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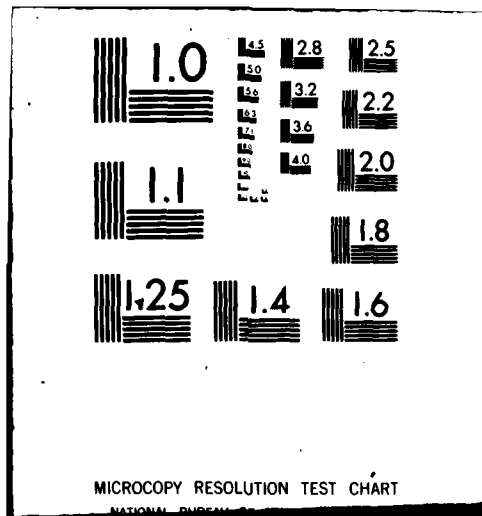
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**ADHESIVE BONDING EXPERIMENTS FOR TITANIUM 6
ALUMINUM 4 VANADIUM (Ti6Al4V)
Part I. Anodization Treatments**

WILLIAM L. BAUN

*MECHANICS & SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION*

DECEMBER 1979

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Final Report for period July 1978 to August 1979

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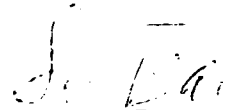
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Evaluations of surface treatments for adhesive bonding of Ti6Al4V were carried out using lap shear, peel and thick-thin wedge tests. Anodization to form dense oxides from 100-3000 A in thickness had little effect on bond strength or durability. Properties were governed by chemical pretreatments. Fluorine present in the anodization bath can cause oxide/alloy failures and should be avoided.			

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Part I

FOREWORD

This technical report was prepared by W. L. Baun, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (AFML/MBM), Wright-Patterson Air Force Base, Ohio. This work was initiated under Project 2419, "Nonmetallic and Composite Materials" and was administered by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The Work Unit Monitor is Dr. T. W. Haas.

This report covers work conducted inhouse during the period July 1978 to July 1979.

The author is grateful to James S. Solomon for the Auger electron spectra. Donald Thomas is thanked for his careful experimental work on some of the anodizations.

The work of A. K. Behme, Jr., in bonding and testing specimens was invaluable in the evaluation of surface treatments.

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SECTION I

INTRODUCTION

The need for lighter, higher strength structures makes it necessary to develop new methods of joining materials such as by adhesive bonding. Adhesive joints possess a more uniform stress distribution, are lighter, and are better sealed against corrosion than conventional joints. Titanium and its alloys, because of their lightweight, thermal stability and high strength, are in use in numerous applications and are development for further aerospace applications. Conventional methods of joining titanium alloys such as welding, bolting, and riveting are used, but reliable methods of joining titanium alloys by adhesive bonding must be developed. McDevitt and co-workers^{1,2} have shown that the surface composition of many aluminum alloys bears little resemblance to the bulk composition. Segregation during heat treatment, preferential dissolution, and impurities left behind by surface preparations can either improve or degrade the properties of that surface for adhesive bonding. Aluminum alloys, currently the most popular material used, lose temper and soften at elevated temperatures. Titanium and its alloys are used and are under consideration for further use in the aerospace industry, because of its potential operation at higher temperatures. The operation of the adhesive bond in temperatures near 350°F places a severe burden on both the adhesive and the interfacial region between the adhesive and adherend in the joint. Joint failures under adverse conditions have often been blamed on the adhesive, but is quite possible that the interfacial region governed by the surface preparation on the adherend may also contribute to such failures. Chemical treatments have been developed to give optimum bonding surfaces which produce durable bonded joints. This involves creating a

surface of the proper structure and surface roughness and also the correct chemistry to insure long-time durability under operating conditions. Reports from this laboratory^{3,4,5} have shown the results of surface analysis for treatments on titanium and titanium alloys such as stripping of the natural oxide, preparation for anodization, and other treatments which replace the natural oxide with a chemically-formed oxide or conversion coating which is bondable and durable.

In this work, we are investigating the possibility of combining certain pre-treatments with anodization to provide a bondable, durable surface. Anodization on titanium and other valve metals is attractive, because it lends itself to the technology already developed for aluminum alloys. In addition, oxides on alloys from several hundred to several thousand nanometers in thickness produce brightly colored films which may be used as an aid for inspectability and other non-destructive examination applications. Anodized films also are exceptionally uniform in thickness and provide galvanic corrosion resistance to other metals in contact with titanium. The latter advantage is seldom considered since titanium itself is so corrosion resistant. Anodized films also may provide reproducible and stable carriers for additives in the film to be used for adhesive bonding. This may be especially true for the formation of one of the forms of TiO_2 , anatase, which contains a large number of vacancies and these sites could be available for additive ions. Anodization of titanium is easily carried out in acidic, neutral, and basic aqueous solutions. In addition, titanium and its alloys may be anodized in non-aqueous solutions, such as liquid salts (eutectics) at elevated temperatures and various salts in non-aqueous media such as ethylene glycol.

SECTION II

EXPERIMENTAL

1. SURFACE CHEMICAL TREATMENTS

Chemical pre-treatments and anodizations were carried out on samples for peel, lap shear, and wedge opening testing. In order to conserve space, each of the steps in the preparations are given a code number. This code number is identified in Table 1. A typical treatment might consist of cleaning with an abrasive pad plus detergent, etching with hydrofluosilicic acid, anodizing with phosphoric acid at 30 volts, followed by a warm water wash. This preparation then, based on the data in Table 1, would be shown as 1, 3, 4, 11. All chemicals were of reagent grade quality.

