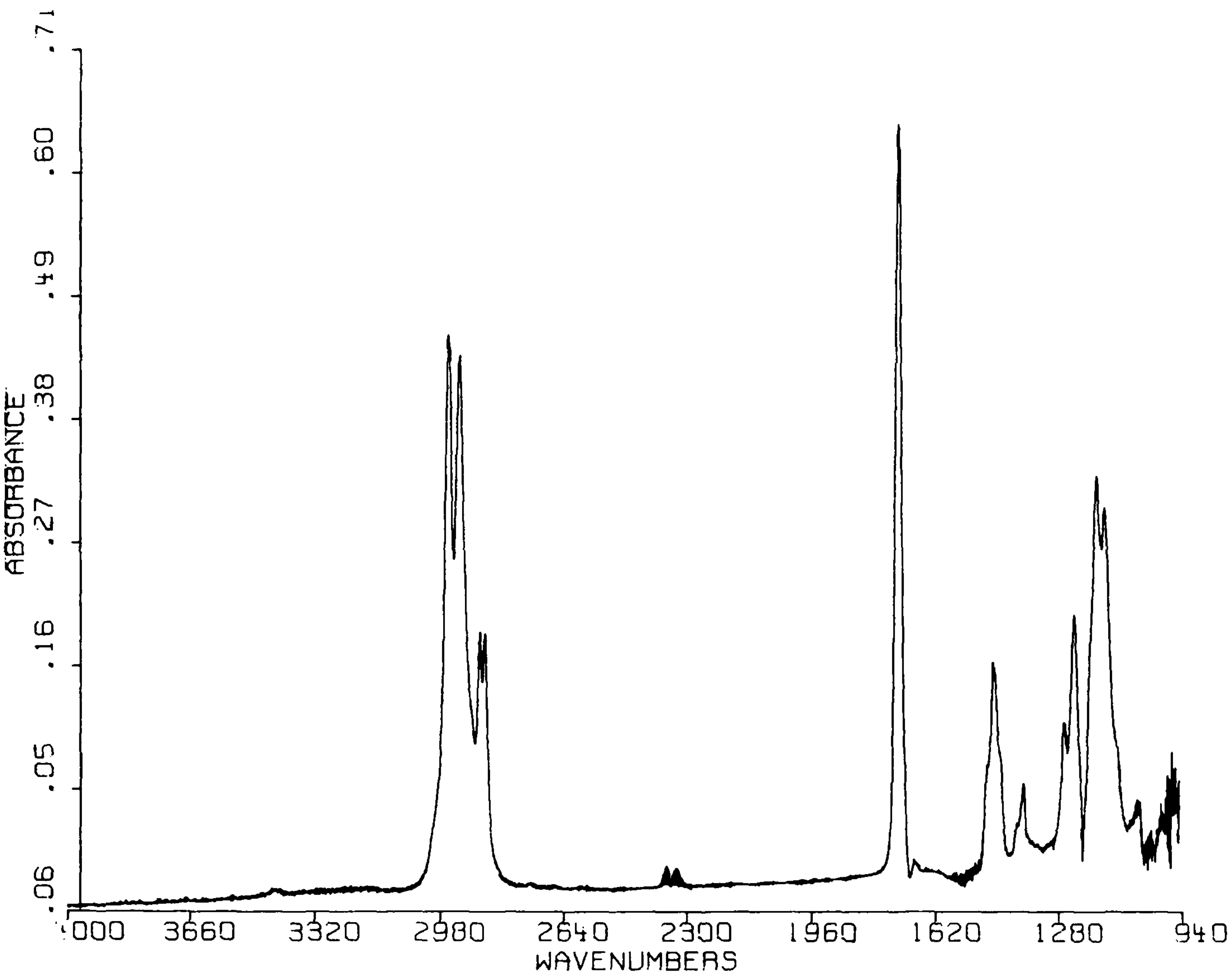
1. Grazing angle specular reflectance attachment for the Nicolet 5DX FTIR



