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ROCKWELL INTERNATIONAL THOUSAND OAKS CA SCIENCE CENTER
TREATMENT OF AM 355 STEEL FOR ADHESIVE BONDING. (U)

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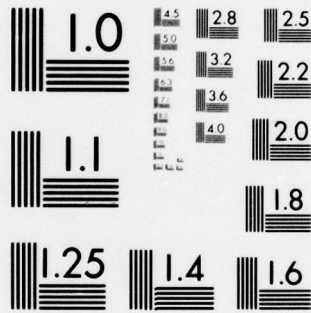
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TREATMENT OF AM 355 STEEL FOR ADHESIVE BONDING

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compared to the less than 1 hour time to failure obtained using the present method. It was found that increased bond durability, measured by the wedge test, was directly related to the increased chromium content of the surface oxide layer produced using these and other treatments.

Experiments indicate that AM355 is essentially impermeable to hydrogen, i.e. the diffusion coefficient was unmeasurable using an electrochemical technique sensitive to 0.1 ppm of mobile hydrogen.

Although both methods mentioned above are commercially applicable, the HNO₃ anodize appears the best because of the absence of carcinogenic dichromates, the lower production cost and slightly better bond results.



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I. INTRODUCTION

A surface treatment for AM355 stainless steel is required which will give the resulting adhesive bond optimum strength, as well as environmental durability. This treatment should not degrade the strength of the metal, for example, through hydrogen embrittlement, and should yield a surface which is stable enough that a 24 hour delay between the treatment and bonding has no effect. The treatment should also be applicable to commercial use and give consistently strong, durable bonds.

Prior to the start of this project, the manufacturer of the helicopter, Hughes Helicopter, investigated a number of preparation methods.⁽¹⁾ The method which showed most promise though, an electrolytic, acid-chromate treatment,⁽²⁾ was feared to subject the specimen to hydrogen, possibly resulting in embrittlement of the metal.

A patent for a treatment developed at Boeing⁽³⁾ was one of the few sources of information on stainless steel treatments for adhesive bonding where environmental durability was stressed. In it were summarized data from bonds prepared using six state-of-the-art methods. Snogren⁽⁴⁾ has compiled a number of surface treatments for stainless steel. Unfortunately, the tests administered to the bonded samples were, with exception of lap shear, not the same tests used in this study. In general, methods in the literature to date consist of some or all of the following steps: 1. Solvent cleaning, 2. Abrading, 3. Alkaline clean, and 4. Acid treatment. Electrochemical



methods, more explicitly, anodizing techniques, have been used quite successfully^(3,4) in acid solutions. Acid treatments where hydrogen may be generated may or may not be a problem. Austenitic stainless steel typically is essentially impervious to hydrogen, martensitic steel on the other hand, is susceptible to hydrogen diffusion. Steps would, therefore, have to be taken to avoid the situation or drive off any absorbed hydrogen. AM355 is a mix of austenitic and martensitic structures, leading to questions about its permeability to hydrogen.

"Dry" surface preparation techniques, such as flame treatment,⁽⁴⁾ ion beam texturing,⁽⁵⁾ and ultraviolet irradiation,^(6,7) have been investigated although not in the context of adhesive bonding. Flame treating and irradiating a metal surface with U.V. can not only remove hydrocarbon layers, but also, in some cases, promote oxide growth. Ion beam texturing consists of sputtering a low sputter yield material into the metal surface while ion milling. The resultant surface appears textured, i.e., consists of ridges, cones or rods depending on the materials.

The purpose of this project is to develop a method of treating AM355 stainless steel such that optimum adhesive bond strength and durability are obtained. The major properties to be addressed are:

1. Effect of the treatment on adherend properties, i.e., if hydrogen is formed and embrittles the metal.
2. Effect of solution aging, contamination and restoration on the strength and durability of the adhesive bond.



3. Durability of the bond, tested using the wedge test and stress durability test (ASTM D2919).
4. The bond must exhibit 100% cohesive failure during a T-peel test.
5. The treatment must produce a surface which remains bondable for at least 24 hours in normal bond shop condition.
6. The process developed must be commercially feasible.

II. EXPERIMENTAL RESULTS

1. Surface Treatments

Of the various surface treatments tried, some were developed outside the Science Center but were included for the sake of comparison. The following are a listing of these. In all cases, samples were first degreased by immersion in methyl ethyl ketone (MEK) and air dried. Unless otherwise specified, they were then subjected to a given treatment followed by a deionized water rinse and blow drying using nitrogen.

Procedure 1. Electrolytic Coloring Process (U.S. Patent 3,804,730)

The samples were anodized in a 402g/l $K_2Cr_2O_7 \cdot 2H_2O$ - 475g/l H_2SO_4 solution at 65 - 70°C. The potential of the AM355 sample was monitored with respect to a saturated calomel electrode (SCE) and the current density between



the sample and the Pb cathode adjusted between 0.025 - 0.25 A/dm². After an 8 mV rise in potential the process is complete.

Procedure 2. Sulfuric Acid/Dichromate Anodize

Samples were anodized in 26 volume percent (v/o) H₂SO₄, 40 weight percent (w/o) Na₂Cr₂O₇·2H₂O for 20 min, 75°C using a Pb cathode and a potential of 2 volts.

Procedure 3. Boeing Phosphoric Acid Anodize

Anodize in 9 v/o H₃PO₄, Pb cathode, room temperature for 10 minutes and 9.6 volts.

Procedure 4. H₂SO₄ Anodize (U.S. Patent 4,064,020)

Anodize at 2.3 v in 500g/l H₂SO₄ for 10 minutes at room temperature using a Pb cathode.

Procedure 5. H₂SO₄ Anodize - CrO₃ Passivate (U.S. Patent 4,064,020)

Anodize as in Procedure 4 followed by passivation in 5 w/o CrO₃ at 38°C for 20 minutes.

Procedure 6. Alkaline Cleaner

Immerse in 20 w/o KMnO₄, 5 w/o NaOH, 80 - 90°C for 20 minutes (Procedure 6a) or 40 minutes (6b).



The following procedures were developed at the Science Center.

Procedure 7. Degrease Only

Samples were degreased in MEK and air dried.

Procedure 8. H₂O

Samples were immersed in 75 - 80°C deionized water for 60 minutes.

Procedure 9. HNO₃/dichromate

Samples were immersed in 50 v/o HNO₃, X w/o Na₂Cr₂O₇·2H₂O, 75 - 80°C for 1 hour. X = 0, 1, 2, 3, 5, 10 corresponding to Procedure 9a - 9f, respectively.

Procedure 10. HNO₃ Anodize

Samples were anodized in 50 v/o HNO₃ for 60 min in the following manners:

- 10a. Room temperature, potentiostat at +0.9 V (vs SCE), stainless steel (304) tank cathode (resultant current ~ 0.6 $\mu\text{A}/\text{cm}^2$).
- 10b. Same as 10a but +1.10 V, (resultant current ~ 50 $\mu\text{A}/\text{cm}^2$).
- 10c-f. Room temperature, stainless steel tank cathode, galvanostat at:
1 mA/cm² (10c.), 1.5 mA/cm² (10d.), 3 mA/cm² (10e.),
6 mA/cm² (10f.).
- 10g. 75 - 80°C, stainless tank cathode, galvanostat at 1 mA/cm².



10h. 75 - 80°C, stainless (304) cathode, potentiostat at +1.142 V
(vs SCE), resultant current density ~ 2 mA/cm².

10i. 75 - 80°C, stainless tank cathode, galvanostat at 3 mA/cm².

Procedure 11. H₂SO₄ Etch

Samples were etched in 50 v/o H₂SO₄ , 75 - 80°C for 2 (11a.), 5
(11b.), or 10 min (11c.).

Procedure 12. H₂SO₄ /Dichromate

Samples were immersed in 50 v/o H₂SO₄ , X w/o Na₂Cr₂O₇·2H₂O,
75 - 80°C for 60 min. X = 1, 2, 5, 10 corresponding to 12 a - d.

Samples were immersed in 30 v/o H₂SO₄ , 40 w/o Na₂Cr₂O₇·2H₂O,
75 - 80°C for 60 min (12e.) or 50° for 60 min (12f.). Method was varied over
a wide range of parameters which will be discussed in a separate section.
(Preparation of 40 w/o dichromate, 30 v/o H₂SO₄: weigh out dichromate, add
H₂SO₄, mix well (it won't dissolve), cautiously add H₂O.)

Procedure 13. H₂SO₄ - Passivate

Samples were etched in 50 v/o H₂SO₄ , 75 - 80°C for 5 min, rinsed
with distilled water and passivated in either 50 v/o HNO₃ (13a.) or 50 v/o
HNO₃, 10 w/o Na₂Cr₂O₇·2H₂O (13b.) for 1 hr at 75 - 80°C.



Procedure 14. MICRO* - HNO₃

Samples were immersed in MICRO*, 50°C for 1 hr, rinsed and immersed in 50 v/o HNO₃, 75 - 80°C for 1 hr.

Procedure 16. NaOH

Samples were immersed in NaOH (450g NaOH, 800 ml H₂O), 50°C for 30 - 120 min.

Procedure 17. NaOH Anodize

Samples were anodized in NaOH (40g/l), room temperature, stainless tank cathode and current density of 0.8 mA/cm² (17a.), 1.6 mA/cm² (17b.), 3.1 mA/cm² (17c.) or 7.8 mA/cm² (17d.).

Procedure 18. Flame

Samples were passed through a CH₄·O₂ flame ~ 2.5 cm. long at various rates just outside the inner blue cone.

18a. 1 sec/in (0.4 sec/cm)

18b. 5 sec/in (2 sec/cm)

18c. 10 sec/in (4 sec/cm)

18d. 50 sec/in (20 sec/cm)

*International Products Corp., P.O. Box 118, Trenton, New Jersey 08601.



Keeping the rate constant (2 sec/cm) but varying the distance from the flame, and estimating metal temperature using welding pencils.

18e. 370 - 430°C

18f. 430 - 480°C

18g. 480 - 540°C

Procedure 19. Ultraviolet (UV) Irradiation

One set of samples (19a.) were exposed to UV for 34 hours using an Osram high pressure Xenon lamp (X80, 1000 V/HSC). This lamp has 30% of its power at 300 nm, 1% at 280 nm and $< 1000 \rightarrow \sim 100 \text{ mW/cm}^2$. This corresponds to 10 - 100 mW/cm^2 of 280 nm radiation.

Another set of samples (19b.) were initially pretreated by immersion in MICRO*, 50°C for 2 hours, rinsed, dried and irradiated as in 19a.

2. Bond Strength

Samples were brush primed using 10% solid EA9210 primer (Hysol). Care was taken so the primer coat was not too thick. No extreme precautions were taken to ensure reproducible primer thickness. The primed samples were air dried 30 min then baked at 150°C for 30 min. The samples were then bonded using 0.060 lb/ft^2 (0.293 kg/m^2) EA9628H (Hysol) adhesive. The adhesive was cured for 1 hour at 121°C (250°F) following an approximately 20 min warm-up. Pressure was kept at 50 psi (3.5 kg/cm^2). Most samples were 0.040 in. x 1 in. x 5 in. (0.1 x 2.5 x 12.7 cm) AM355. Some wedge test samples and some of the stress durability test samples run at 50°C were 6 in. (15.2 cm) in length.



Wedge tests were done at 50°C, 99 - 100% relative humidity. The wedge was 0.318 cm x 2.54 cm x 2.54 cm (0.125 in. x 1 in. x 1 in.) aluminum 2024T3. Stress durability tests were done at 50°C or 60°C, 100% relative humidity stressed with 2000 psi (13.8 mPa).

Table I is a compilation of the bond strengths and durability obtained using the surface treatments listed in the preceding section. It was found that lap shear values could be quite good while bond durability, measured by the wedge and stress durability tests, could be poor. Wedge tests were, therefore, used as a more general indication of the initial success of a treatment. The treatments which yielded a crack growth of < 0.1 in./24 hr (0.25 cm/24 hr) were, 2. H₂SO₄/dichromate anodize, 9f. HNO₃/dichromate, 10. HNO₃ anodize, 12e. H₂SO₄/dichromate, 13. H₂SO₄ etch - HNO₃ (or HNO₃/dichromate) and 14. NaOH. The latter five of these were developed at the Science Center. Stress durability tests (ASTM D-2919) at 50°C and 60°C were run on samples given these treatments. Results for these tests given for treatments 2, 3, and 6 at 60°C are taken from the references given in parenthesis. Since the same adhesive, primer and metal were used, values should be comparable. The stress durability test indicates that the HNO₃ anodize, H₂SO₄ - HNO₃/dichromate and the H₂SO₄/dichromate treatments yield the most durable bonds.

3. Surface Properties

In order to possibly gain an understanding of the nature of the oxide layer which is conducive to forming strong durable bonds and investigate tools that may be used for nondestructive surface inspection, ellipsometry, surface



TABLE I
BOND STRENGTH
(Sheet 1 of 3)

Procedure	Lap Shear psi/% IF* (mPa)	Wedge Test in./24 hr. (cm/24 hr)	Stress Durability	
			hr	
			50°C	60°C
1. Electrolytic Coloring	5500/40 (38)			
2. H ₂ SO ₄ /dichromate anodize	6300/20 (43)	0.07 (0.18)	134, 324, 1070 [†]	347, 470, 347 ⁽¹⁾
3. H ₃ PO ₄ anodize	5400/25 (37)		68, 92 ⁽¹⁾	
4. H ₂ SO ₄ anodize	5700/10 (39)	0.2 (0.51)		
5. H ₂ SO ₄ anodize - CrO ₃	5400/15 (37)	0.3 (0.76)		
6a. KMnO ₄ /NaOH 20 min	6000/55 (41)	1.0 (2.5)	20, 21 ⁽¹⁾	
b. KMnO ₄ /NaOH 40 min	5400/30 (37)	1.4 (3.6)	138, 115, 103, 159 ⁽¹⁾	
7. Degrease Only	5000/30 (34)	2.7 (6.9)		
8. H ₂ O		1.0 (2.5)		
9a. 50 v/o HNO ₃		0.35 (0.89)		
b. 50 v/o HNO ₃ /1 w/o dichromate		0.40 (1.0)		
c. 50 v/o HNO ₃ /2 w/o dichromate		0.20 (0.51)		
d. 50 v/o HNO ₃ /3 w/o dichromate	5200/20 (36)			
e. 50 v/o HNO ₃ /5 w/o dichromate		0.20 (0.51)		
f. 50 v/o HNO ₃ /10 w/o dichromate		0.10 (0.25)	237, 419, 714	
10a. HNO ₃ anodize Room Temp. 0.6 μA/cm ²		1.8 (4.6)		
b. HNO ₃ anodize Room Temp. 50 μA/cm ²		0.7 (1.8)		
c. HNO ₃ anodize Room Temp. 1 mA/cm ²	5900/25 (41)	0.15 (0.38)		194, 226, 318
d. HNO ₃ anodize Room Temp. 1.5 mA/cm ²		0.3 (0.76)		
e. HNO ₃ anodize Room Temp. 3 mA/cm ²	5900/20 (41)	0.06 (0.15)		318, 547, 705
f. HNO ₃ anodize Room Temp. 6 mA/cm ²		0.04 (0.10)		
g. HNO ₃ anodize 75 - 80°C 1 mA/cm ²	5900/40 (41)		276, 329, 470	

*Primer-adhesive interfacial failure

†Test temperature changed to 60° during course of test.



TABLE I
BOND STRENGTH
(Sheet 2 of 3)

Procedure	Lap Shear psi/% IF (mPa)	Wedge Test in./24 hr, (cm/24 hr)	Stress Durability hr	
			50°C	60°C
10h. HNO ₃ anodize 75 - 80°C 2 mA/cm ² i. HNO ₃ anodize 75 - 80°C 3 mA/cm ²	6500/20 (45)	0.05 (0.13)	615 [†] , 728 [†]	507, 581, 636
11a. H ₂ SO ₄ etch 2 min b. H ₂ SO ₄ etch 5 min c. H ₂ SO ₄ etch 10 min		1.0 (2.5) 0.9 (2.3) 1.0 (2.5)		
12a. 50 v/o H ₂ SO ₄ /1 w/o dichromate b. 50 v/o H ₂ SO ₄ /2 w/o dichromate c. 50 v/o H ₂ SO ₄ /5 w/o dichromate d. 50 v/o H ₂ SO ₄ /10 w/o dichromate e. 30 v/o H ₂ SO ₄ /40 w/o dichromate f. 30 v/o H ₂ SO ₄ /40 w/o dichromate	5500/* (38) 5200/* (36)	1.7 (4.3) 1.5 (3.8) 1.5 (3.8) 1.4 (3.6) 0.06 (0.15) 0.1 (0.25)	509, 782, 1062 424, 864, 865	368, 386, 469 490, 783 73, 75, 129
13a. H ₂ SO ₄ - HNO ₃ b. H ₂ SO ₄ - HNO ₃ /dichromate		0.1 (0.25)		
14a. MICRO*, 10 v/o b. MICRO*	5600/55 (39) 5800/60 (40)	1.1 (2.8) 0.3 (2.0)		
15. MICRO* - HNO ₃		0.2 (0.51)		
16. NaOH		0.1 (0.25)	58, 74, 100	
17a. NaOH anodize 0.8 mA/cm ² b. NaOH anodize 1.6 mA/cm ² c. NaOH anodize 3.1 mA/cm ² d. NaOH anodize 7.8 mA/cm ²		0.6 (1.5) 0.4 (1.0) 0.6 (1.5) 0.5 (1.3)		

*Interfacial Failure

†Test temperature changed to 60° during course of test.