2. EQUIPMENT

a. ISS/SIMS

The primary characterization techniques used were ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS). This dual method uses a low energy beam (1 to 3 keV) to probe the surface. The ISS method (3M Company, St. Paul, Minnesota) measures the energy loss when the probing ion scatters from the outermost layer at the surface. The SIMS technique⁷ measures the mass spectrum of the sputtered ions which are removed from the surface by the primary ion beam. Advantages and operating parameters were outlined in an earlier report⁸ and the experimental setup was shown in earlier reports^{3,4,5}. Appendices of mass and scattering information appear in this report and are also included in earlier reports on titanium to aid the reader in spectral interpretation.

b. AES

Auger Electron Spectrometry (AES)⁹ is based on a process of radiationless de-excitation of an excited atom by

TABLE I
KEY FOR IDENTIFICATION OF
SURFACE TREATMENTS OF Ti 6-4

<u>Code Number</u>	<u>Treatment</u>
1	Abrasive Pad* & Detergent
2	Etch 2 min, R.T. 170 ml HNO_3 , 30 ml HF 800 ml H_2O
3	Etch 2 min, R.T. 15% Hydrofluosilicic acid
4	30v Anodize, 0.1 m H_3PO_4
5	60v Anodize, 0.1 m H_3PO_4
6	100v Anodize, 0.1 m H_3PO_4
7	150v (sparking) 2.0 m H_3PO_4
8	30v Anodize, 0.05 m NaOH
9	60v Anodize, 0.05 m NaOH
10	100v Anodize, 0.05 m NaOH
11	Warm tap H_2O wash, 5 min.

*3M Brand "Scotchbrite"

emission of electrons. This mechanism is often more probable than the radiative de-excitation by emission of an x-ray. For the matrix and alloy elements of concern in this work, the Auger electron yield per K electron vacancy is much higher than for the other mechanism of de-excitation (x-ray emission). The instrument used in this work is the Model 540 thin film analyzer (Physical Electronics, Inc., Eden Prairie, Minnesota).

SECTION III

RESULTS AND DISCUSSION

1. LAP SHEAR TESTS

Samples were prepared using various of the procedures outlined in Table 1 on titanium 6 aluminum 4 vanadium for testing by lap shear, crack extension tests and Bell peel. Lap shear specimens were prepared and bonded with B. F. Goodrich 729-3 adhesive. The standard 1/2 inch overlap lap shear specimens were tested in a Tinius Olsen machine using a crosshead speed of .02" per minute. A summary of lap shear data is shown in Figure 1. Here the ultimate strength and bond breakage is shown for several surface treatments which are noted within the boxes. These results indicate that the etch appears to dominate the properties of the anodized film and that the anodized oxide generally does not improve lap shear strength. The hydrofluosilicic acid seems more effective alone or as a pre-treatment for anodizing than does the combination of HNO_3 and HF pre-treatment. Based on the lap shear strength values, there would seem to be no point in anodization. The only positive aspect to anodization is found in the formation of brightly colored oxides which are an aid to diagnoses of bond failure. In this region of oxide thicknesses used for this group of specimens the colored films make the locus a failure quite obvious. There is no confusion as to whether the failure took place at the adhesive oxide interface or at the oxide/alloy interface as sometimes happens in the aluminum system where the aluminum oxide is colorless. All of the oxides in this series are of the dense variety, except for No. 36 which was formed in two molar phosphoric acid at 150 volts during sparking. Under these conditions a very porous film is formed, (perhaps crystalline) such as that shown in the scanning electron micrograph in Figure 2. Even though this oxide film is morphologically