2. FTIR spectra of E-8385 aluminum alkoxide

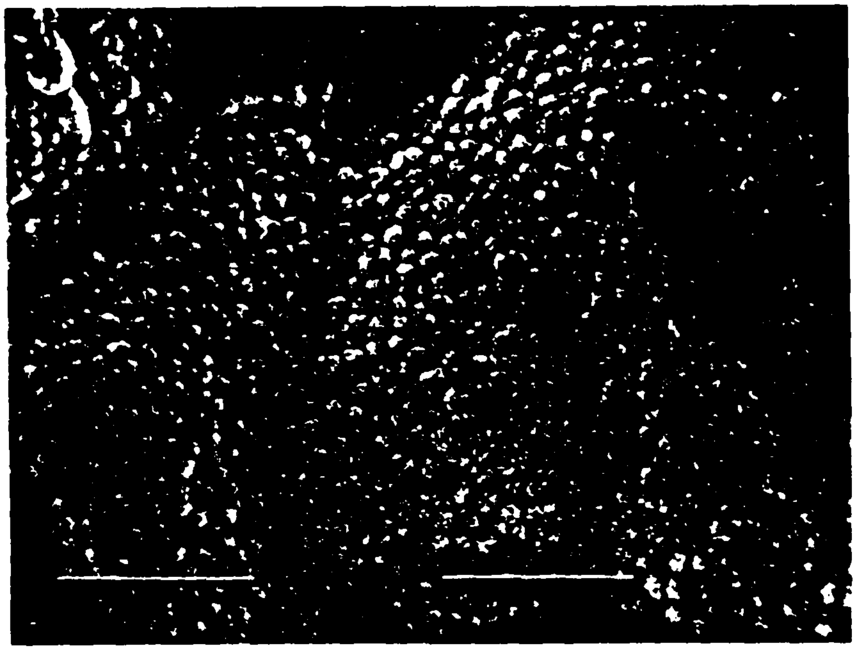


3. FTIR spectra of PEHMA films on ferrotype plates

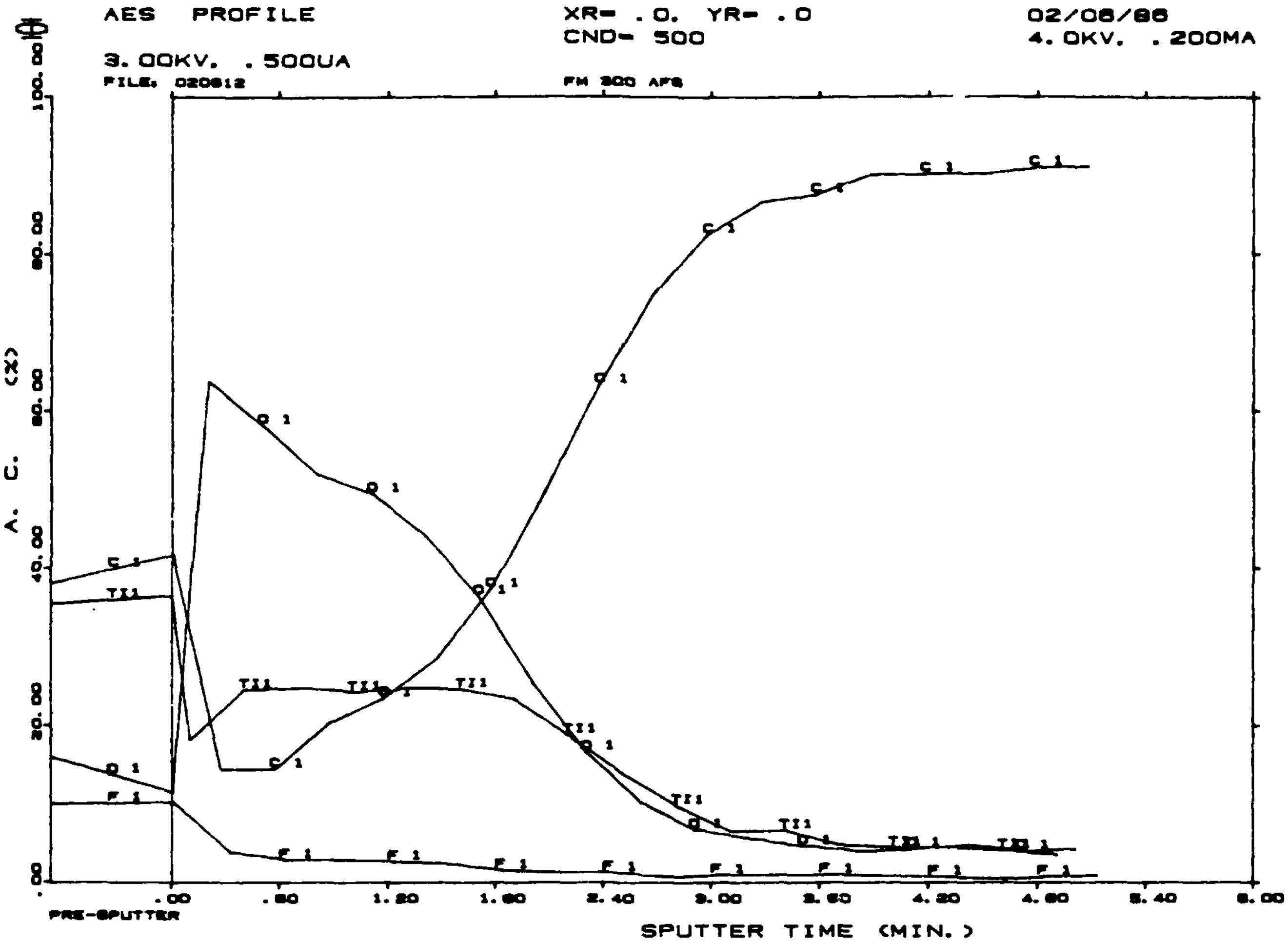