TABLE I
BOND STRENGTH
(Sheet 3 of 3)

Procedure	Lap Shear (psi/% IF) (MPa)	Wedge Test in./24 hr, (cm/24 hr)	Stress Durability hr	
			50°C	60°C
18a. FLAME 0.4 sec/cm	5000/45 (34)			
b. FLAME 2 sec/cm	5300/30 (37)			
c. FLAME 4 sec/cm	4200/85 (29)	0.9 (2.3)		
d. FLAME 20 sec/cm	3800/85 (26)			
e. FLAME 370 - 430°C		0.9 (2.3)		
f. FLAME 430 - 480°C		1.6 (4.1)		
g. FLAME 480 - 540°C		1.4 (3.6)		
19a. UV		1.6 (4.1)		
b. MICRO* - UV		0.6 (1.5)		

*Primer-adhesive interfacial failure

†Test temperature changed to 60° during course of test.



potential different (SPD), photoelectron emission (PEE) and water contact angle (θ_{H_2O}) measurements were made. Table II is a summary of these measurements along with wedge test results. Smith has described these techniques, i.e., the instruments and interpretation of the measurements, elsewhere.⁽⁹⁾ Essentially, SPD and θ_{H_2O} are extremely sensitive to the outermost layer of the surface, PEE depends upon the nature of the oxide as well as the substrate as does ellipsometry. Ellipsometry can be used to determine film (oxide) thickness and can often yield information about roughness.

4. Morphology, Scanning Electron Microscope Studies

The scanning electron microscope (SEM) has been used to monitor to morphology of a surface which has undergone surface treatment. Figures 1a - 1p are photomicrographs of a number of surfaces given their respective treatments. Comparison of a treated surface with the degreased only surface enables determination of the effect the treatment has on morphology.

The $KMnO_4/NaOH$ (6b) treatment, Fig. 1c, d, FLAME (18c) treatment, Fig. 1g, h, HNO_3 /dichromate (9f) treatment, Fig. 1k, l, H_2SO_4 /dichromate (12e) treatment, Fig. 1m, n, have little effect in actually altering the roughness of the surface. Visual observation of these samples showed that indeed the surface had been modified, particularly for the latter three treatments, because their new oxide layers appeared colored.

MICRO*, Fig. 1e, f, caused some enlargements and smoothing of pits and cracks although there was no visual difference from the non-treated sample.



TABLE II
SURFACE PROPERTIES
(Sheet 1 of 2)

Procedure	Ellipsometry		SPD (V)	PEE (nA)	θ_{H_2O} (deg)	Wedge in./24 hr, (cm/24 hr)
	Δ (deg)	ψ (deg)				
1. Electrolytic coloring	3.7	46.2	-0.65	0.20	19	
2. H ₂ SO ₄ /dichromate anodize	102.3	25.7	-0.52	0.22	0	0.07 (0.18)
3. H ₃ PO ₄ anodize	129.9	36.5	0	1.0	70	
4. H ₂ SO ₄ anodize	108.8	28.1	6.08	0.80	46	0.2 (0.51)
5. H ₂ SO ₄ anodize - CrO ₃	106.3	27.4	-0.31	0.40	38	0.3 (0.76)
6a. KMnO ₄ /NaOH 20 min	108.2	30.1	-0.45	0.70	50	1.0 (2.5)
b. KMnO ₄ /NaOH 40 min	108.8	30.1	-0.43	0.80	56	1.4 (3.6)
7. Degrease Only	111.5	31.6	0.07	0.90	65	2.7 (6.9)
8. H ₂ O	118.5	31.6	-0.07	0.48	66	1.0 (2.5)
9a. 50 v/o HNO ₃	128.7	30.5	-0.21	1.2	40	0.35 (0.89)
b. 50 v/o HNO ₃ /1 w/o dichromate	90.0	33.4	-0.63	0.58	14	0.40 (1.0)
c. 50 v/o HNO ₃ /2 w/o dichromate	81.7	36.0	-0.71	0.52	11	0.20 (0.51)
e. 50 v/o HNO ₃ /5 w/o dichromate	85.4	33.2	-0.69	0.47	8	0.20 (0.51)
f. 50 v/o HNO ₃ /10 w/o dichromate	90.2	32.0	-0.72	0.51	3	0.10 (0.25)
11a. H ₂ SO ₄ etch 2 min			0.09	2.0	47	1.0 (2.5)
b. H ₂ SO ₄ etch 5 min			0.19	1.4	44	0.9 (2.3)
c. H ₂ SO ₄ etch 10 min			0.17	1.7	47	1.0 (2.5)
12a. 50 v/o H ₂ SO ₄ /1 w/o dichromate	111.8	26.2	-0.17	0.29	16	1.7 (4.3)
b. 50 v/o H ₂ SO ₄ /2 w/o dichromate	106.1	24.5	-0.25	0.25	16	1.5 (3.8)
c. 50 v/o H ₂ SO ₄ /5 w/o dichromate	83.8	17.5	-0.22	0.16	12	1.5 (3.8)
d. 50 v/o H ₂ SO ₄ /10 w/o dichromate	84.4	16.8	-0.44	0.14	11	1.4 (3.6)
e. 30 v/o H ₂ SO ₄ /40 w/o dichromate	66.4	10.3	-0.96	0.18		0.06 (0.15)
13a. H ₂ SO ₄ - HNO ₃			0.01	1.4	7	0.10 (0.25)

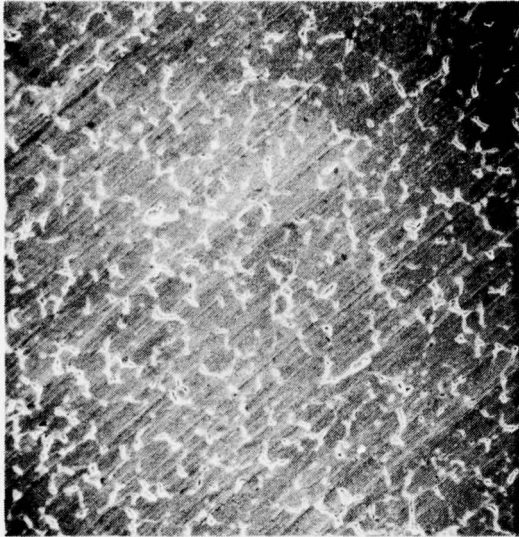
TABLE II
SURFACE PROPERTIES
(Sheet 2 of 2)

Procedure	Ellipsometry		SPD (V)	PEE (nA)	θ_{H_2O} (deg)	Wedge in./24 hr, (cm/24 hr)
	Δ (deg)	ψ (deg)				
14a. 10 v/o MICRO*	126.4	31.2	-0.31	1.3	35	1.1 (2.8)
b. MICRO*	126.8	31.3	-0.08	1.3	43	0.80 (2.0)
15. MICRO* - HNO ₃	128.8	30.0	-0.24	1.4	32	0.20 (0.51)
16. NaOH	121.8	30.7	0.17	1.0	56	0.10 (0.25)
18a. FLAME 0.4 sec/cm	110.8	30.8	0.15	0.30	70	
b. FLAME 2 sec/cm	56.6	34.2	-0.23	4.6	38	
c. FLAME 4 sec/cm	354.8	17.4	-0.31	4.4	7	0.9 (2.3)
d. FLAME 20 sec/cm	40.8	19.9	-0.73	1.2	10	
19a. UV	117.9	31.2	0.02	0.6	50	1.6 (4.1)
b. MICRO* - UV	121.1	31.0	-0.09	1.4	66	0.6 (1.5)

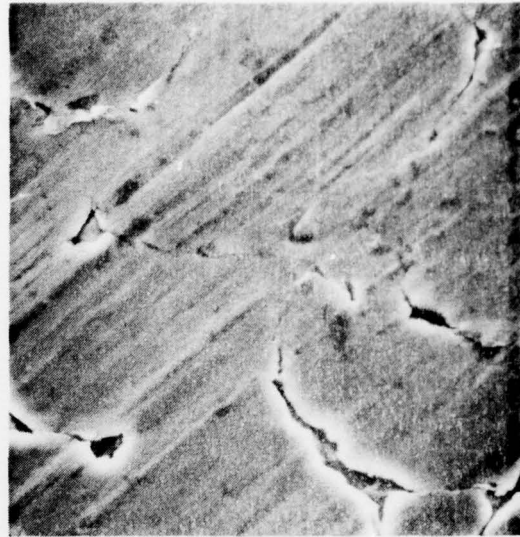


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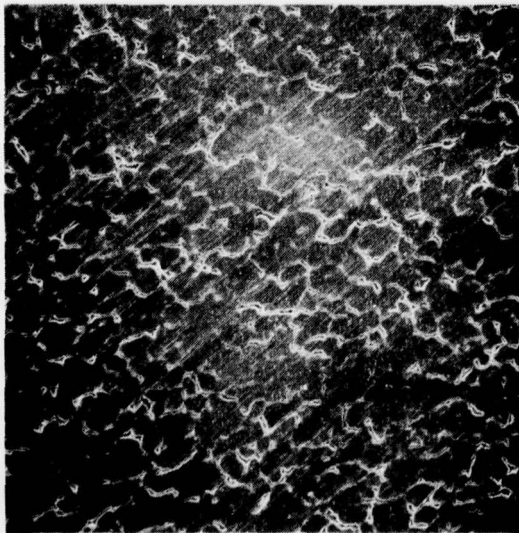


a. 10μ \square , 300x



b. 1μ \square , 3000x

DEGREASE ONLY
(TREATMENT 7)



c. 10μ \square , 300x



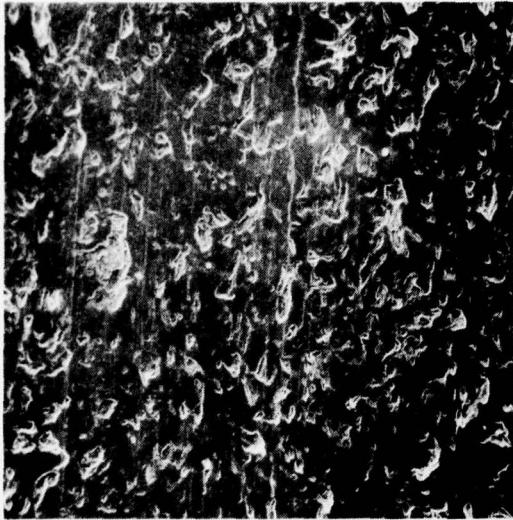
d. 1μ \square , 3000x

$KMnO_4/NaOH$

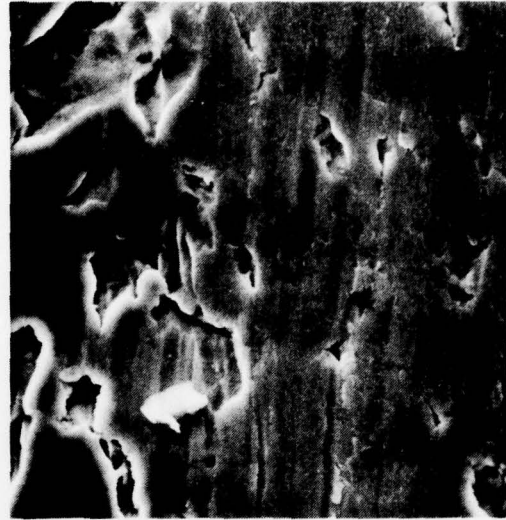
Fig. 1 Scanning electron photomicrographs.



SC79-5529

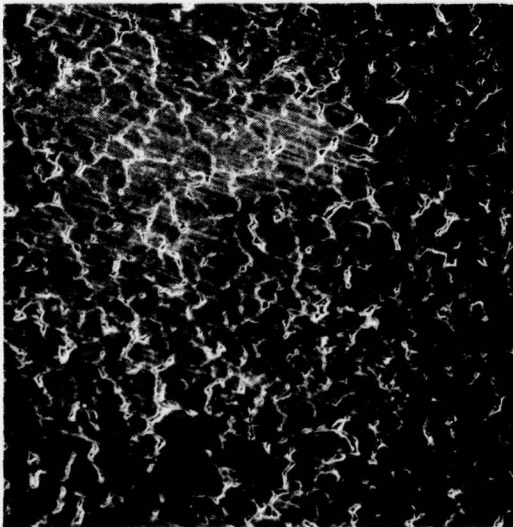


e. 10μ \square , 300x



f. 1μ \square , 3000x

MICRO*
(TREATMENT 14b)



g. 10μ \square , 300x



h. 1μ \square , 3000x

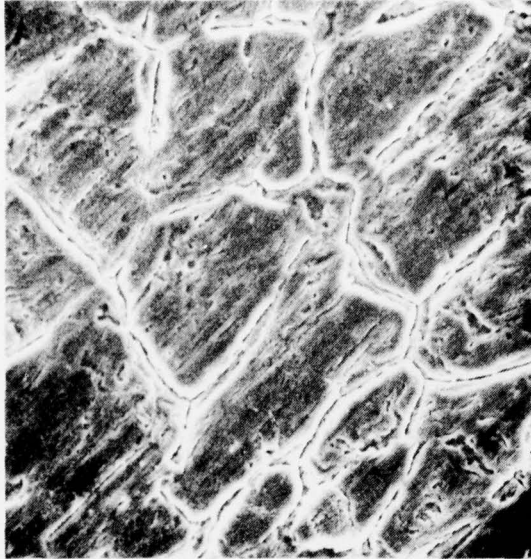
FLAME
(TREATMENT 18c)

Fig. 1 (continued)

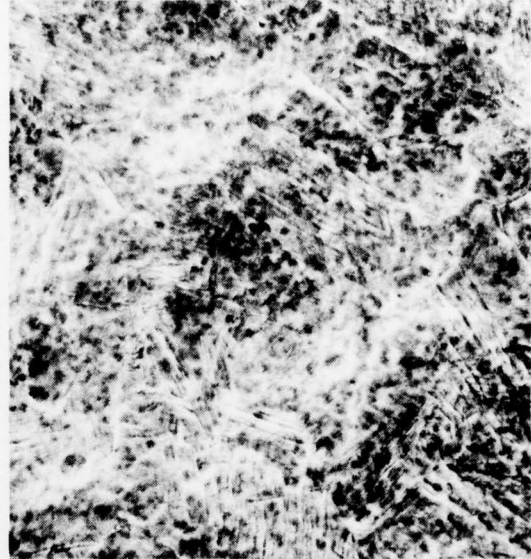


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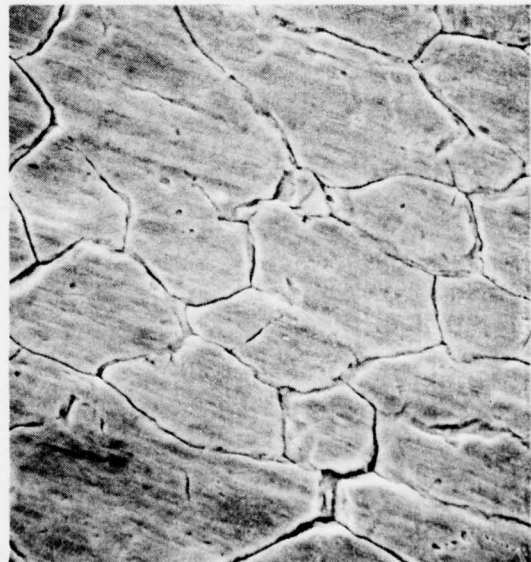
i. H_2SO_4 ANODIZE - CrO_3 (PROCEDURE 5)
 1μ □ , 2000x



j. H_2SO_4 - HNO_3 (PROCEDURE 13a)
 1μ □ , 2000x



k. HNO_3 ANODIZE (PROCEDURE 10h)
 1μ □ , 2000x

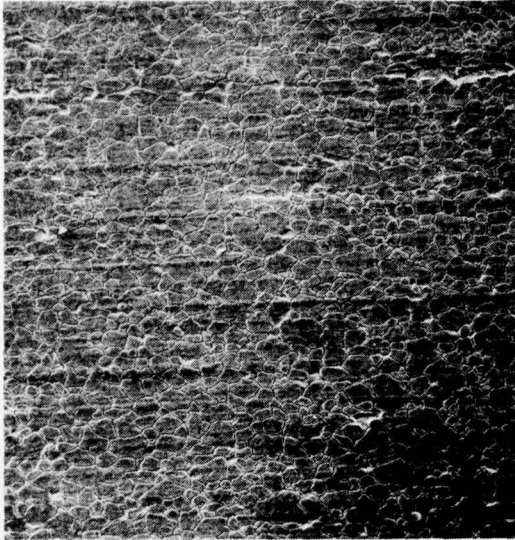


l. HNO_3 /DICHROMATE (PROCEDURE 9f)
 1μ □ , 2000x

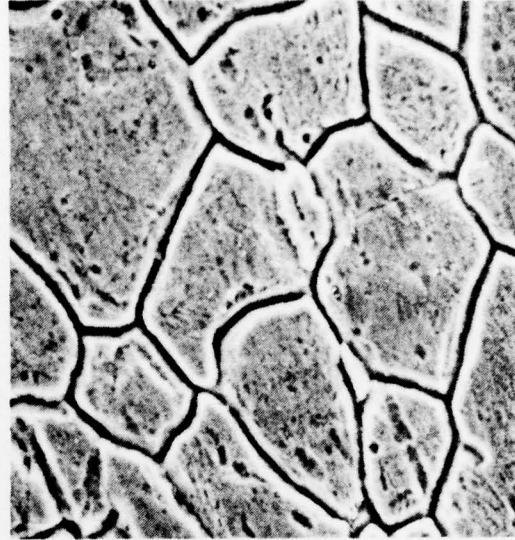
Fig. 1 (continued)