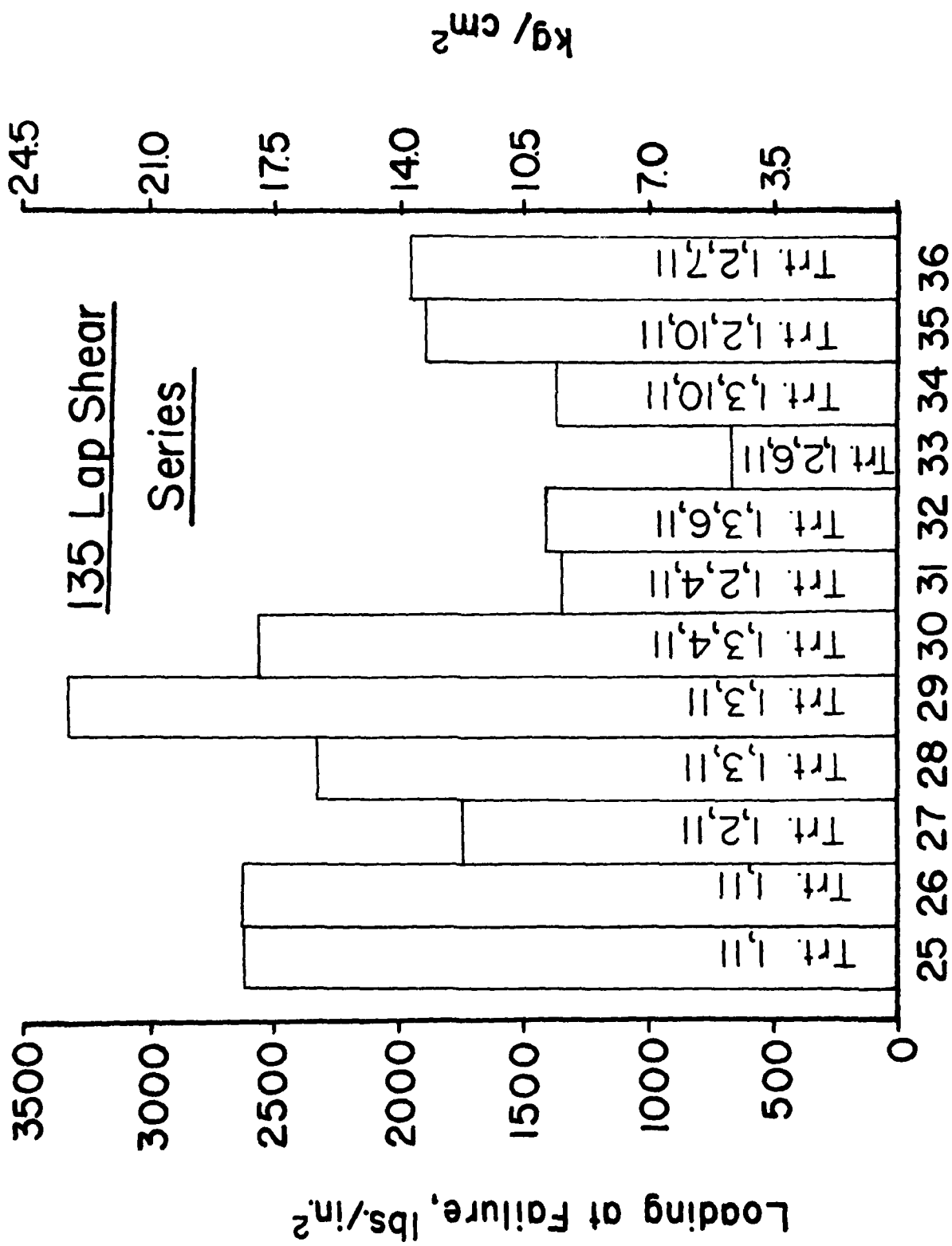


Figure 1. Lap Shear Data for Specimens Given Treatments
Shown in Table I.

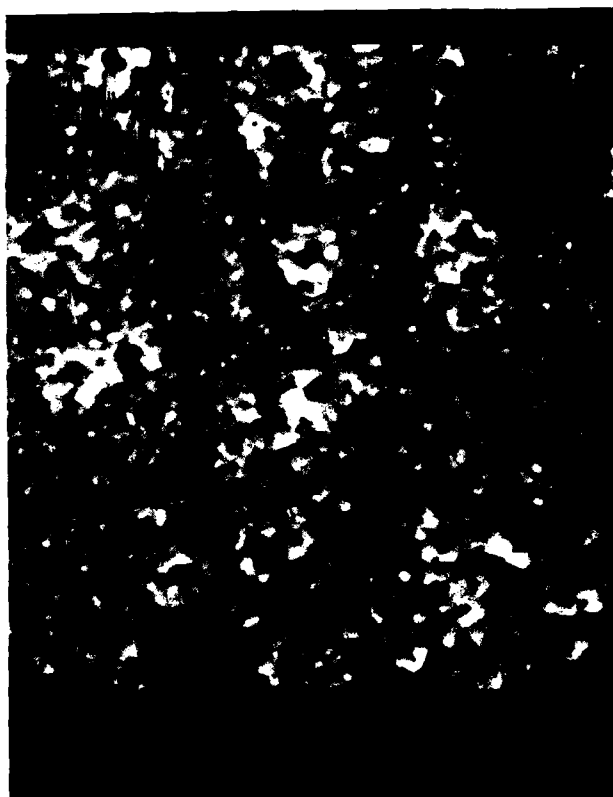


Figure 2. SEM Photograph of Porous Oxide Formed at 150V in 2.0M H_3PO_4 .

much different and undoubtedly allows for much greater penetration in the adhesive, the ultimate strength of the joint was still approximately the same as for the other anodization treatments and somewhat less than for surfaces which were only cleaned.

2. PEEL TESTS

A standard Bell test was conducted. The specimens consisted of one thick specimen approximately 0.04" (1mm) in thickness and one thin specimen approximately 0.02" (0.5mm) in thickness which were etched in the etches shown and then 1/2 of each specimen was anodized. The concept was to etch the first half of the specimen to establish the peel strength of the etch only, then to see if the anodization improved or degraded the peel strength. In each case, performance was degraded by anodization in one tenth molar phosphoric acid. The exact amount of degradation was not determined since the test operators did not allow the peel to proceed beyond the point at which the peel strength dropped as the failure passed through the anodize. At that point, the test was terminated for every specimen rather than allowing the test to continue so that the peel strength could be determined both for the anodized and for the etched specimen. Only these thin anodized films formed in phosphoric acid were evaluated. No other thicker or porous films as formed in phosphoric acid were evaluated in this series or films formed in other electrolytes. A method to produce porous films at low voltages has been developed and will be reported separately¹⁰. Peel tests over the whole specimen on other anodized specimens showed average results such as shown in Figure 3, where peel strength was either approximately the same (solid curve) or slightly decreased (dashed curve) in the anodized area.

3. CRACK EXTENSION TESTS (WEDGE)

Crack extension tests were carried out on unequal thickness adherends¹¹, one adherend being one half the thickness of the other. This thick/thin crack extension test was used in an