4. FTIR spectra of PEHMA solution

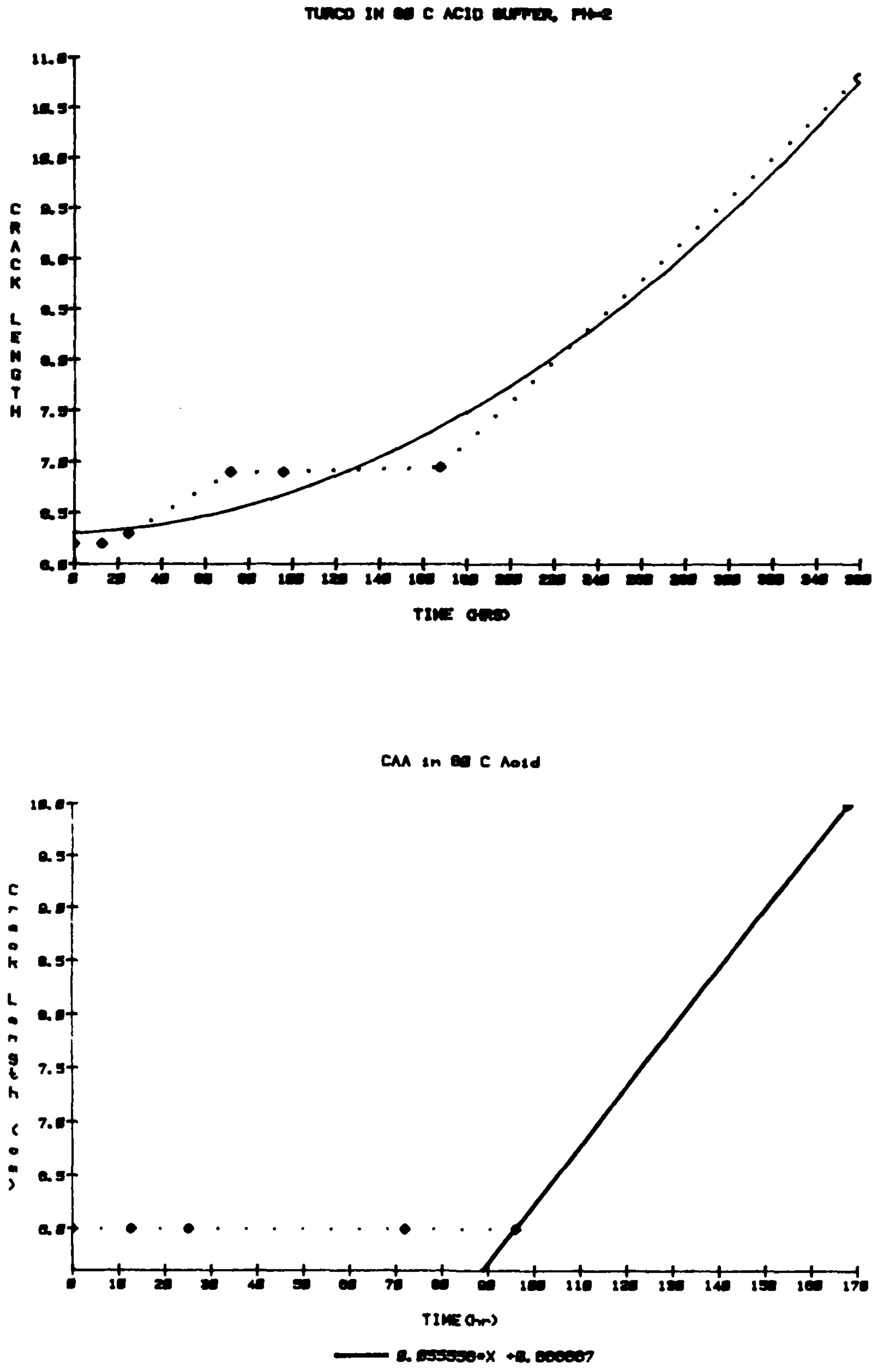
5a. STEM photomicrograph at 50,000 x of MFS of CAA Ti-6-4 foil peeled from FM-300