SC79-5531

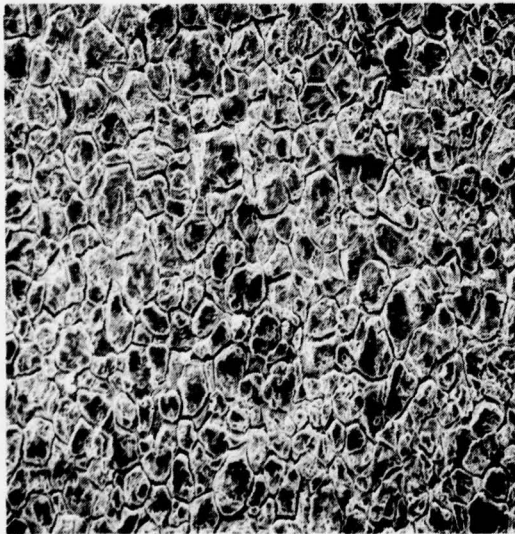


m. 10μ \square , 200x



n. 1μ \square , 2000x

H_2SO_4 /DICHROMATE
(PROCEDURE 12e)



o. 10μ \square , 300x



p. 1μ \square , 3000x

H_2SO_4 /DICHROMATE ANODIZE
(PROCEDURE 1)

Fig. 1 (continued)



The acid anodizing treatments (5, 10h, 2) Fig. 1i, h, o, p, show increased corrosion along grain boundaries and in the case of the H_2SO_4 /dichromate anodize, Fig. 1o, p, much etching had taken place. All these surfaces appeared rougher visually (non shiny surface after treatment), the H_2SO_4 anodize - CrO_3 and HNO_3 anodize treated samples appearing whitish and the H_2SO_4 /dichromate anodize treated samples varying in color depending upon current density used while anodizing.

Samples etched in H_2SO_4 and passivated in HNO_3 , Fig. 1j, show much etching had taken place. These samples also appeared whitish.

5. Auger Electron Spectroscopy (AES) Studies

AES was run on selected samples to attempt a correlation between bond character and oxide film composition. Figure 2 is a typical spectrum. After an initial scan was made the oxide layer was ion sputtered for a set amount of time following which another scan, only wide enough to include peaks of interest (in this case oxygen, chromium and iron) was made. This process was repeated until there was no change in the spectra and the oxygen peak at a minimum, indicating base metal had been reached. Figure 3 shows an example of the AES spectra obtained during depth profile analysis. As can be seen, the peak intensities for the various elements change dramatically as the oxide layer is sputtered off. Figures 4 through 14 are plots of the Auger peak-to-peak height (APPH) vs sputter time. These allow comparison of relative concentration of species, i.e., Cr/Fe, as well as relative thickness of the oxide layer. It should be noted that the initial top layer on the surface is contamination such as hydrocarbons. The depth of this layer can be estimated by observing the disappear-



ance of the carbon peak. This was done in two cases and found to be on the order of 20 - 30Å.

Table III summarizes the important facts arising from the AES depth profile analysis and lists wedge test results using the indicated methods. In some cases the sputtering was not continued through the entire oxide layer due to time considerations. The chromium APPH to iron APPH ratio (Cr/Fe) is one of the standout features to note. In the base metal the ratio is fairly constant for all specimens, as is expected. In the oxide the ratio ranges from 0 to 4.1. Figure 15 graphically portrays how wedge test results have varied with the ratio. Not until there is significant chromium enrichment (Cr/Fe ~2) in the oxide layer are there optimum wedge tests obtained. This is consistent with the knowledge that passive films offer increased corrosion resistance and, in the case of stainless steel, show chromium enrichment.



TABLE III
AUGER ELECTRON SPECTROSCOPY RESULTS

Treat- ment	Description	Wedge Test Results in./24 hr, (cm/24 hr)	Cr/Fe max in Oxide	Cr/Fe in Metal	Approximate Sputter Time Through Oxide (min)
7	Degreased	2.7 (6.9)	0.3	0.3	2.5
6b	KMnO ₄ /NaOH	1.0 (2.5)	0.3	0.3	5.0
19b	MICRO*-UV	0.6 (1.5)	0.3	0.2	3
18f	FLAME	1.0 (2.5)	0		>30
13b	H ₂ SO ₄ - HNO ₃ /Dichromate	0.1 (0.25)	2.8	0.3	3.5
5	H ₂ SO ₄ Anodize - CrO ₃	0.2 (0.51)	1.3	0.3	1.5
12e	H ₂ SO ₄ /Dichromate	0.06 (0.15)	4.1		>30
2	H ₂ SO ₄ /Dichromate Anodize	0.07 (0.18)	2.4		>10
9a	HNO ₃	0.35 (0.89)	1.0	0.3	1.5
9f	HNO ₃ /Dichromate	0.1 (0.25)	3.0	0.4	5.5
10h	HNO ₃ Anodize	0.05 (0.13)	2.0	0.3	4

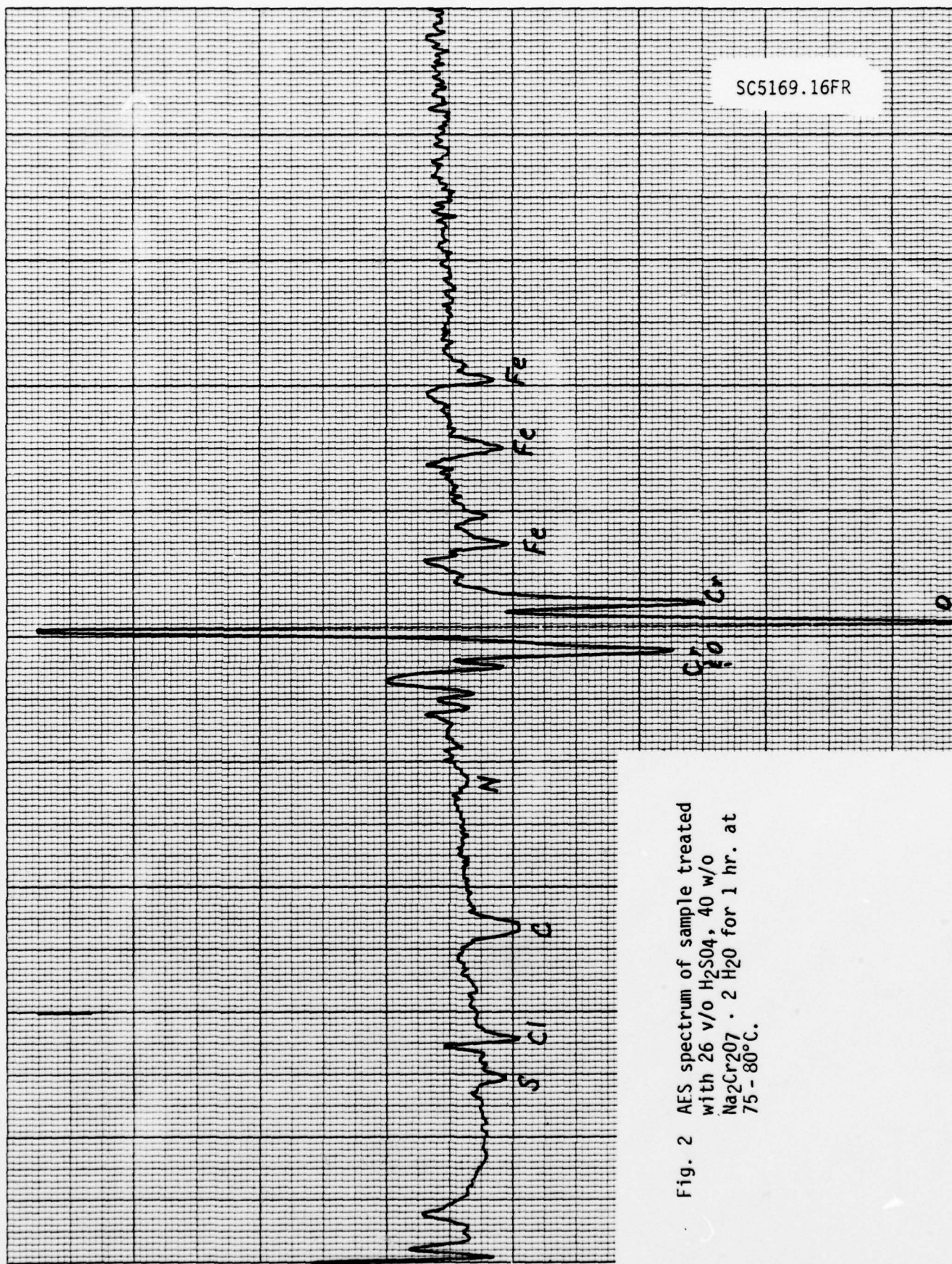


Fig. 2 AES spectrum of sample treated with 26 v/o H₂SO₄, 40 w/o Na₂Cr₂O₇ · 2 H₂O for 1 hr. at 75 - 80°C.

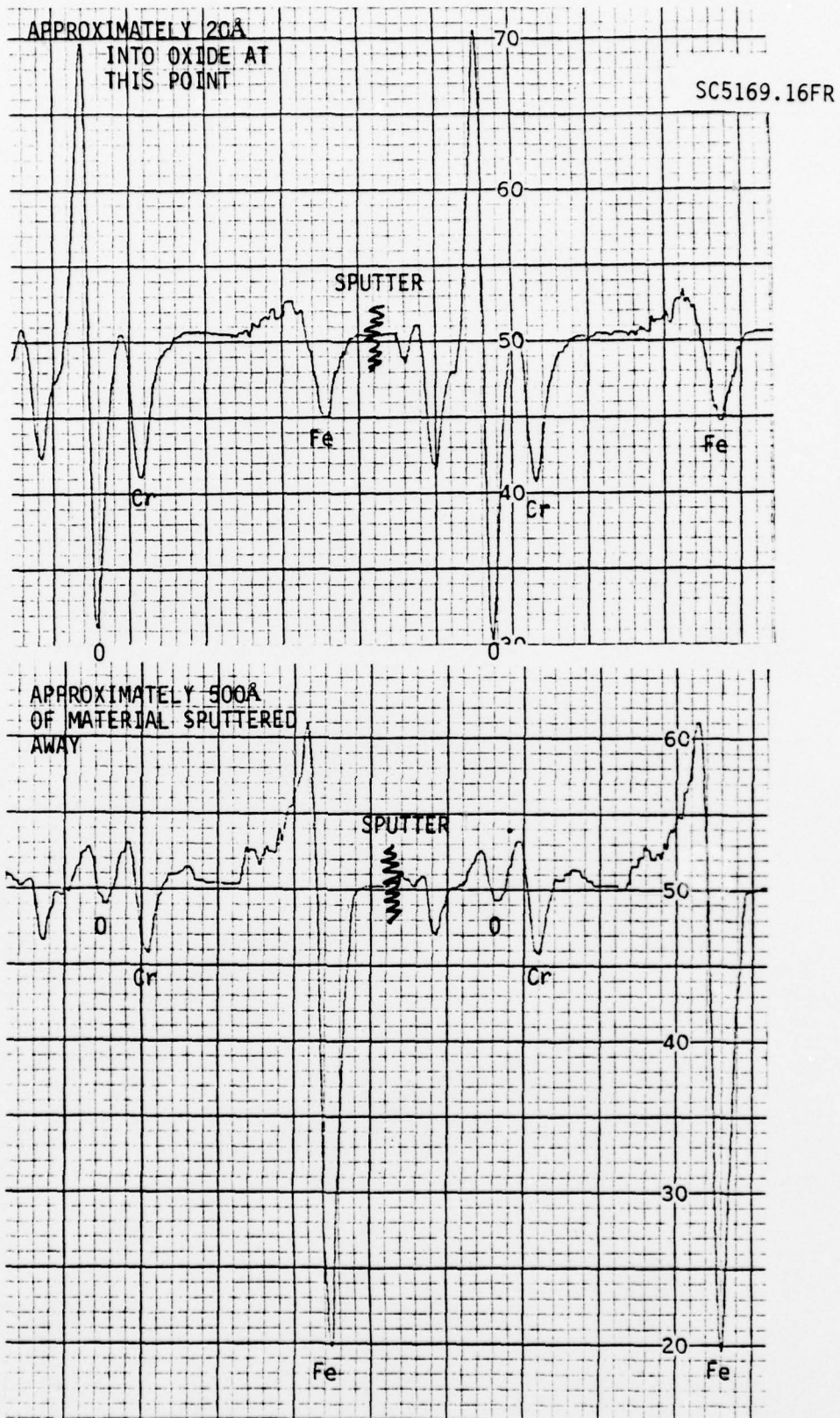
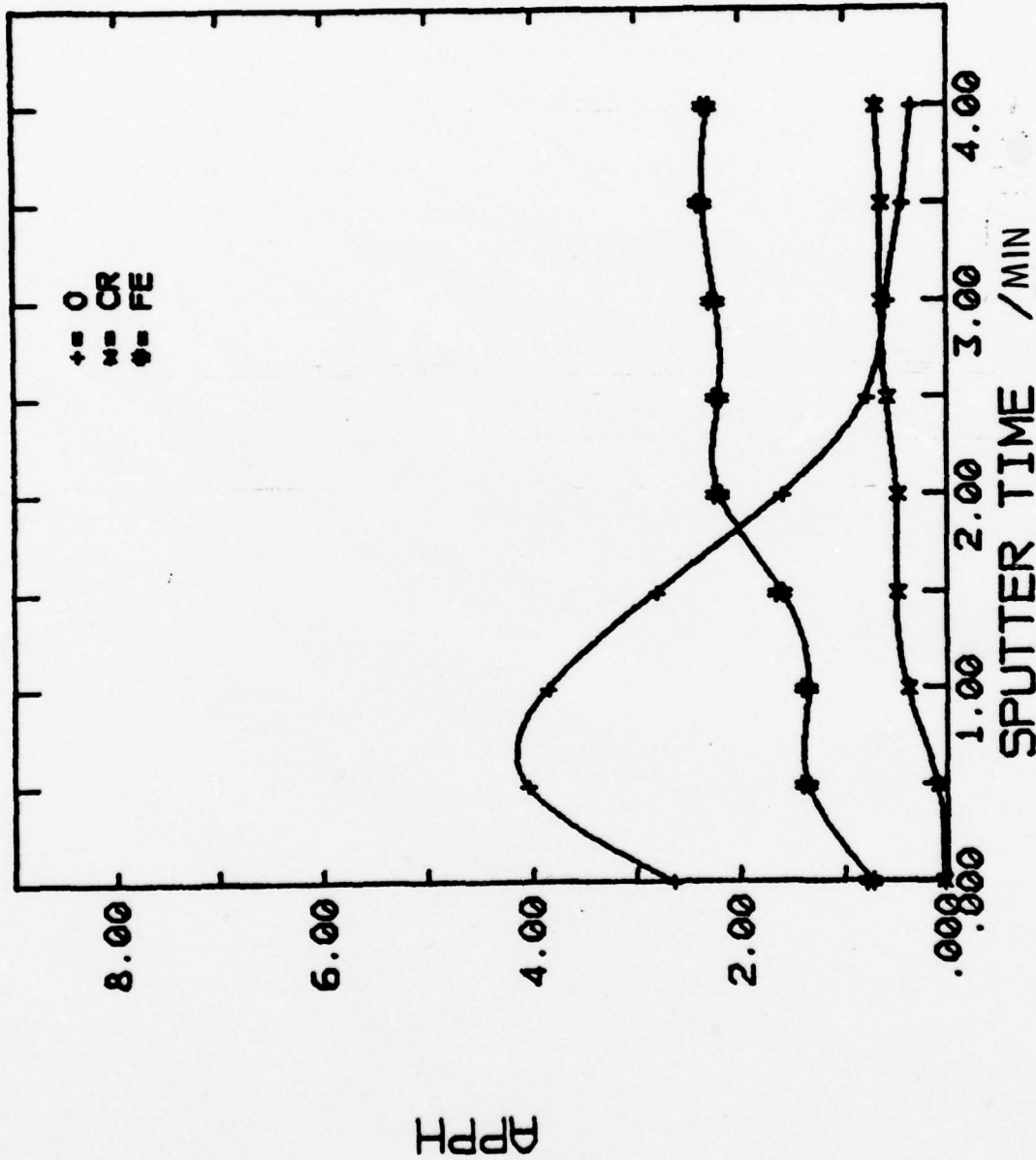


Fig. 3 Example of AES output for depth profile analysis. Sample is sputtered for a period following which the spectrum of a small chosen interval is taken.