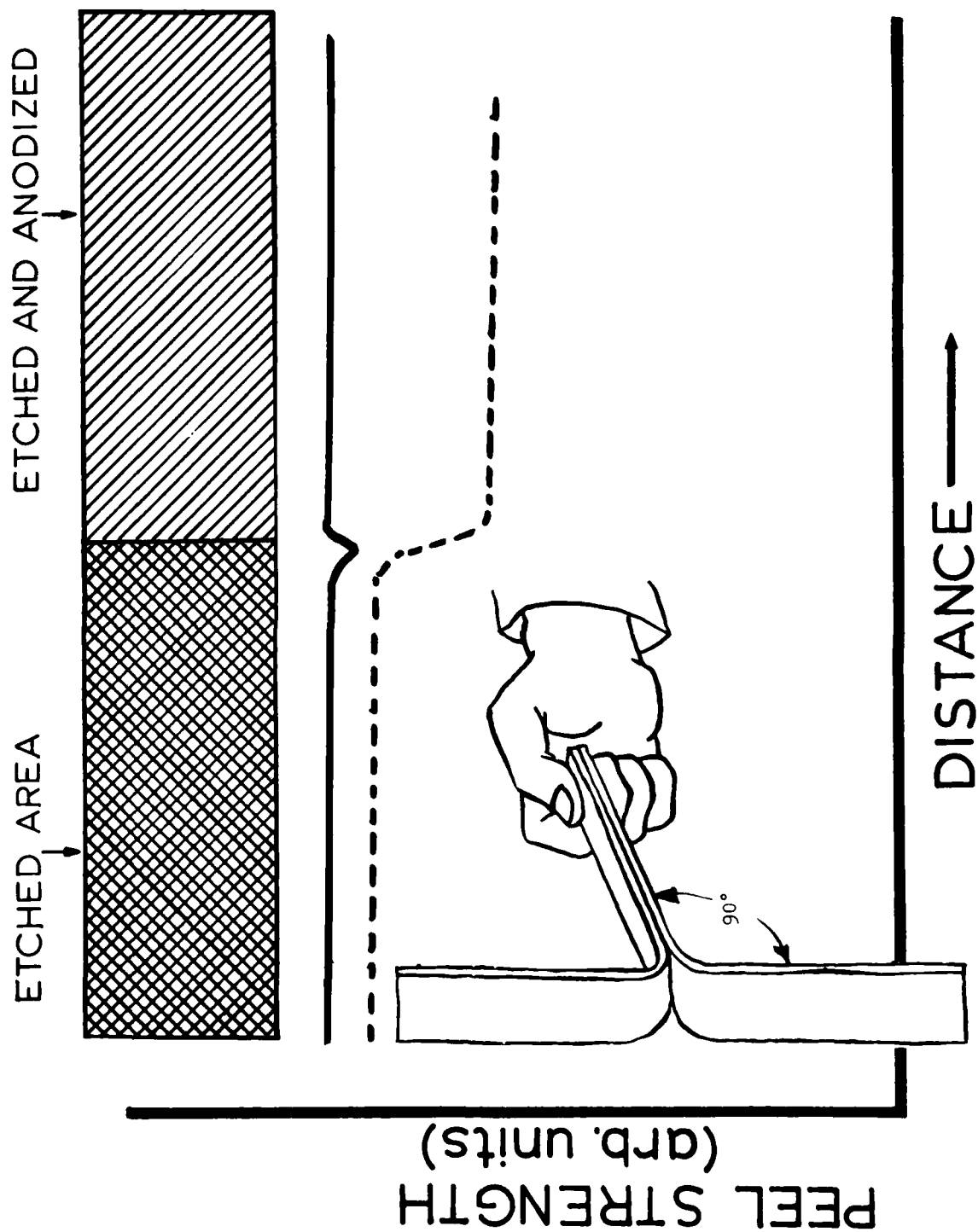


Figure 3. Typical Peel Performance of Specimen Etched Over the Whole Surface and the One Half Anodized.

effort to drive the failure to the interface. In typical thick adherend crack extension tests on well prepared surfaces the locus of failure is often directly down the center of the bond line resulting in cohesive failure in the adhesive. This offers little in the way of a test of the surface preparation of the adherend. The surface preparation of this set of adherends (135) consisted of the pre-treatments shown along with anodization in an acid media (phosphoric) as shown earlier and, in addition, anodization in a basic media (sodium hydroxide). The results of these crack extension tests are shown in Figures 4 through 7. Again, as in earlier testing, the hydrofluosilicic acid appeared to provide the best pre-treatment giving best original bondability and least crack extension. Unlike the phosphoric acid anodize, however, the sodium hydroxide anodize appeared to provide some beneficial aspects to the bonding of titanium in this set but little effect due to oxide thickness was seen. In these figures, the total crack extension during the duration of the test at 160°F. and 95% relative humidity is shown. Intermediate points were within the envelope shown in the figures. In addition to providing the smallest amount of crack propagation during the test, the combination of the hydrofluosilicic pre-treatment and the sodium hydroxide anodize also provided the smallest amount of crack opening upon wedge insertion, suggesting best initial adhesion. Overall performance was largely governed by the pre-treatment.

The crack extension test specimens were examined by ISS and SIMS, and provided interesting results. Specimen 135-11 was prepared by an abrasive pad plus detergent followed by the nitric/hydrofluoric acid etch and a 60-volt anodization in .05 molar sodium hydroxide. Most failure in this specimen was at the oxide adhesive interface. One patch on the specimen of several square centimeters, however, appeared to be interfacial failure at the oxide/alloy interface. ISS and SIMS data for these two surfaces, one from the thin specimen and one from the thick specimen, are shown in Figures 8 and 9. Note that even though the etching step using hydrofluoric acid appeared before