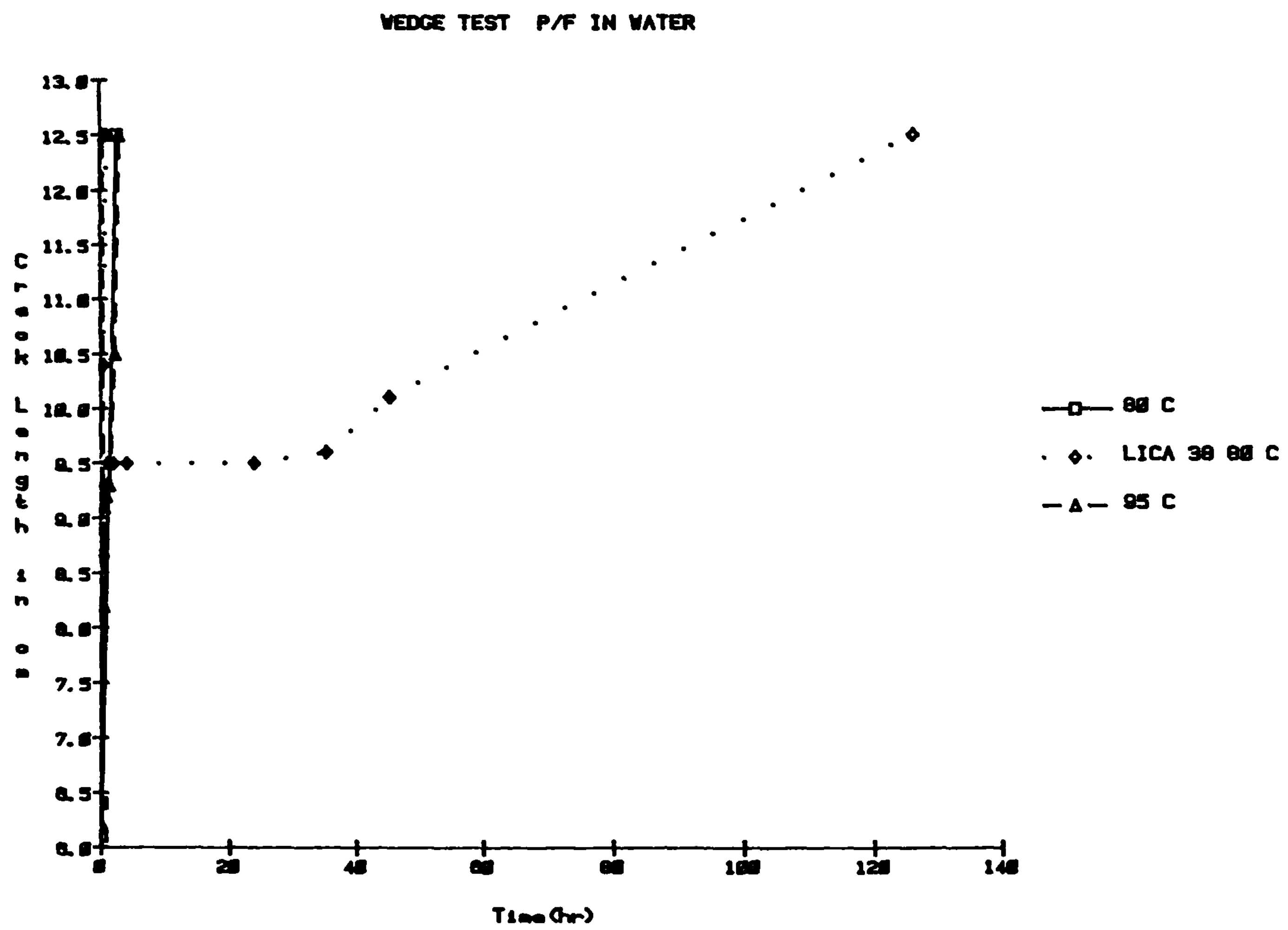
5b. STEM photomicrograph at 50,000 x of AFS of FM-300 peeled from CAA Ti-6-4 foil