AES DECREASED ONLY 2/79

Fig. 4 Auger peak-to-peak height (APPH) vs. sputter time for oxygen (510eV), chromium (529eV) and iron (598eV). Sample had been degreased only.

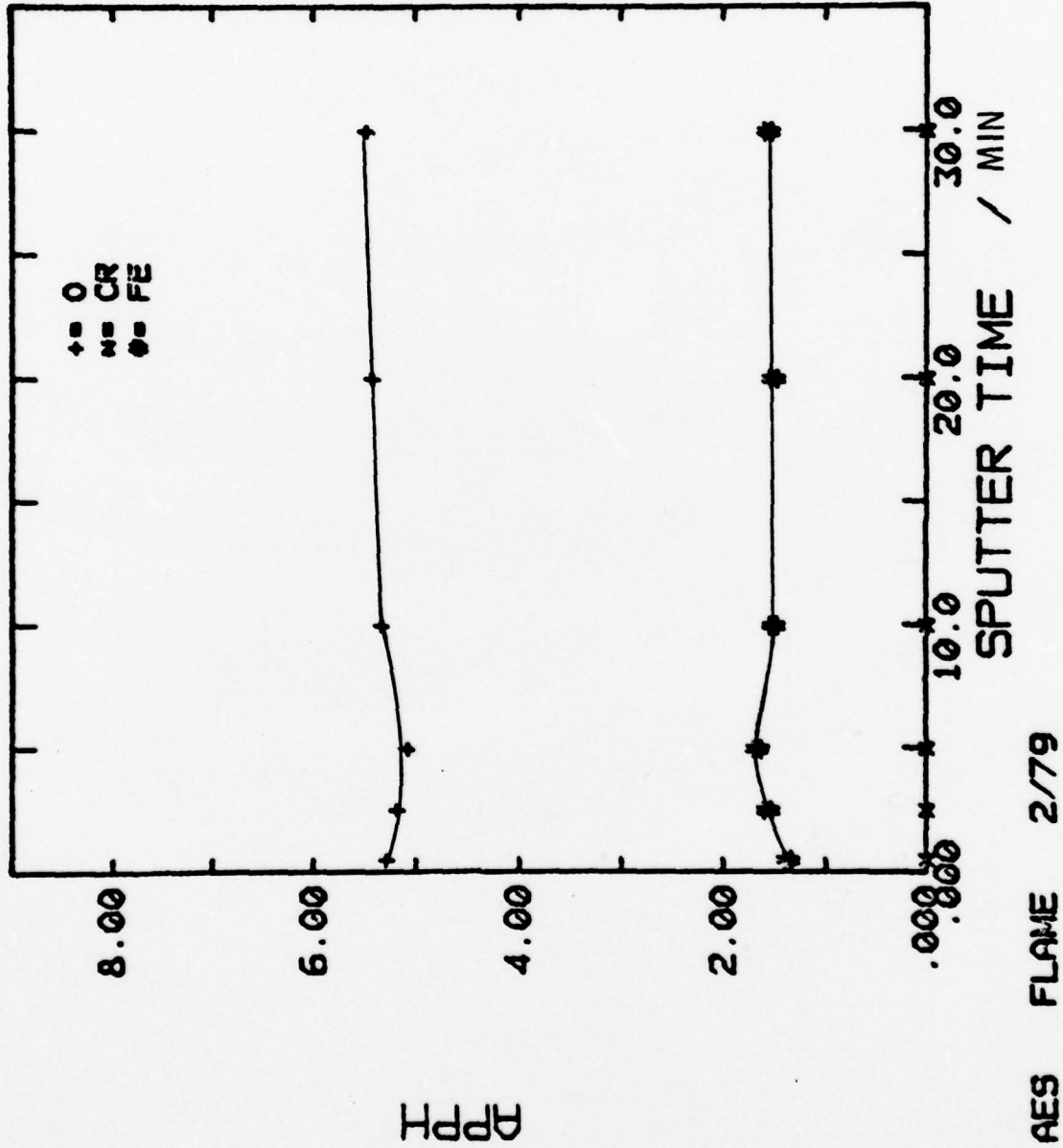


Fig. 5 AES Flame (18f).

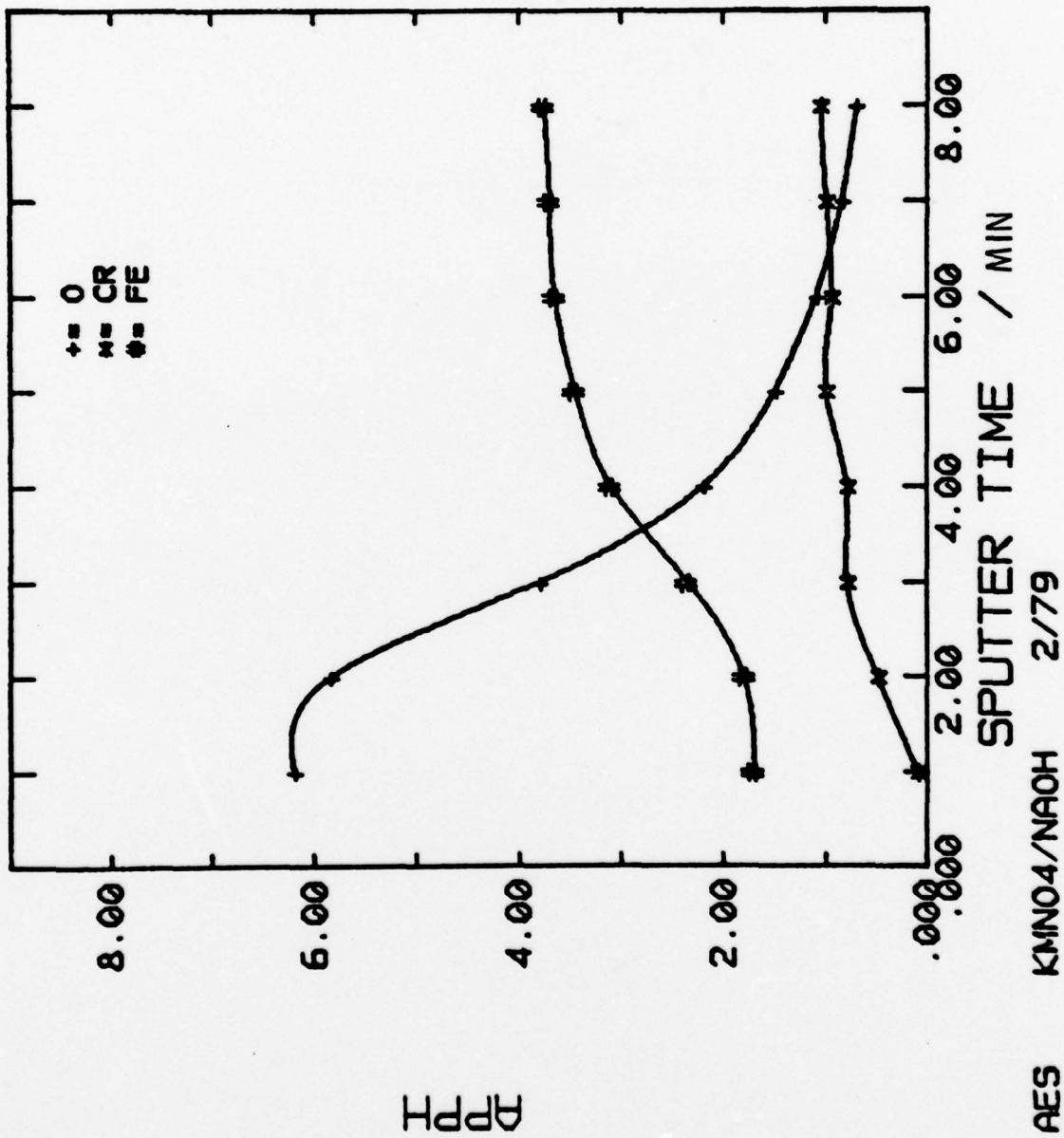


Fig. 6 AES KMnO₄/NaOH (6b).

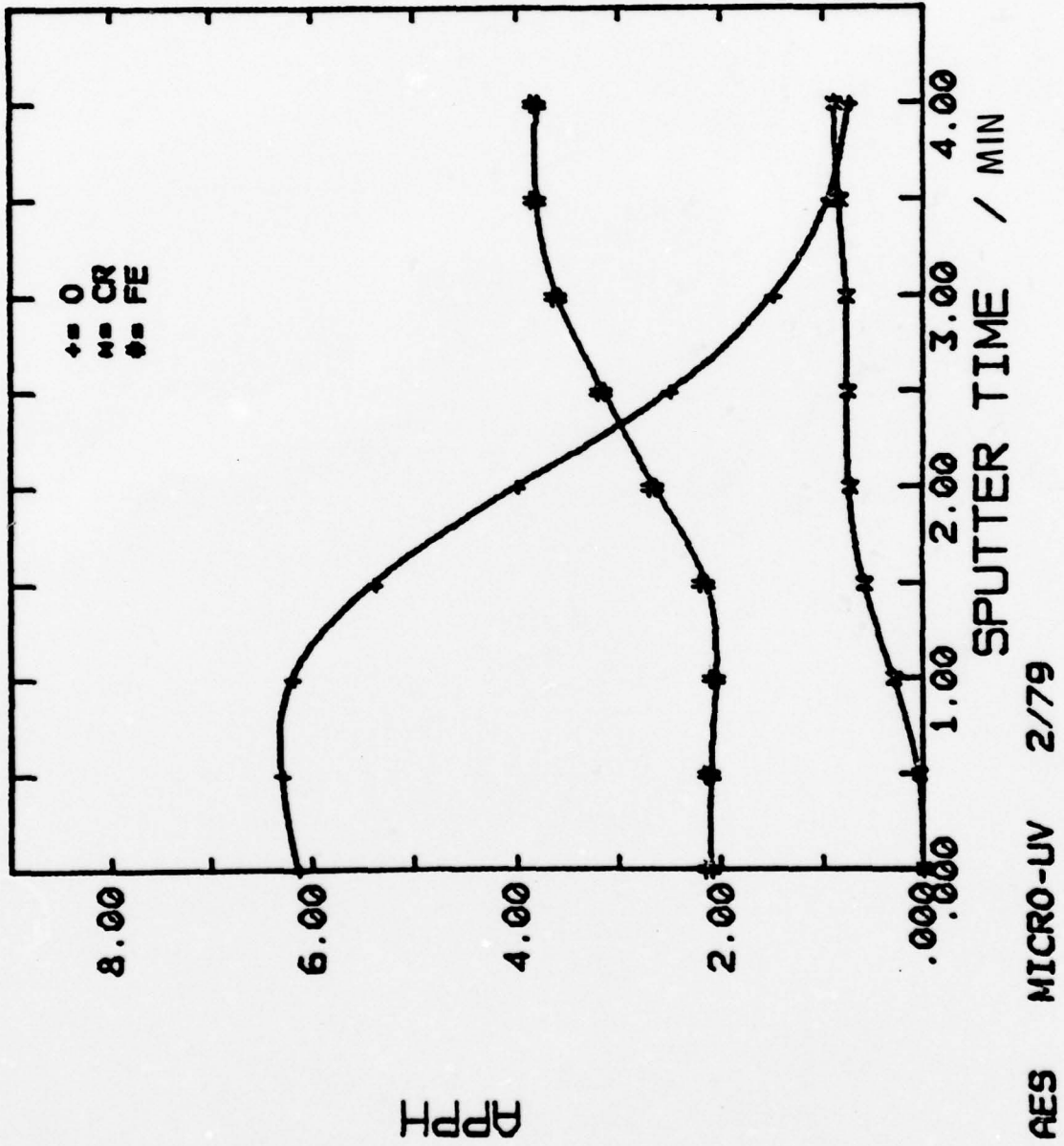


Fig. 7 AES MICRO-UV (19b).

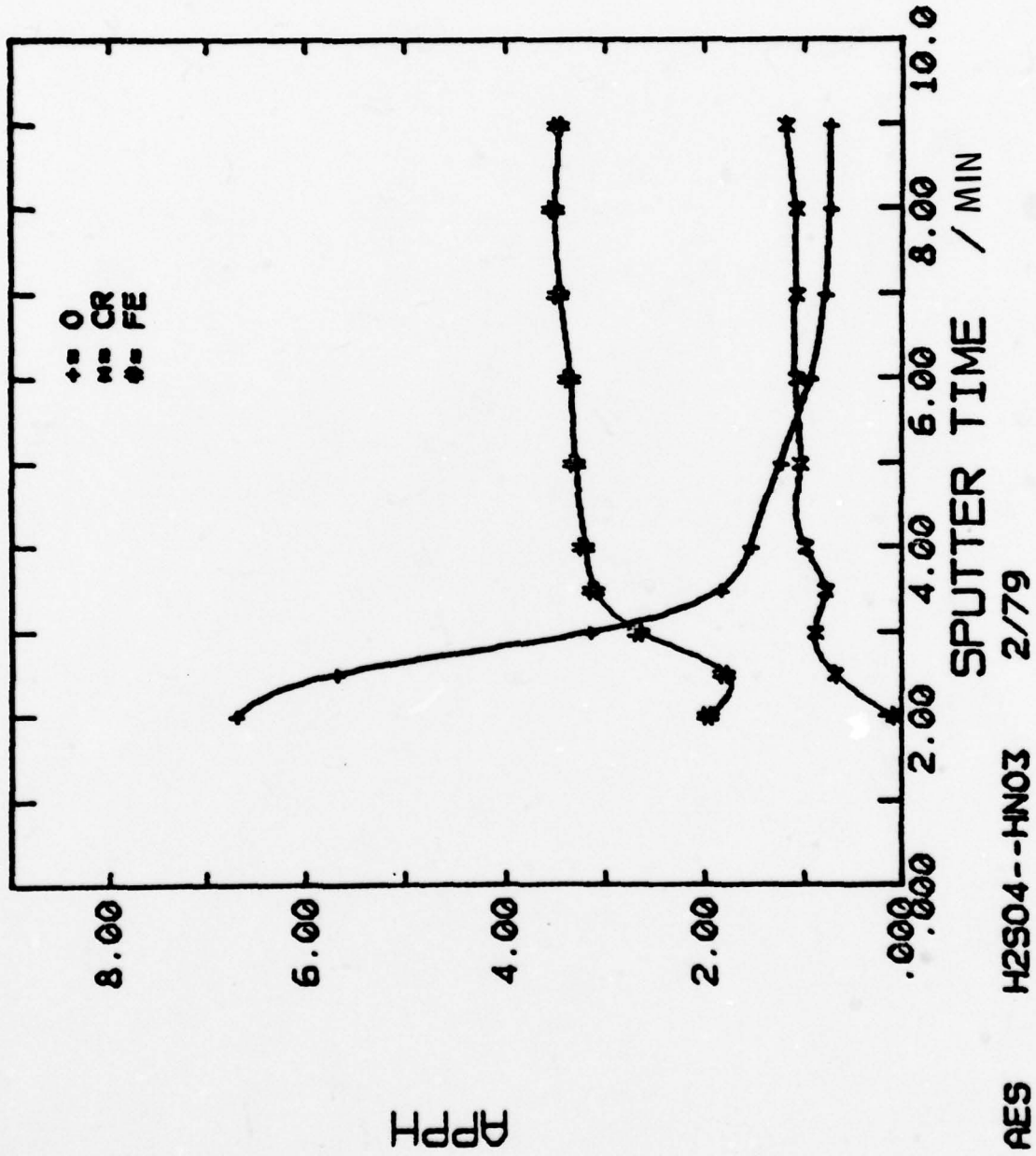


Fig. 8 AES H₂SO₄ - HNO₃ (13b).