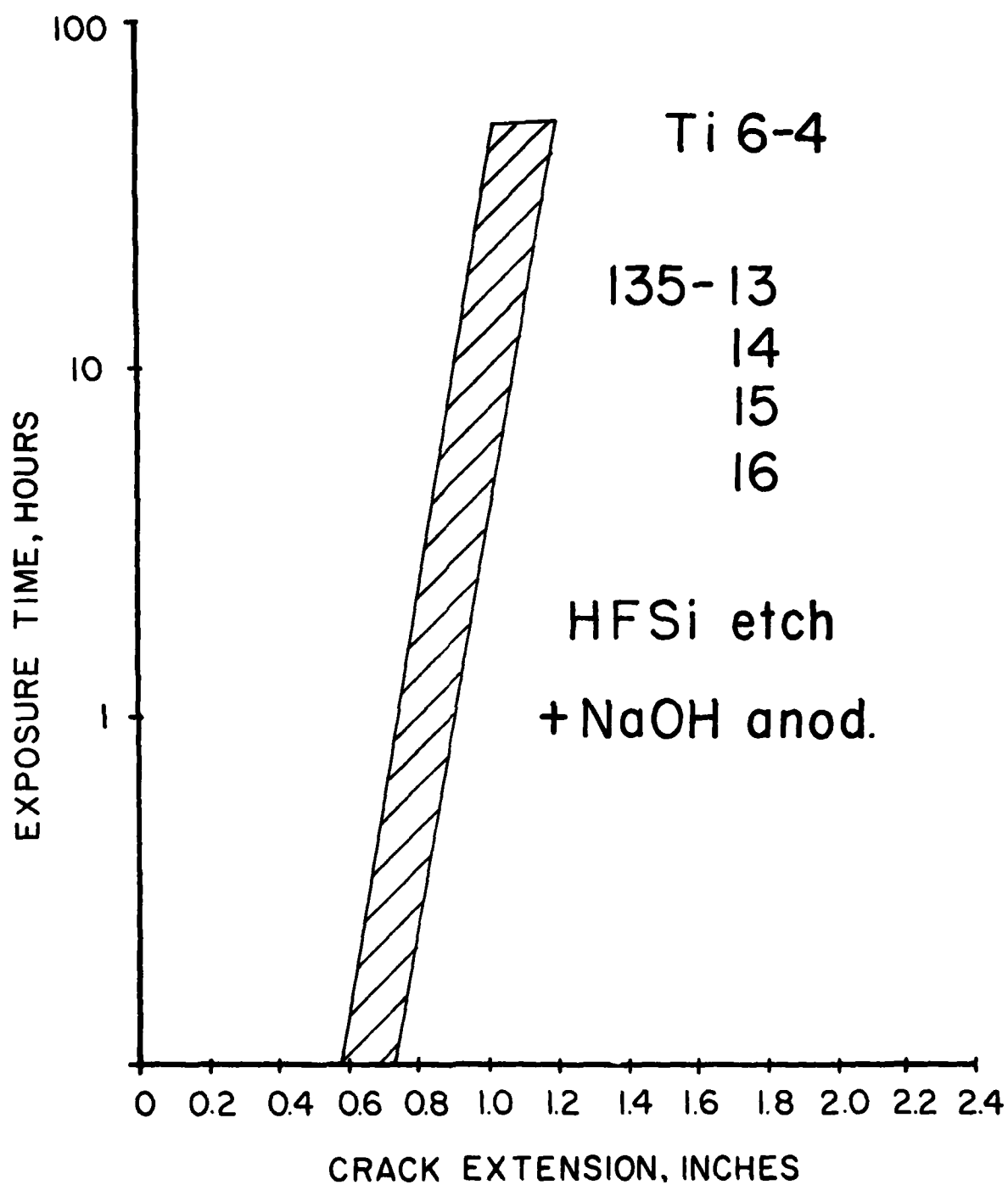


Figure 4. Initial and Crack Growth Data for Thick-Thin Wedge Test of Ti64 Held at 95% Relative Humidity and 160°F. Samples Cleaned, Etched for 2 Minutes in 15% Hydrofluosilicic Acid, and Anodized at Potentials Between 10 and 100 Volts in 0.05M NaOH.

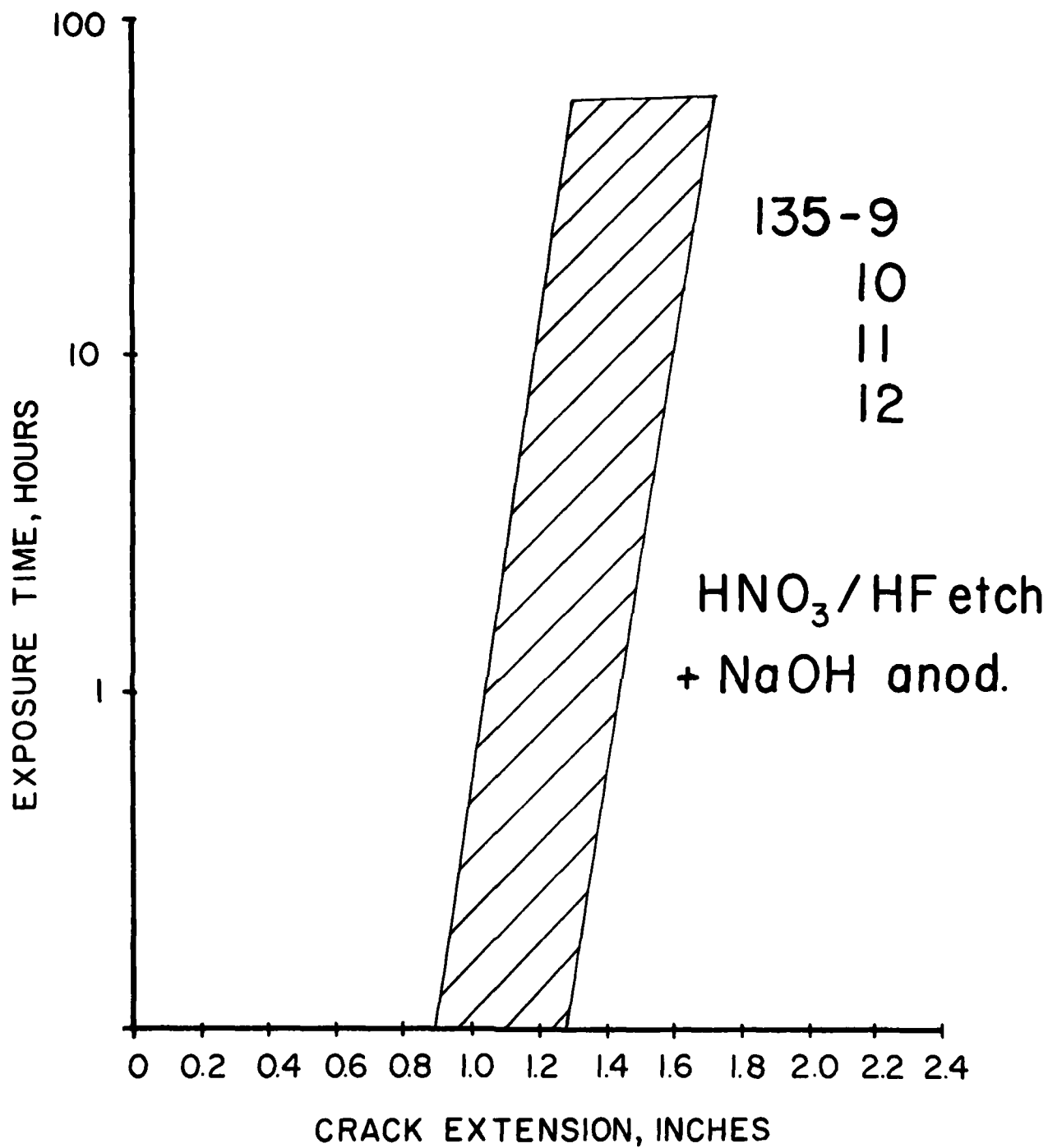


Figure 5. Data as in Figure 4 for Samples Cleaned, Etched for 2 Minutes 30 ml HF, 170 ml HNO₃, 800 ml H₂O, and Anodized in 0.05 NaOH at Potentials Between 10 and 100 Volts.