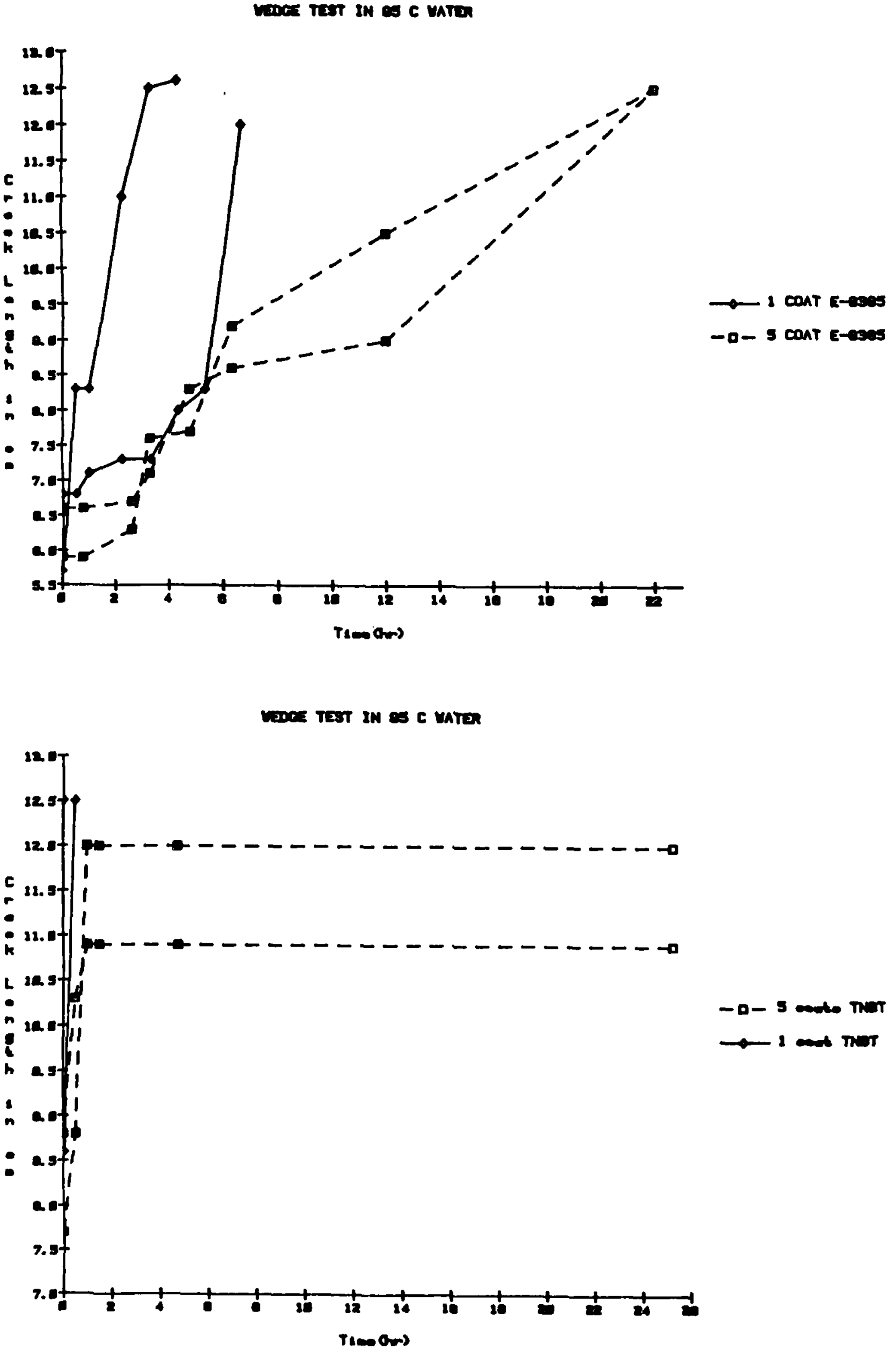
6. AES depth profile of AFS of FM-300 peeled from CAA Ti-6-4