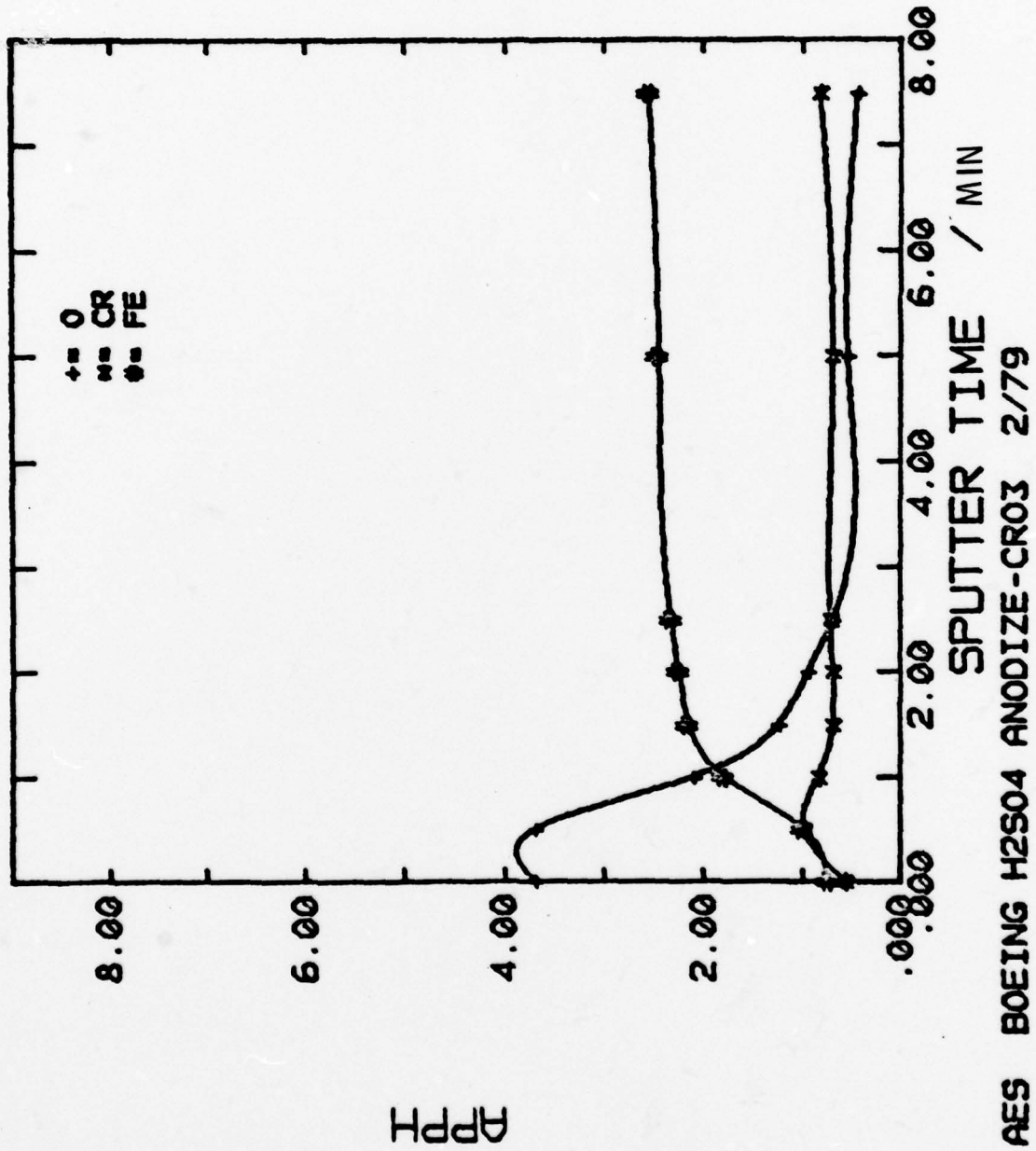


Fig. 9 AES Boeing H₂SO₄ anodize-CrO₃ (5).

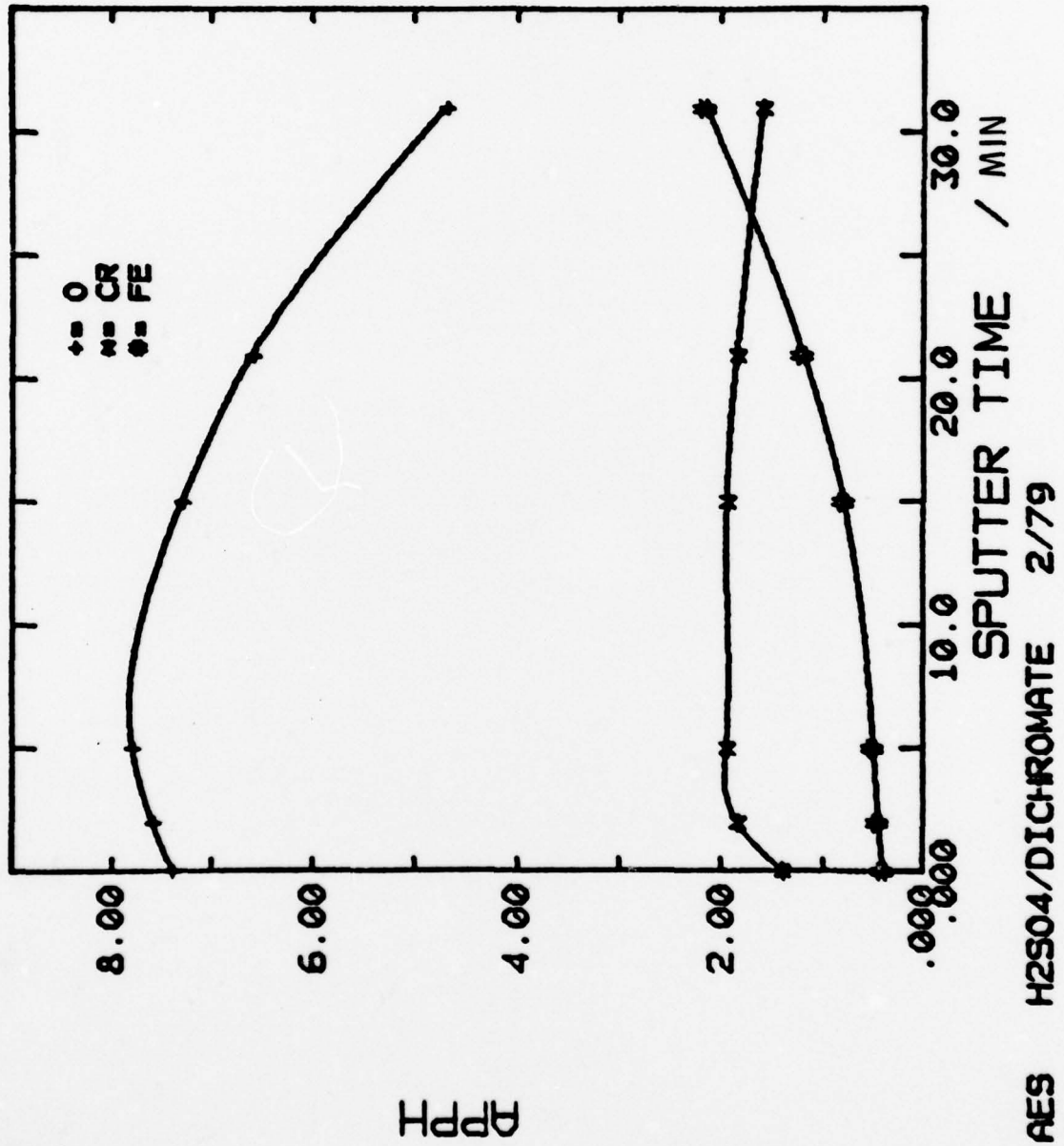


Fig. 10 AES H₂SO₄/dichromate (12e).

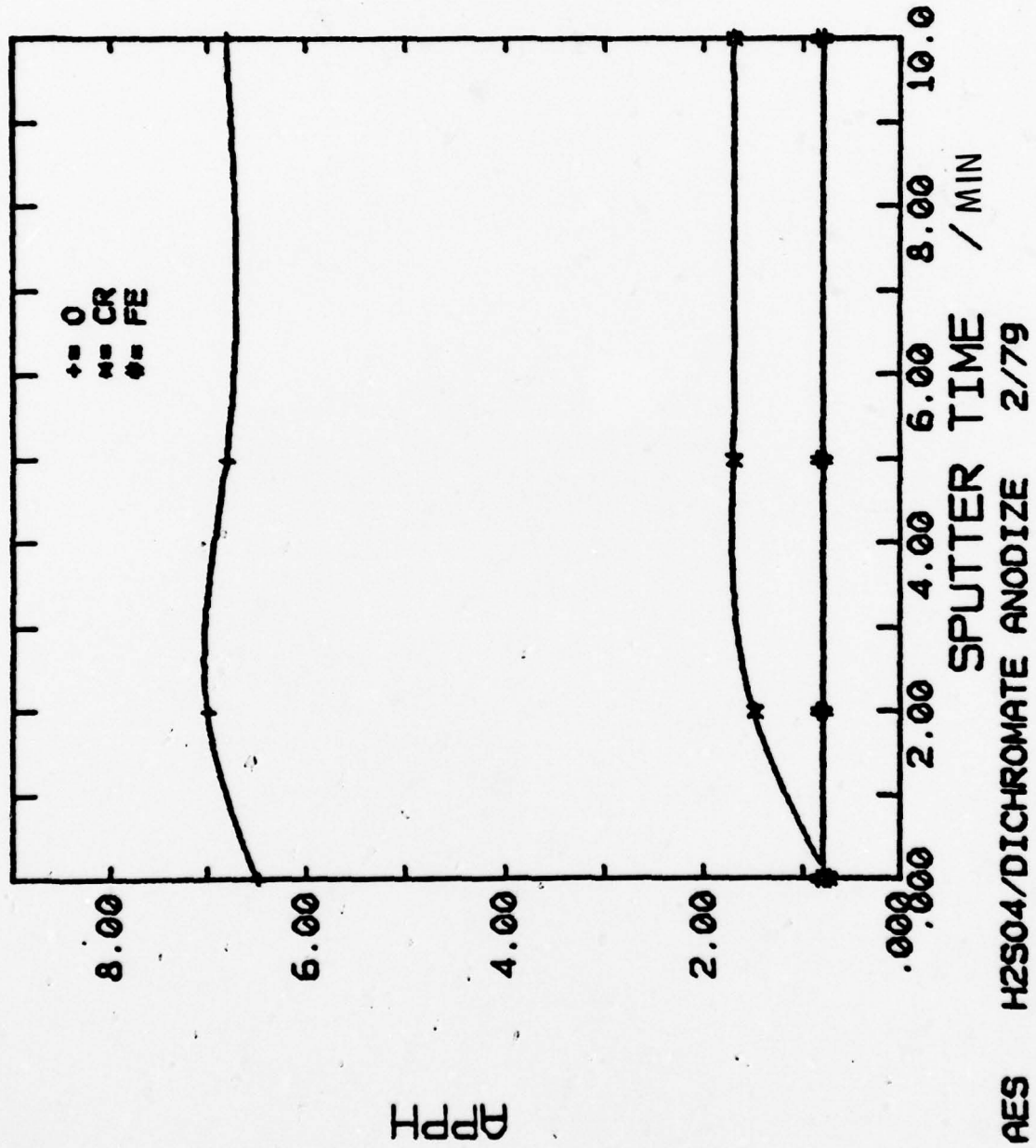


Fig. 11 AES H₂SO₄/dichromate anodize (2).

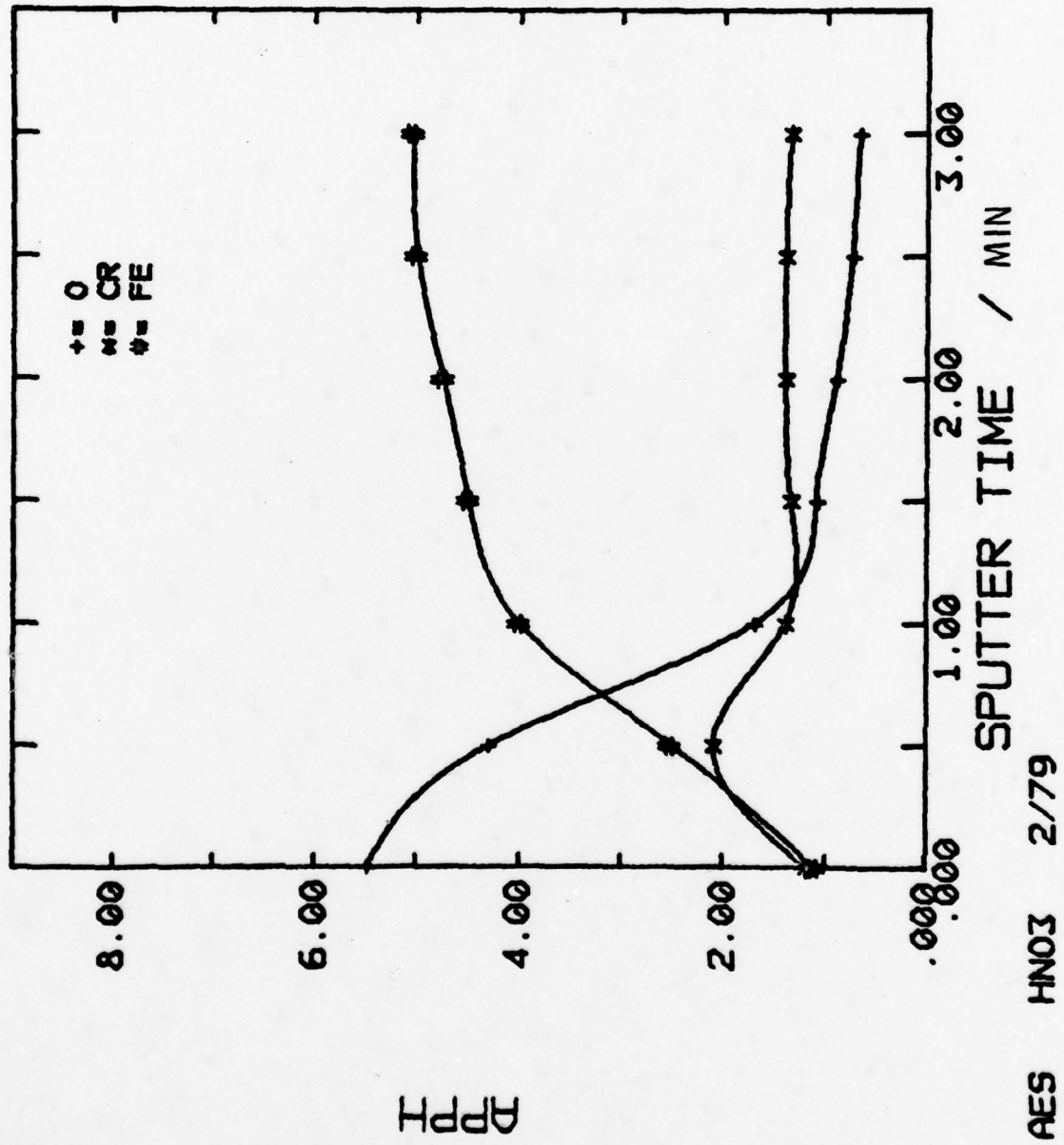


Fig. 12. AES HNO₃ (9a).