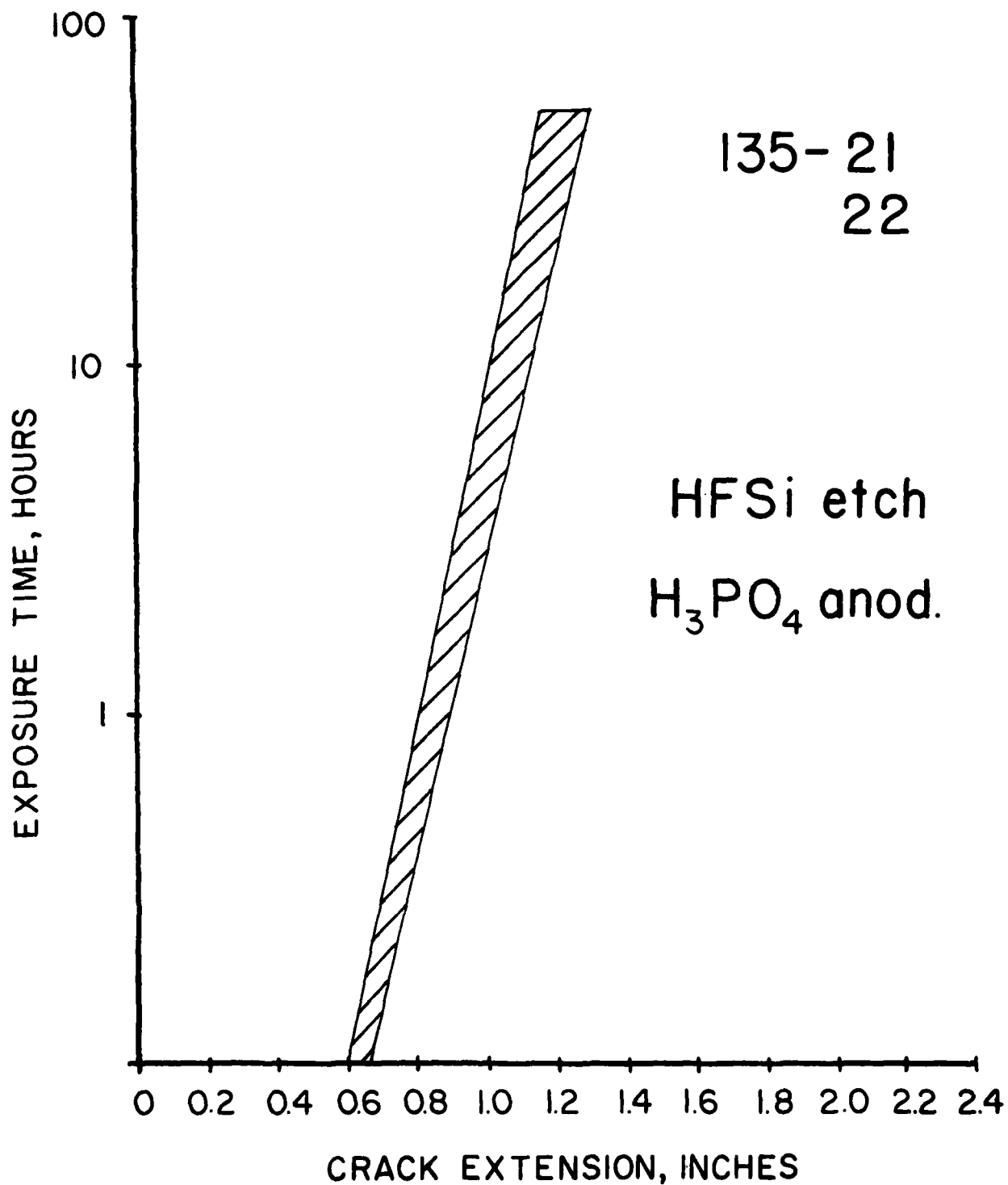


Figure 6. Data as in Figure 4 for Samples Cleaned. Etched in 15% Hydrofluosilicic Acid for 2 Minutes and Anodized in 1.0M H_3PO_4 at Potentials Between 10 and 100 Volts.