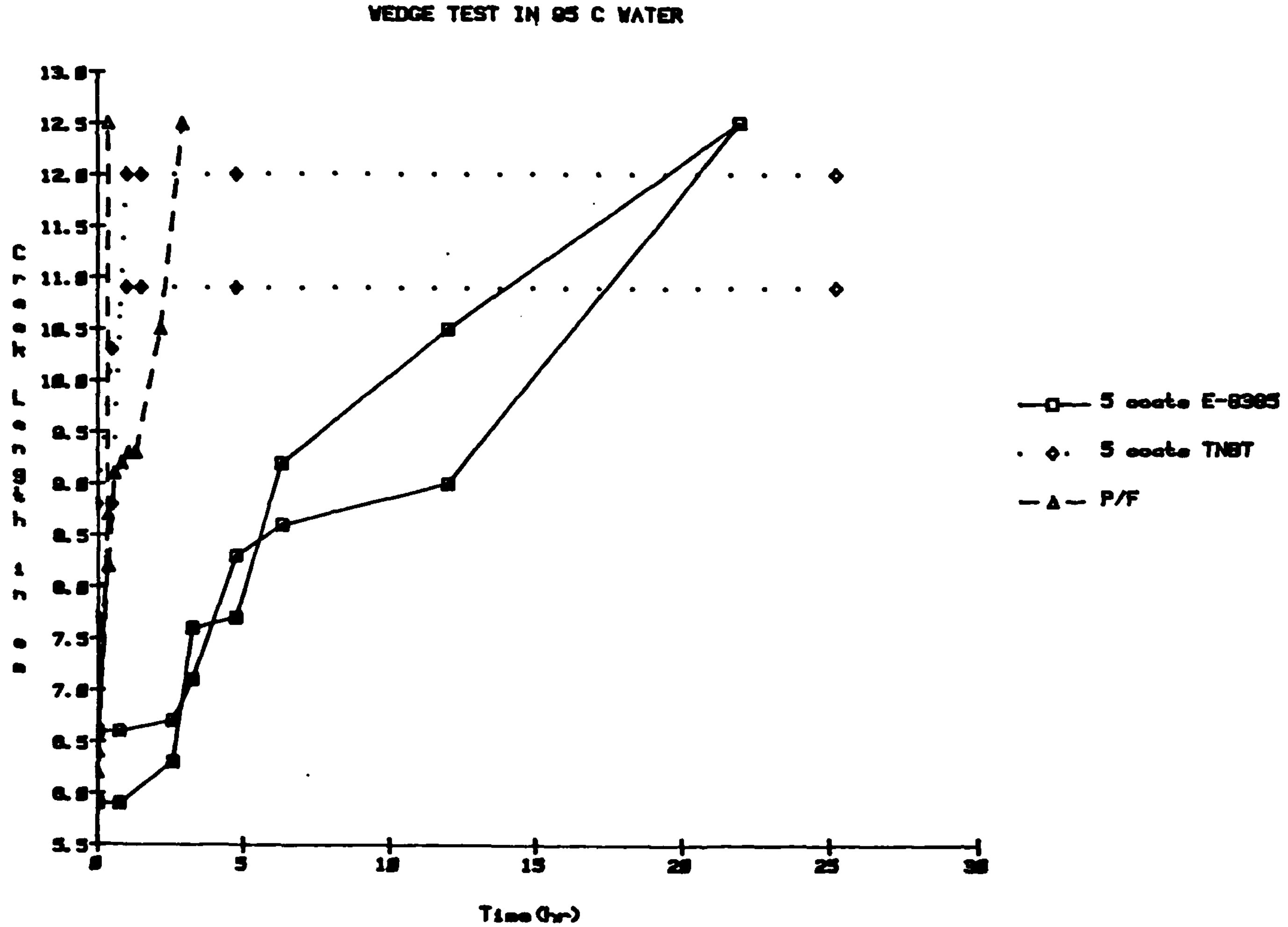
7. Crack length vs. Time of wedge samples placed in acidic buffer at 80° C