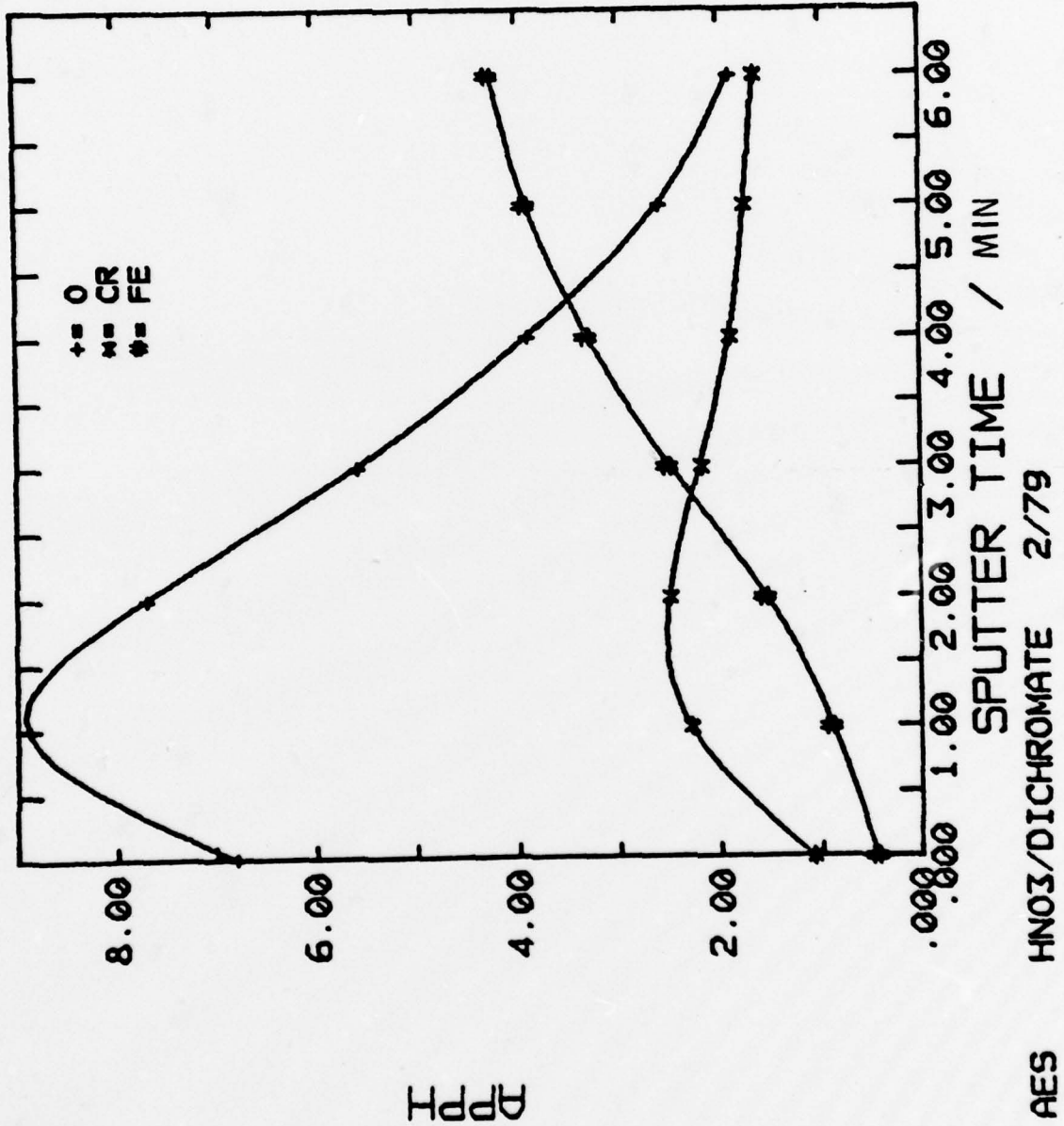


Fig. 13 AES HNO₃/dichromate.

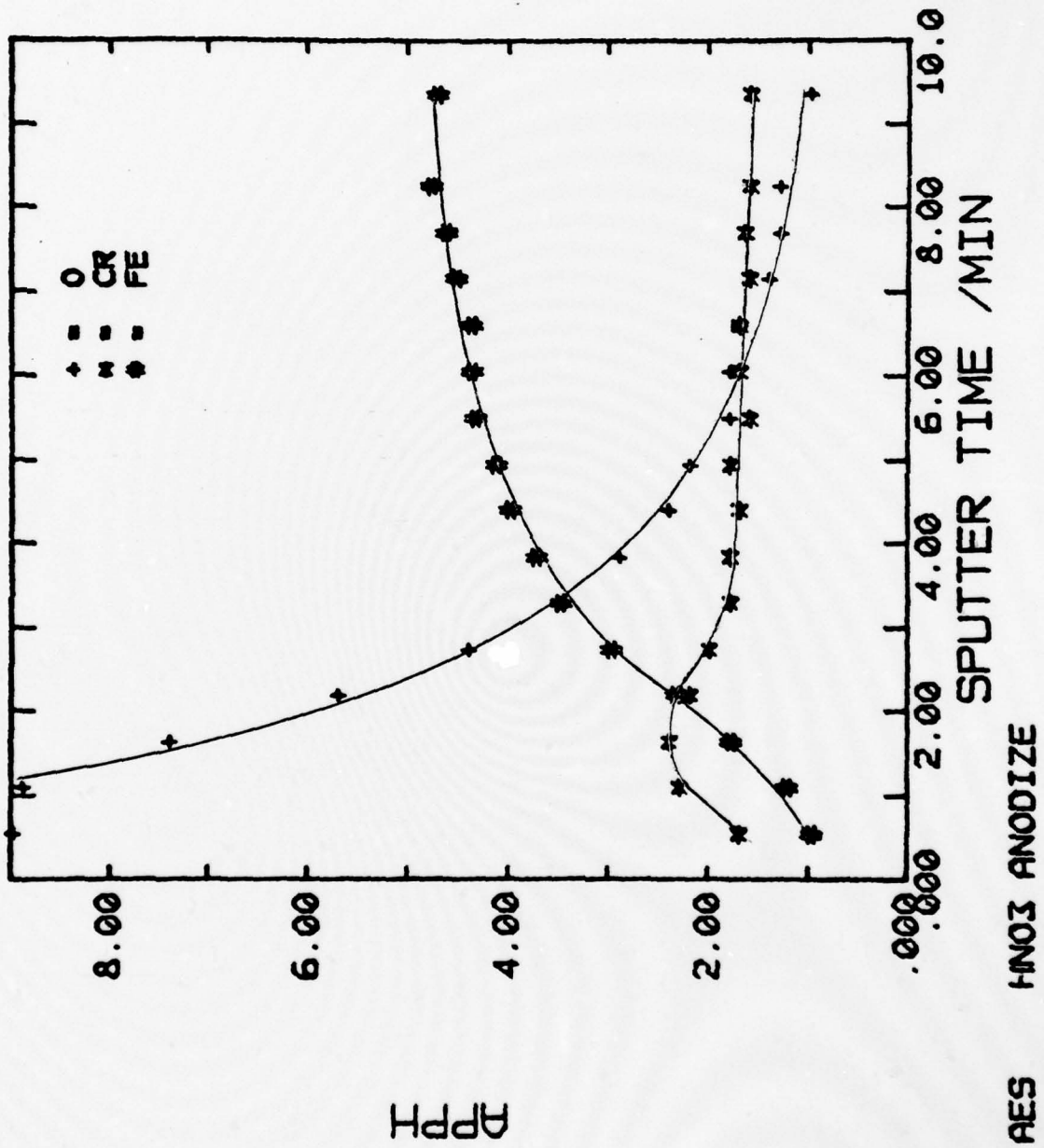


Fig. 14 AES HNO₃ anodize (10h).

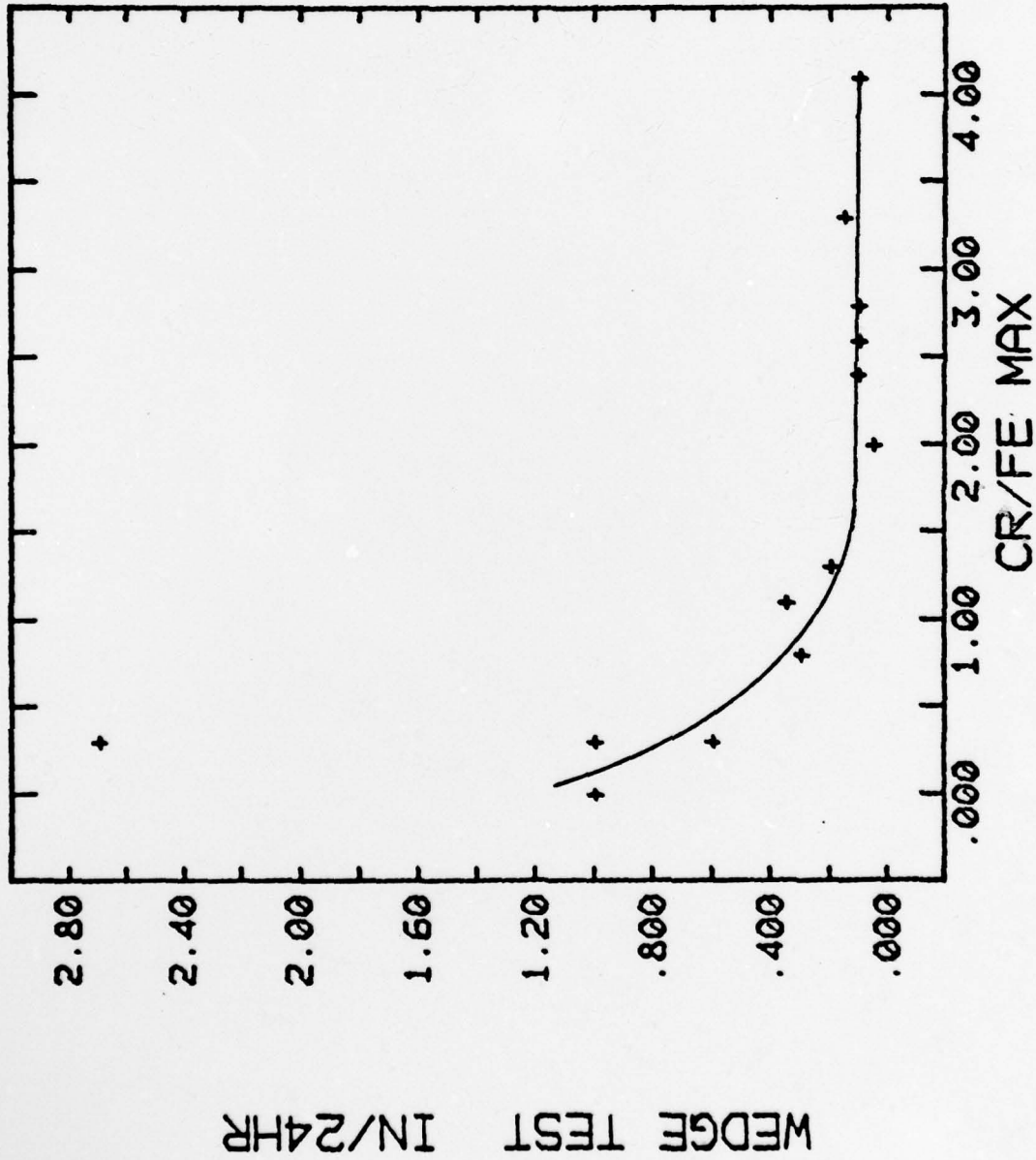


Fig. 15 Wedge test results vs. APPH ratio of chromium to iron. Values taken from Table II



6. X-Ray Photoelectron Spectroscopy (XPS) Analysis

XPS was run on selected samples to provide information about the oxidation state of chromium and iron on the metal surface after treatment. Figure 16 is representative of spectra obtained. Only the sample which had been treated by immersion in H_2SO_4 /dichromate (12e) showed any appreciable Cr (VI) on the surface. In all cases it appeared that Fe (II) was the predominant oxidation state of iron in the oxide.

Using peak areas and sensitivity factors to relate area to species concentration the results found in Table IV were compiled. Although no data were taken for the base metal the Cr/Fe ratio should be about 0.2, demonstrating the large degree of chromium enrichment of the outer surface layer.

TABLE IV
XPS RESULTS

Sample		Cr/Fe
H_2SO_4 /dichromate anodize (2)	initial	9.6
	After 1.5 min sputter	7.0
H_2SO_4 /dichromate (12e)	initial	10.5
HNO_3 anodize (10h)	initial	8.6
	After 1.5 min sputter	5.7

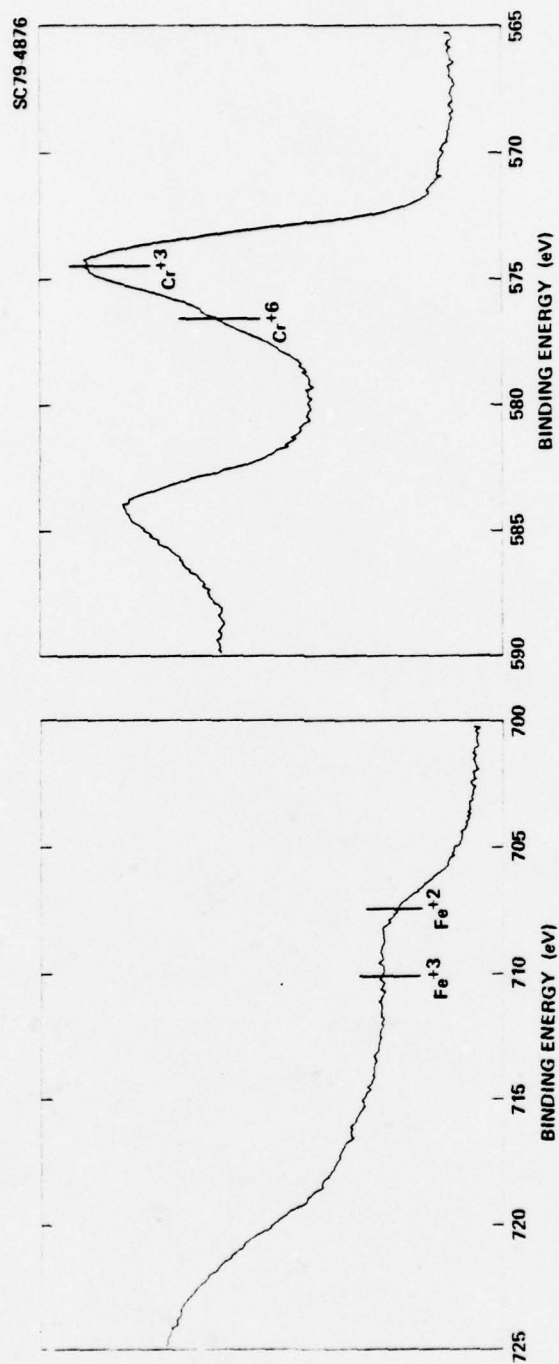


Fig. 16 X-ray photoelectron spectra for H₂SO₄/dichromate (12e) treated sample.



7. Hydrogen Permeation in AM355 Steel

There has been concern recently as to whether a surface preparation process might subject the metal to hydrogen which in turn might diffuse into and embrittle the specimen. In order to determine the susceptibility of AM355 to hydrogen permeation an experiment was designed which would show the kinetics of diffusion through the metal and enable calculation of a diffusion coefficient.

A hydrogen permeation cell, shown in Fig. 17, was used for the following measurements. Initially the sample is passivated on the detection side by potentiostating at 100 mV vs SCE until the residual current dropped below 2 μ A. This produces a surface which should not itself undergo any corrosion reaction as the experiment proceeds and provides a low, fairly constant baseline for current (μ A) measurements. The charging cell is filled with a NaOH/NaCN solution and when an approximately 2 μ A reading is reached, a constant cathodic current density of 10 mA/cm² is applied in the charging cell such that hydrogen is produced at the metal surface. On the detection side the potential is held constant at +100 mV vs SCE. Any hydrogen that permeates through the sample will be oxidized at the metal surface, producing a rise in current. When the metal becomes saturated with respect to hydrogen, noted by the current leveling off, charging can be stopped and the rate with which the hydrogen leaves can be measured. This process yields data needed for calculation of the diffusion coefficient of hydrogen in the metal via plots of fraction of hydrogen diffused out (μ A(t)/ μ A (saturated)) vs square root of time and the thickness of the specimen.