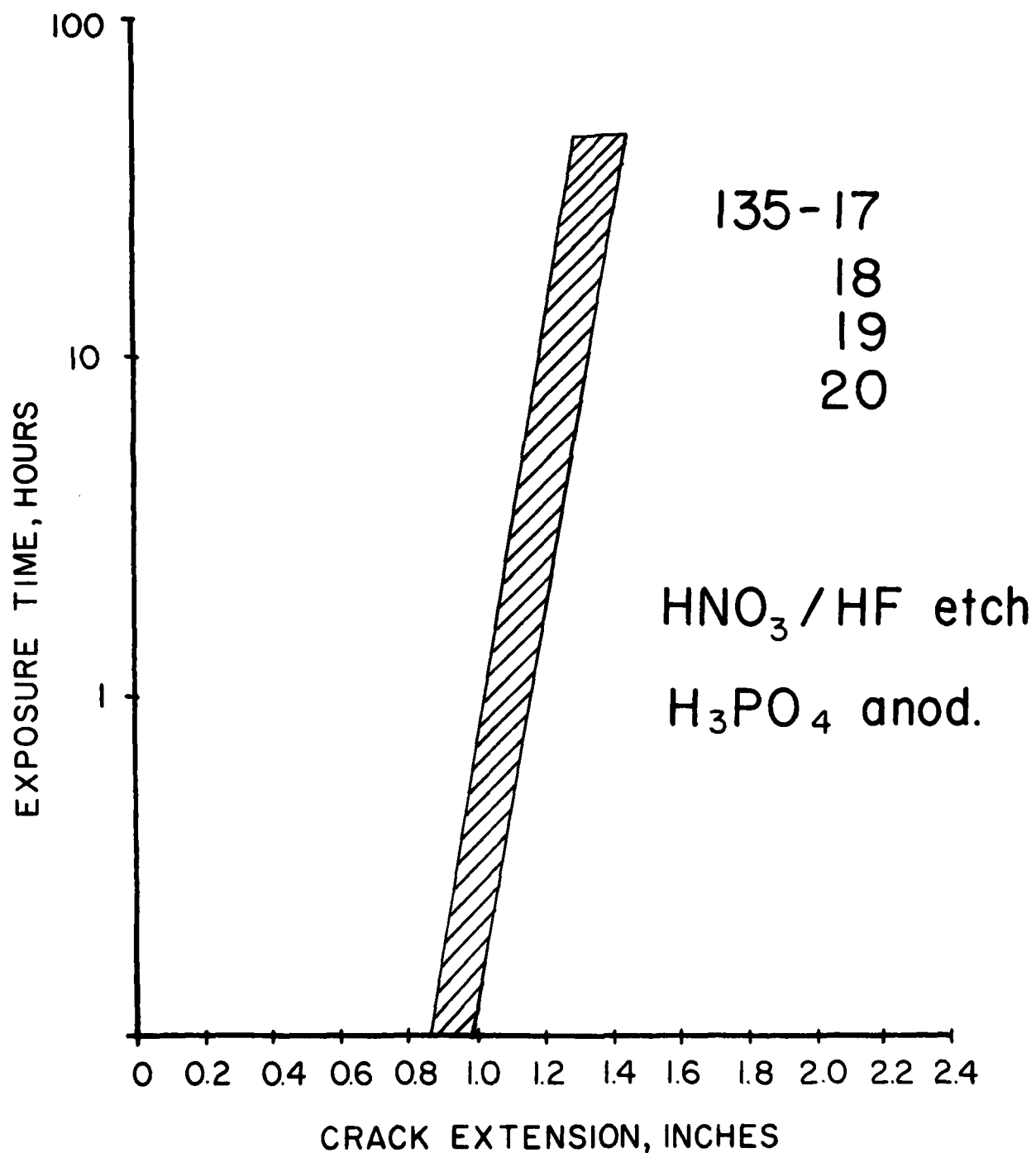


Figure 7. Data as in Figure 4 for Samples Cleaned, Etched in HF/HNO_3 , and Anodized in 1.0M H_3PO_4 at Potentials Between 10 and 100 Volts.

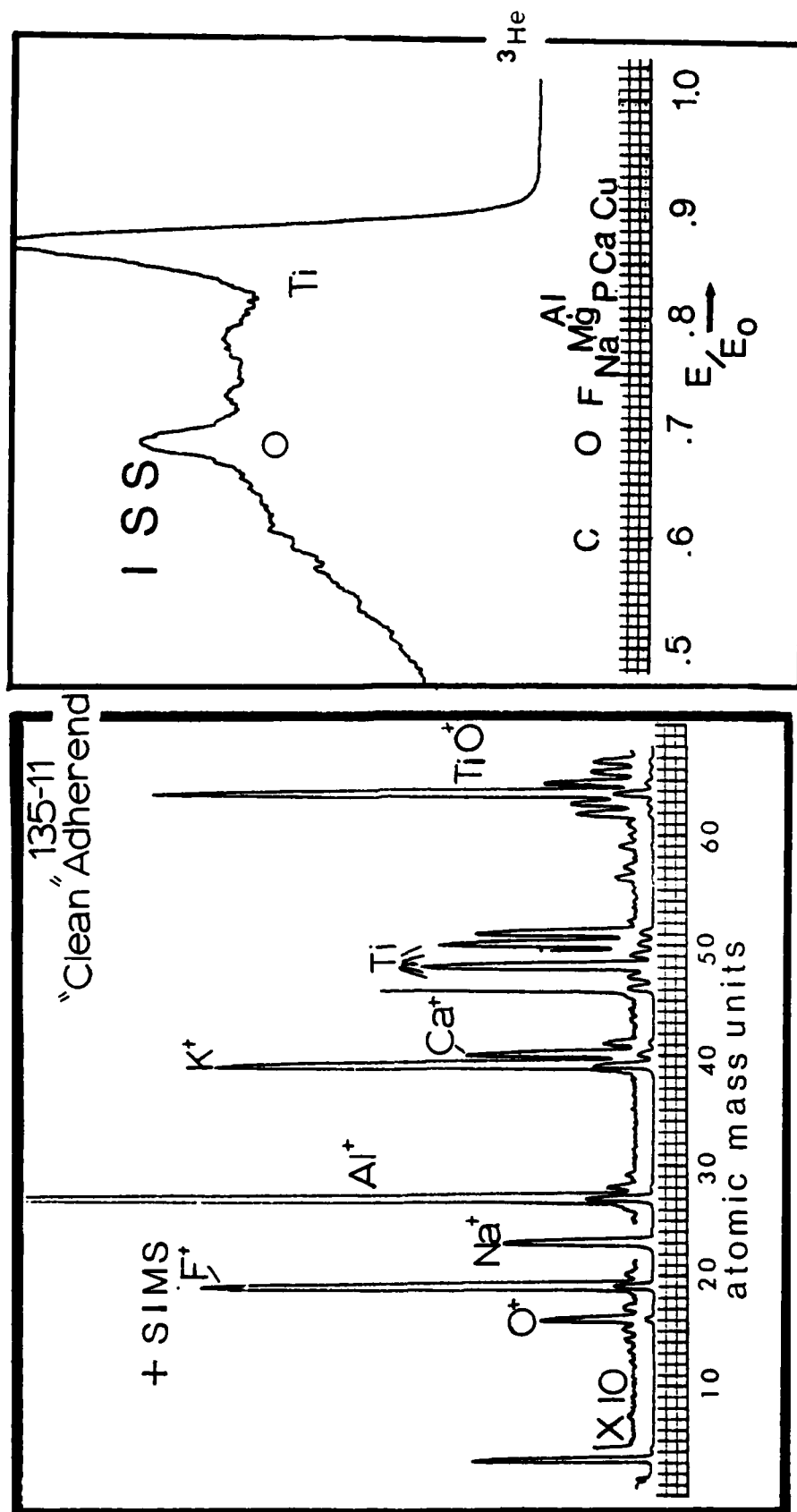


Figure 8. Failure Surface ISS/SIMS Data for Surface Which Appears to be Clean Metal.