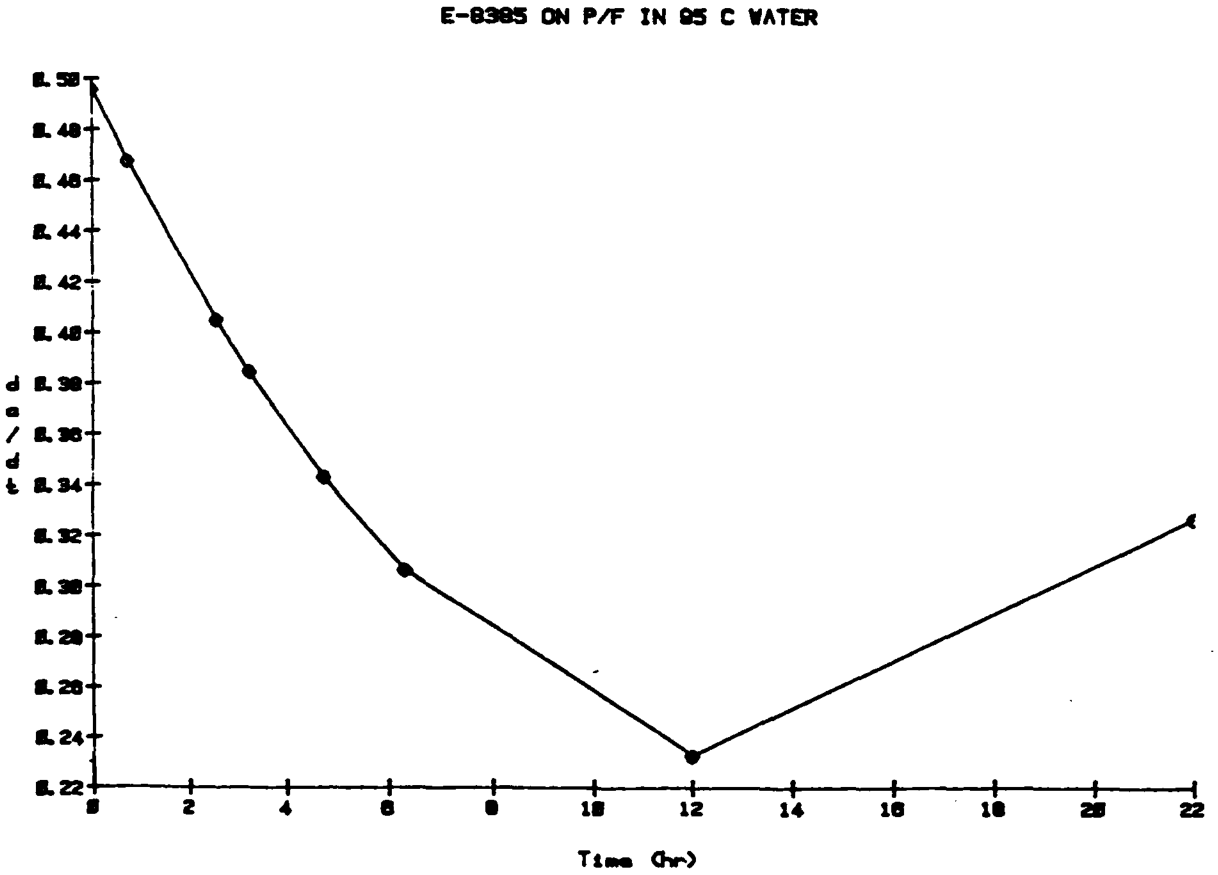
8. Crack length vs Time of P/F wedge samples with and without alkoxide primer