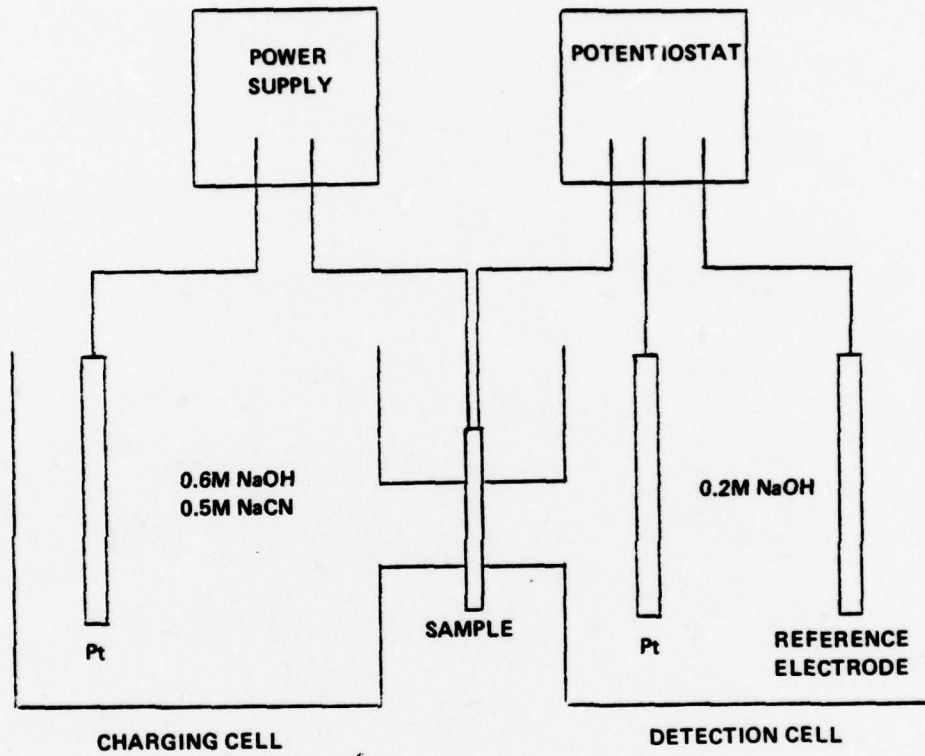


Fig. 17 Hydrogen permeation cell.



Initially a sample of 4130 steel 0.025 in. (0.064 cm) thick was investigated because its permeability to hydrogen has been previously studied. Figure 18 shows the results. As the specimen was charged, hydrogen began diffusing through in less than two minutes. Because this experiment was only to verify that the system was indeed working, the steel was charged for only 30 minutes, not until saturation. When the charging current was turned off the hydrogen in the metal diffused out (current decreased) in exactly the manner expected.

Hydrogen permeability through AM355 was then examined. Figure 19 shows the results obtained from a 0.015 in. thick (0.038 cm) sample. After 40 minutes of charging there was no rise in current, i.e., no hydrogen permeating through. A 0.040 in. (0.102 cm) thick sample was charged for 20 hours with similar results. This leads to the conclusion that the diffusion coefficient is so low that there can be no hydrogen build-up in AM355 in the time used for any surface treatments.

One valid question which could be raised is the effect an increase in temperature might have on the diffusion coefficient since some treatments are done at about 100°C. It has been shown⁽⁸⁾ that the diffusion coefficient for hydrogen in steel (A.I.S.I. 4340 steel and ARMCO iron specifically) follows the Arrhenius relationship that $\log_{10}D$ is directly proportional to $10^3/T$ (°K). This allows the estimation that going from 10°C to 100°C leads to an increase in the diffusion coefficient by about a factor of six, clearly not enough to warrant concern.

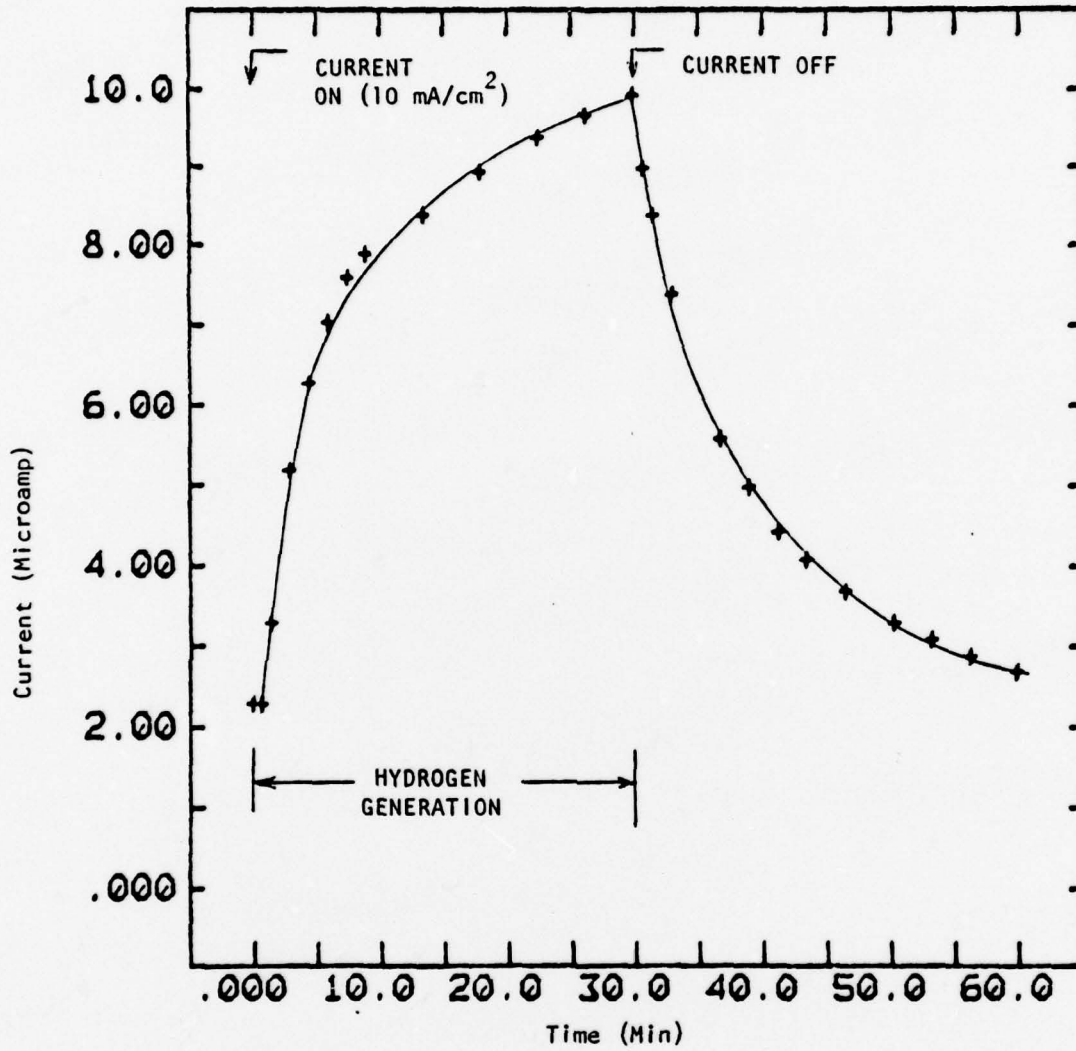


Fig. 18 Hydrogen permeation in 4130 steel. Charging solution: 0.6N NaOH, 0.5N NaCN. Reference cell: 0.2N NaOH. Potentiostat at +100 mV vs SCE. T = 22°C.

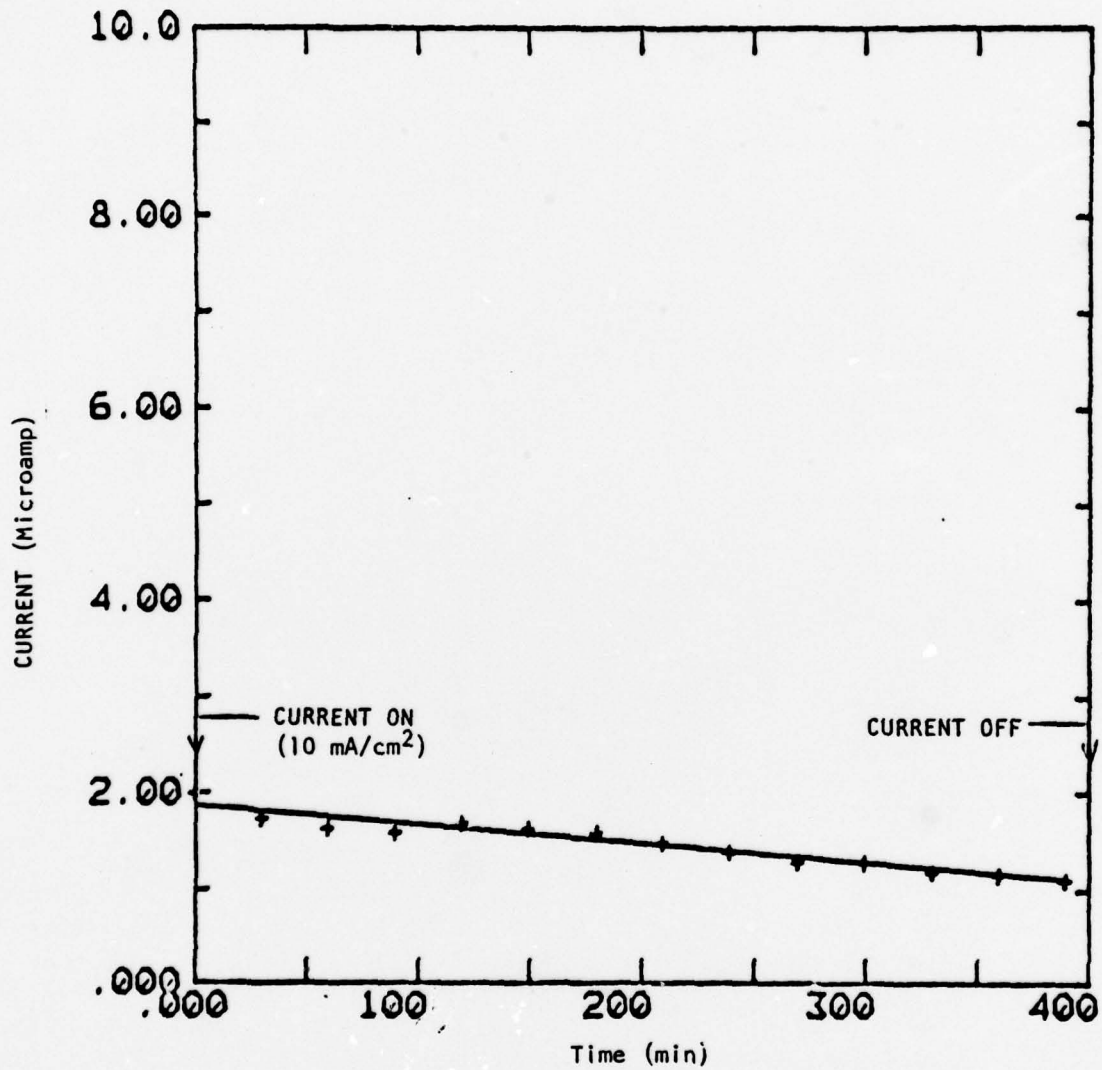


Fig. 19 Hydrogen permeation in AM355 stainless steel. Charging solution: 0.6N NaOH, 0.5N NaCN. Reference cell: 0.2N NaOH. Potentiostat at +100 mV vs SCE. T = 22°C.



8. H₂SO₄/Dichromate Method

As a result of the excellent bond durability and strength obtained using treatment 12e (MEK degrease; 30 v/o H₂SO₄40 w/o Na₂Cr₂O₇·2H₂O, 1 hr, 75 - 80°C, stir; DI rinse; N₂ blow dry) further investigation was warranted to determine the effect of varying certain parameters.

The most significant experiment was varying the temperature of the solution and the time of immersion, all else remaining as described above. Table V summarizes the results. All values are an average of two samples. As can be seen, it is not until relatively high temperatures (70 - 80°C) that consistently good results are obtained. It was observed that only at these temperatures was there a substantial color change on the surface of the metal for a 60 min immersion. In an attempt to obtain a correlation between bond durability and a simple measurement, SPD, PEE and ellipsometry (described in Section 3) were measured for each wedge test sample, the results of which are also given in Table VI. SPD shows a substantial decrease which correlates with the visual observation of surface color change. PEE begins to decrease at the same point. Ellipsometry shows that Δ values, at the lower temperatures, initially increase before decreasing. At the higher temperatures a substantial decrease from non-treated samples occurs within the first 30 min. A final point to note is the increase in wedge test values for 120 min immersion for all but those treated at room temperature. Although the number of samples was extremely limited this recurrence must be accepted as a valid indication that long immersion times, whatever the temperature, are detrimental to bond durability.



TABLE V
H₂SO₄/DICHROMATE
TIME AND TEMPERATURE VARIATION

Solution Temperature	Immersion Time (min)	Wedge Test in./24 hr, (cm/24 hr)	SPD (V)	PEE (nA)	Δ (deg)	ψ (deg)
Room Temp	0	2.5 (6.4)	0.07	0.90	111.5	31.6
	30	1.17 (3.0)	-0.62	0.62	117.5	30.9
	60	0.35 (0.89)	-0.58	0.50	116.8	31.2
	90	0.57 (1.4)	-0.68	0.50	119.0	30.8
	120	0.20 (0.51)	-0.65	0.52	118.8	31.0
40°C	30	0.40 (1.0)	-0.68	0.38	120.7	30.8
	60	0.14 (0.36)	-0.66	0.51	133.5	30.6
	90	0.16 (0.41)	-0.72	0.36	130.8	30.4
	120	0.20 (0.51)	-0.76	0.34	117.6	30.0
50°C	30	0.56 (1.4)	-0.56	0.48	120.3	30.4
	60	0.15 (0.38)	-0.68	0.35	128.6	30.4
	90	0.30 (0.76)	-0.66	0.45	110.3	28.8
	120	0.62 (1.6)	-0.70	0.62	94.0	27.2
60°C	30	0.17 (0.43)	-0.68	0.64	116.4	29.8
	60	0.14 (0.36)	-0.74	0.64	82.0	27.0
	90	0.05 (0.13)	-0.79	0.57	43.5	30.7
	120	0.32 (0.81)	-0.94	0.38	321.5	23.0
70°C	30	0.10 (0.25)	-0.80	0.33	53.2	29.0
	60	0.05 (0.13)	-0.90	0.18	314.8	20.4
	90	0.07 (0.18)	-0.94	0.14	56.9	22.2
	120	0.12 (0.30)	-0.92	0.17	57.2	21.5
80°C	30	0.14 (0.36)	-0.94	0.14	78.7	8.2
	60	0.07 (0.18)	-0.96	0.18	66.4	10.3
	90	0.06 (0.15)	-1.00	0.16	68	6.6
	120	0.12 (0.30)	-0.96	0.18	79	10



TABLE VI
VARIATIONS OF H₂SO₄/DICHROMATE (12e) TREATMENT

Variation From Treatment 12e		Wedge Test (in./24 hr)/ (cm/24 hr)/ (# samples)
Standard Method (12e)		0.057 σ = 0.032 (91) (0.14, σ = 0.08)
Delay before priming	24 hr	0.06/0.15/8
	7 days	0.09/0.22/3
	13 days	0.07/0.17/4
Delay before bonding	24 hr	0.05/0.13/2
	7 days	0.05/0.13/3
	13 days	0.05/0.13/4
Delay time between treatment and rinse	0.5 min	0.04/0.10/4
	1 min	0.04/0.14/4
	5 min	0.12/0.30/4
	10 min	0.06/0.15/4
Contamination	no degrease	0.10/0.25/4
	dip in stearic acid	0.10/0.25/2
	coat with LPS* (lubricant)	0.10/0.25/2
	dip in parafin oil	0.08/0.20/2
Damage treated surface	sand with fine grit	0.04/0.10/2
	sand with coarse grit	0.06/0.15/2
	scrape off top layer	0.05/0.13/2
	extensively scratch metal	0.04/0.10/2
Change time of immersion and solution temperatures	75°C, 55 min	0.05/0.13/3
	85°C, 65 min	0.03/0.08/3
	50°C, 60 min	0.10/0.25/4
	50°C, 120 min	0.12/0.30/4
	50°C, 180 min	0.14/0.36/4
No stirring of solution		0.06/0.15/4
Drip dry		0.07/0.17/2
Tap water rinse		0.04/0.1/2
No degrease, no stirring, tap water rinse, drip dry		0.05/0.13/4
No primer		0.27/0.69/8



Table VI lists wedge test results of sample where treatment 12e has been varied. As is listed in the table the average wedge test value using the standard method, an average of 91 samples, is 0.057 in./24 hr where $\sigma = 0.032$ (0.14cm/24hr, $\sigma = 0.08$). If a sample is treated, a delay of up to two weeks before priming or priming, curing the primer and then storing the sample prior to bonding, appears to be of no consequence. The effect of delay between the H_2SO_4 /dichromate bath and rinsing is ambiguous. It appears that a five minute delay leads to poorer bond durability than a ten min delay, although short delays (0.5 - 1 min) lead to excellent results. This experiment was done twice, the trends being the same each time. In order to test the need for the initial degrease step some samples were not degreased and others, to carry the test to extreme, were dipped or coated with various contaminating substances such as stearic acid, LPS (a greaseless lubricant) and paraffin oil. As can be seen in Table VI the H_2SO_4 /dichromate solution, especially at this elevated temperature, is very effective in removing contamination. Because of the possibility of a treated surface being scratched or somehow damaged either in transportation or when laying up pieces for bonding, tests were made where treated samples were sanded, scraped and scratched. There was no loss in bond durability due to this damage. More tests were also done where time of immersion and temperature of the solution were varied. Once again it was found that treatment at 50°C, regardless of the immersion time, is not as good as treatment at 75 - 80°C. The 55 min immersion at 75°C and 65 min immersion at 85°C was to demonstrate that by holding the time and temperature parameters at $80^\circ \pm 5^\circ C$ and $60^\circ \pm 5$ min, good results could be obtained. Finally, it was found that the solution need not be stirred, the samples could be rinsed with tap water (although because tap water



composition varies from local to local this should be taken with caution) and samples could be drip dried. The effect of primer was also studied. It was found that priming is very important, at least for bond durability.