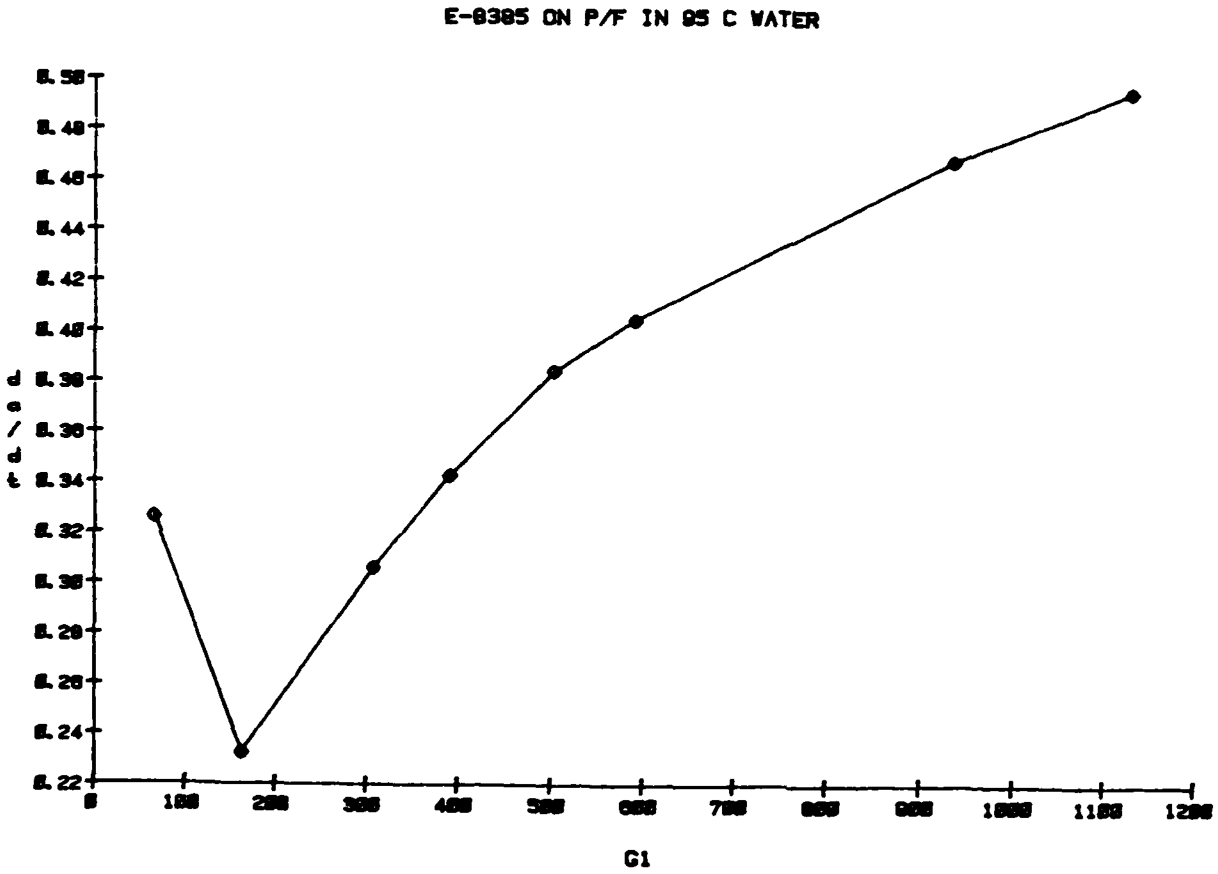
9. Crack length vs Time of P/F wedge samples with one and five coats of E-8385 and TNBT



10. Crack length vs Time of P/F wedge samples with five coats of E-8385 and TNBT



11. Rate of crack growth vs Time of P/F wedge samples with 5 coats of E-8385



12. Rate of crack growth vs. G_1 of P/F wedge sample with 5 coats of E-8385.

END

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