T peel tests were run on samples given the standard treatment (12e) except the solution was not stirred. Table VII list the results. Samples 1 - 6 were prepared on a different day than samples 7 - 12. There is quite a discrepancy in actual peel strength. This may be more a function of adhesive properties or a mistake in curing the adhesive, for in both sets there was total cohesive failure.

TABLE VII
H₂SO₄/DICHROMATE T-PEEL* RESULTS

Sample	Kg/cm	lb/in.
1	2.2	12.1
2	2.0	11.0
3	2.0	11.0
4	1.9	10.4
5	2.0	11.0
6	2.0	11.2
		Avg 11.1 σ = 0.55
7	2.9	16.1
8	2.7	14.8
9	2.7	15.0
10	2.7	15.0
11	2.8	15.4
12	2.6	14.8
		15.2 σ = 0.50

100% cohesive failure for all samples.

*ASTM D 1876-72
0.009 in. x 1 in. x 12 in. (0.23 mm x 25.4 mm x 305 mm) samples



III. DISCUSSION OF RESULTS

1. Surface Treatments

Of the initial surface treatments tried, five produce exceptionally good surfaces for forming strong durable bonds. They are:

1. H_2SO_4 /dichromate (12e)
2. H_2SO_4 /dichromate anodize (2)
3. H_2SO_4 etch - HNO_3 /dichromate passivate (13b)
4. HNO_3 /dichromate (9f)
5. HNO_3 anodize (10)

the number in parenthesis corresponds to the treatment number given previously.

Of these five methods, the H_2SO_4 /dichromate immersion (12e) and the HNO_3 anodize (10) seem to be the most promising. The H_2SO_4 /dichromate anodize (2) offers no advantage over simple immersion in the solution. Treatment in a HNO_3 /dichromate solution (9f) produces bonds which are not quite as durable as bonds prepared from samples treated with either of the two optimum methods. The H_2SO_4 etch - HNO_3 /dichromate passivate (13b) process is not as attractive because of the multiple treatment steps required, and as a consequence, increased production cost, with no benefit of increased bond durability and strength.

All but the HNO_3 anodize method require elevated temperatures which, because of the carcinogenic nature of dichromate fumes and energy requirements



for heating large amounts of solution for industrial application, may make them somewhat less attractive than the HNO_3 anodize which can be done at room temperature. Nitric acid fumes, even at room temperature and the concentration used (50 v/o), are still a problem, though not nearly as great. The energy requirement for anodizing ($3\text{mA}/\text{cm}^2$, $\sim 1\text{V}$) is also not nearly as great as the energy needed to heat tanks of solution.

Suitable tanks for solutions must also be considered. Stainless steel passivates in the presence of nitric acid and nitric/dichromate solutions. Sulfuric acid/dichromate solutions attack stainless to a degree, seen by the increased grain boundary corrosion noted previously, although the effect of longer term exposure is not known. A tank lined with lead or other inert coating (e.g., teflon) may be necessary, or perhaps some sort of cathodic protection, i.e., polarizing the tank at some potential to inhibit corrosion.

Disposal of rinse water might also be a problem when using dichromates, depending upon the number and size of pieces being processed daily. An initial "rough" rinse may be possible, where one tank is repeatedly used as an initial rinse to remove most of the acid, dichromate solution although such experiments have not been done.

The sulfuric acid dichromate solution is more difficult to prepare than the nitric acid solution. It was found that the acid must first be added to the sodium dichromate, a slurry made, following which water is added. If water is added first to the dichromate, then acid added, the dichromate will not completely dissolve. The reason for this is not known conclusively but



perhaps the high temperatures generated by mixing in the former manner is needed, although heating a solution to $\sim 100^{\circ}\text{C}$ prepared this way did not dissolve the dichromate after four hours. The cost of the H_2SO_4 /dichromate solution is also considerably greater than the HNO_3 solution. To give a rough indication of the difference, using prices from a chemical supply company for comparable amounts, the sulfuric/dichromate solution is 2 - 3 times more expensive.

Quality control of the solutions and solution life are still other problems to be addressed. One sulfuric acid/dichromate solution was used on and off for about six months. There was some precipitate formed which accumulated in the storage bottle but good results were consistently obtained using the solution. No tests were made to determine amounts of species (CR(VI), CR(III), dissolved Fe and other contaminants) present since no loss in bond durability and strengths as a function of solution age had been observed. Snogren⁽⁴⁾ in his book lists quality control methods for chromate and acid solutions which could be employed. Tracking bond strengths as a function of concentration of the species of interest should eventually yield information on when the solution needs renewing. Monitoring the oxidation power of the solution might be another method. This is done by measuring the potential between a reference electrode (e.g., saturated calomel) and a platinum electrode.⁽¹⁰⁾



2. Adhesives and Primer

Primer thickness and curing conditions of the primer and adhesive are very important for optimum bond results. It was found that air drying the primer for time as short as 1 hour prior to curing resulted in poor adhesion between the primer and adhesive. A 30 min air dry is now specified by the primer manufacturer as well as the helicopter manufacturer. Curing the primer at a lower temperature or shorter time than specified (30 min; 120°C, Hysol; 150°C Hughes) also resulted in poor primer-adhesive adhesion. This was determined by noting the distance between the initial crack tip and the wedge on wedge test specimens. On a normal sample, the crack would begin 0.7 - 0.8 in. (1.8 - 2.0 cm) from the end of the wedge. When the initial crack would exceed that, sometimes up to 1.3 in. (3.3 cm), it would invariably be found, upon splitting the sample, that there was much primer-adhesive interfacial failure. It is, of course, important to take the initial distance of the crack from the wedge into account when comparing wedge test results. A crack that began 0.2 in. (0.5 cm) farther from the wedge would have considerably less force on it than a normal sample and, therefore, all else being equal, would be expected to not propagate as far. The initial crack length was not reported in this report for it was for the most part constant as mentioned above. Thickness of the cured primer is designated to be 0.1 - 0.3 mil (0.00025 - 0.00076 cm). It was found that fairly thick coats of primer did not affect the wedge test results but too thin of a coat and no primer produced increasingly poorer results. Unfortunately, no complete set of experiments have been done to correlate primer thickness and crack growth. Baking the primer too long also appeared to have no effect on the wedge test.



The adhesive curing cycle and pressure are also important. The differences between the T-peel results (Table VII) for the two groups of samples may have been caused by pressure differences resulting in bond line thickness differences.

Although beyond the scope of this project, determination of and adherence to primer and adhesive parameters are extremely important for obtaining optimum bond strength and durability.

3. Hydrogen Permeation

It was found that AM355 is not susceptible to hydrogen permeation. Experiments determined that the diffusion coefficient for hydrogen in AM355 is extremely small, so that one can safely assume that in the time a surface treatment is administered, essentially no hydrogen would (if present) diffuse into the metal. The method used for this study is sensitive to 0.1 ppm of hydrogen.

4. Chemistry and Morphology

The chemistry and morphology of treated surfaces will be discussed only with regard to their effect on bond durability and strength.

It was found that only surfaces which had significant chromium enrichment also yielded the most durable bonds. This is probably because of the corrosion resistance of chromium oxides as compared to iron oxides. XPS showed that the chromium exists as Cr(III), except for a small amount of Cr(VI) found on H₂SO₄/dichromate (12e) treated samples, which possibly was



adsorbed onto the surface. These chromium rich oxide films can be formed by two mechanisms. The first, and most probably predominant, is that at very low pH's and in solution of high oxidizing power the stable species is a mixed chromium-iron oxide. XPS suggests this mixed oxide because of the large amount of Fe(II) consistently present. Observing, using XPS, the composition of these oxides as functions of potential, pH and dichromate concentration might help elucidate the nature and composition of this stable oxide. Another possibility is that at the low pH, highly polarized state the steel is in, iron and iron oxides form and dissolve much faster than chromium oxide, and Fe(II) slower than Fe(III). At the same time it becomes increasingly passive. The passive film might then consist of Cr_2O_3 , Fe_2O_3 and Fe_3O_4 oxides. The other mechanism possible, particularly in the H_2SO_4 /dichromate immersion (12e) is that Cr(VI) oxidizes metallic iron which in turn dissolves off leaving reduced Cr(III), or Cr_2O_3 at the surface. This seems feasible in light of the Cr(VI) found on the surface by XPS. The HNO_3 anodize and H_2SO_4 /dichromate anodize though do not show any Cr(VI) present but do show almost the same amount of chromium present on the surface (Table IV). In fact, if one were to subtract the Cr(VI) contribution to the total Cr present on the H_2SO_4 /dichromate treated surface, the Cr/Fe ratios would be fairly comparable. This would seem to indicate that this mechanism is not as probable as the first.

AES data for surfaces treated with HNO_3 , HNO_3 /dichromate and HNO_3 anodizing are probably best for demonstrating the effect pH and polarization have in determining oxide composition. AM355 is polarized at a more noble



potential when immersed in the HNO_3 /dichromate solution than when in HNO_3 alone, and shows a greater degree of chromium enrichment. Since the outer oxide layer is not the point of maximum enrichment it seems probable that dichromate does not actually react at the surface and become incorporated into the film. When the steel is anodized (i.e., potentiostated) in HNO_3 at the potential it is at when in the HNO_3 /dichromate solution, significantly greater chromium enrichment is found. Oxide thickness of the potentiostated sample is also very close to the thickness of the film formed in the dichromate solution, which is much thicker than the film formed in HNO_3 alone.

The contribution of surface roughness to bond strength and durability is not completely understood. Roughness certainly will increase the actual surface area. A difference in actual surface area of an order of magnitude is easily possible comparing polished and microscopically roughened (e.g., by anodizing) samples of equal dimensions. Since adhesion depends upon intermolecular attractions between the adhesive and substrate such an increase would have to be beneficial. Of course, once the ultimate strength of the adhesive is exceeded, i.e., completely cohesive failure, any effort to increase bonding is superfluous. Roughness also aids the wettability of the substrate by the adhesive. The more wettable a surface the more actual intimate contact the adhesive will make with the substrate and as a result the stronger the bond will be. The only possibility roughness has to increase bond durability is if a mechanical interlock type effect won't allow the adhesive to pull away from the oxide when the bond is under stress.



As was seen in the SEM studies very few of treated samples exhibited a large degree of roughening, and those that did showed no increased bond durability because of it. Etching in H_2SO_4 is perhaps the best example. Experiments were done where AM355 was etched for various lengths of time in sulfuric acid. Wedge test results were extremely poor in all cases. When similarly etched samples were subsequently passivated in HNO_3 /dichromate bond durability was almost as good as any other method. Anodizing in H_2SO_4 dichromate greatly increased the roughness but produced less durable bonds than those simply immersed in the same solution which showed only some grain boundary corrosion. The HNO_3 /dichromate (9f) treated samples showed very little difference in roughness from untreated samples yet formed extremely durable bonds.

It is evident from these results that bond durability is dependent far more on surface chemistry than roughness for AM355 but that roughness probably aids in total strength of the bond.

5. Surface Properties

SPD, PEE, θ_{H_2O} and ellipsometry are all simple measurements to make which can give information as to the nature of the surface. Since the use of different treatments produces widely varied surfaces, chemically as well as morphologically, as seen in the previous section, it is not surprising that there is no general correlations between any one of these measurements with bond durability and strength. However, surface characterization is reproducible for any particular surface treatment and can be used for quality assurance by nondestructive inspection.



Surface property measurements on samples exposed to the H_2SO_4 -dichromate solution for varying time and temperature yield some general information. Even short exposure at room temperature produces a substantial improvement in wedge test results and fairly dramatic changes in SPD and PEE. Visual inspection shows that not until long exposure time, 120 min at $50^\circ C$ and >30 min at $60^\circ C$, are there visual changes on the surface. Above $60^\circ C$ color of the surface appears in less than 30 min. Ellipsometry shows that Δ and Ψ values begin to change rapidly at the same points, as well as PEE and SPD decreasing rather abruptly. A rise in Δ values indicate a decrease in film thickness indicating that at low temperatures and/or short exposure time the H_2SO_4 -dichromate solution is attacking the original outer layer. The drop in Δ then corresponds to an increase in film thickness, corresponding to the change of colors of the surface. The color change follows the sequence expected using an interference step chart. At the higher temperatures the initial decrease in film thickness is completed before 30 min. It may be that this initial decrease is due more to the removal of a contaminant layer than attack of the original oxide. The other possibility is a rapid dissolution of surface iron oxide followed by slower oxidation - dissolution of metallic iron.

6. H_2SO_4 /dichromate Process

Using method 12e the average obtained on 92 samples in the wedge test was 0.057 in./24 hr, $\sigma = 0.032$ (0.14cm/24hr, $\sigma = 0.08$). For five samples given the stress durability test at $60^\circ C$, 100% RH and 2000 psi (13.8 mPa), the average time to failure was 499 hours.



Many parameters involved in the H_2SO_4 /dichromate immersion method (12e) were explored to find out which were necessary or what degree of control was needed in order to obtain consistently good bonds.

It was found that high temperatures ($>70^\circ C$) are needed in order to obtain maximum strength and durability. Immersion times of about 60 min gave the best results. There seemed to be no problem delaying between treating and priming and bonding, delays of up to two weeks showed no adverse effects.

A rather strange effect was found in the effect of delay time between removal from the H_2SO_4 /dichromate bath and rinsing. Delays of 0.5, 1, and 10 min showed no effect but a delay of 5 min produced a weaker bond. This experiment was done twice on two different days using duplicate samples, the trend in bond results being the same each time. More work should be done to further investigate this.

Contaminating the surface prior to treatment proved that the method is quite effective in removing such. Damaging the surface layer by scratching, scraping and sanding also had no effect on bond durability.

It was found that stirring of the solution was not necessary and that the samples could be drip dried after the final rinse. Tap water rinsing showed no adverse effect but because of the variability of tap water from one location to another one would have to repeat this experiment at the location where the process would be used.



Incorporating all these final results, it was found that samples not initially degreased but immersed in 75 - 80°C, 30 v/o H₂SO₄/40 w/o Na₂Cr₂O₇·2H₂O for 60 min, rinsed with tap water and air dried yielded as good wedge test results as using any other set of parameters.

Finally, it was found that primer is necessary for optimum results.

7. HNO₃ Anodize Process

Bond durability using the HNO₃ anodizing treatment was excellent. Wedge test results were about 0.05 in./24 hr (0.13cm/24hr). The average time to failure for samples given the stress durability test at 60°C, 100% RH and 2000 psi (13.8 mPa) was 523 hours using a room temperature anodizing treatment (10e).

Anodizing AM355 in 50 v/o HNO₃ at low potentials (~ 1 V) and small current densities (~ 1 - 5 mA/cm²) produces surfaces which give optimum bond durability and strength.

Preliminary experiments show that anodizing at room temperature is as effective as when elevated temperatures (75 - 80°C) are used. Current densities as low as 1.5 mA/cm² produced wedge test results of 0.03 in./24 hr. (0.08cm/24hr). Lap shear values were also extremely high for samples prepared in this manner.



IV. CONCLUSIONS

1. The optimum surface treatments considering bond results, cost and simplicity are the H_2SO_4 /dichromate immersion (12e) and the HNO_3 anodize (10e). Preliminary experiments indicate that the HNO_3 anodize is the best choice of treatments considering all factors.
2. Bond durability using the above methods is far greater than any literature values and is much greater than bonds prepared using the current method (Hughes procedure HP4-121).
3. Increases in bond durability have been found to be a function of the increased chromium content of the oxide layer. Treatments which produce such enrichment show dramatic improvement in stress humidity and wedge tests. The thickness and roughness of the oxide layer does not seem to be as important as its chemical composition.
4. Although optimum bond durability and strength cannot be determined using a simple surface measurement such as SPD, PEE, ellipsometry or θH_2O , such measurements might be used to show certain treatment errors and can be used for quality assurance of the surface treatment.
5. It was found that the diffusion coefficient for hydrogen in AM355 is extremely small, in fact unmeasurable using a method sensitive to 0.1 ppm of mobile hydrogen. This implies that even if hydrogen were produced at the surface relatively none would be incorporated into the metal.



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