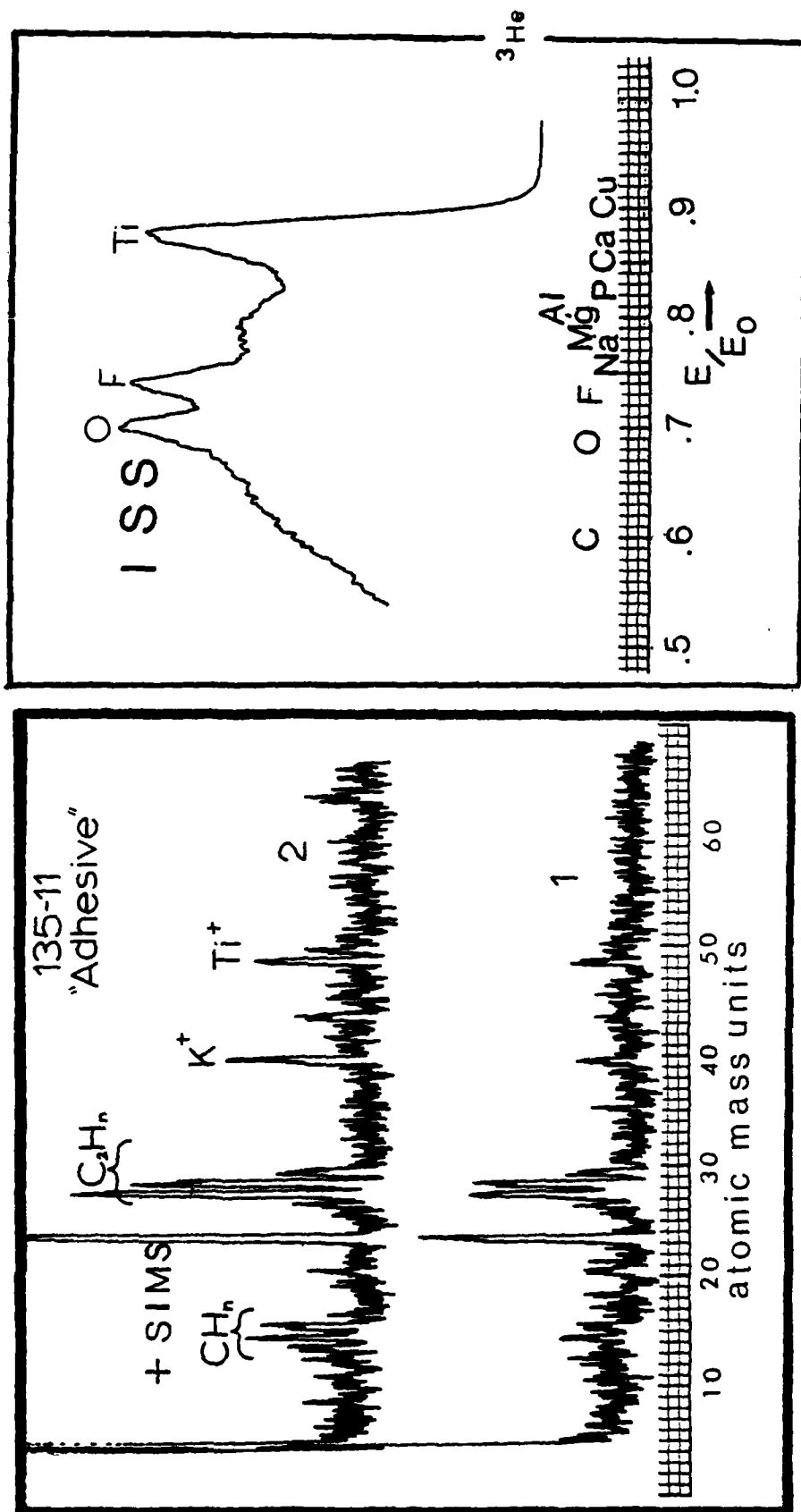


Figure 9. Failure Surface ISS/SIMS Data Matching Figure 8 - Adhesive Side.

the anodization step, appreciable fluorine appears at this interfacial failure site. The specimen in the figures shown here as "clean adherend" represents the region in which oxide has been stripped from the alloy. The specimen labeled "adhesive" is from the thick adherend where the majority of the adhesive remained following bond failure. An interesting phenomenon is shown in the SIMS results for fluorine. Note that on the clean adherend there is appreciable amount of fluorine in the SIMS spectrum, but little in the ISS spectrum. In the figure labeled adhesive, little fluorine shows up SIMS spectrum but considerable in the ISS spectrum, which illustrates that the SIMS data most represents the yield from a surface, not the actual amount present. The fluorine on the surface of the non-conducting adhesive has a very small yield, as shown by the poor signal to noise ratio. A yield on the metal side or the clean adherend side is very high for all of the ions present; therefore, more credence about the amount actually present should be placed in the results shown in the ISS spectrum. SIMS proves to be a very powerful complement to other methods of surface spectroscopy, but has definite limitations from the quantitative standpoint. The important point here is that even though the etch was followed by an anodization, fluorine has reached or remained at the failure interface region.

Another type of failure that was observed in this set of specimens is typified by data from specimen 135-15, as shown in Figures 10 and 11. This type of failure is a very unusual one that does not have the appearance of the interfacial oxide/metal failure and does not have the typical "adhesive" failure as typified by many bond failures. In this specimen the crack extension test adherend, which was thin, shows rather typical spectral data for an oxide on titanium as well as a large quantity of sodium. Some carbon also is seen on this surface. Spectral data for the crack extension test adherend which was

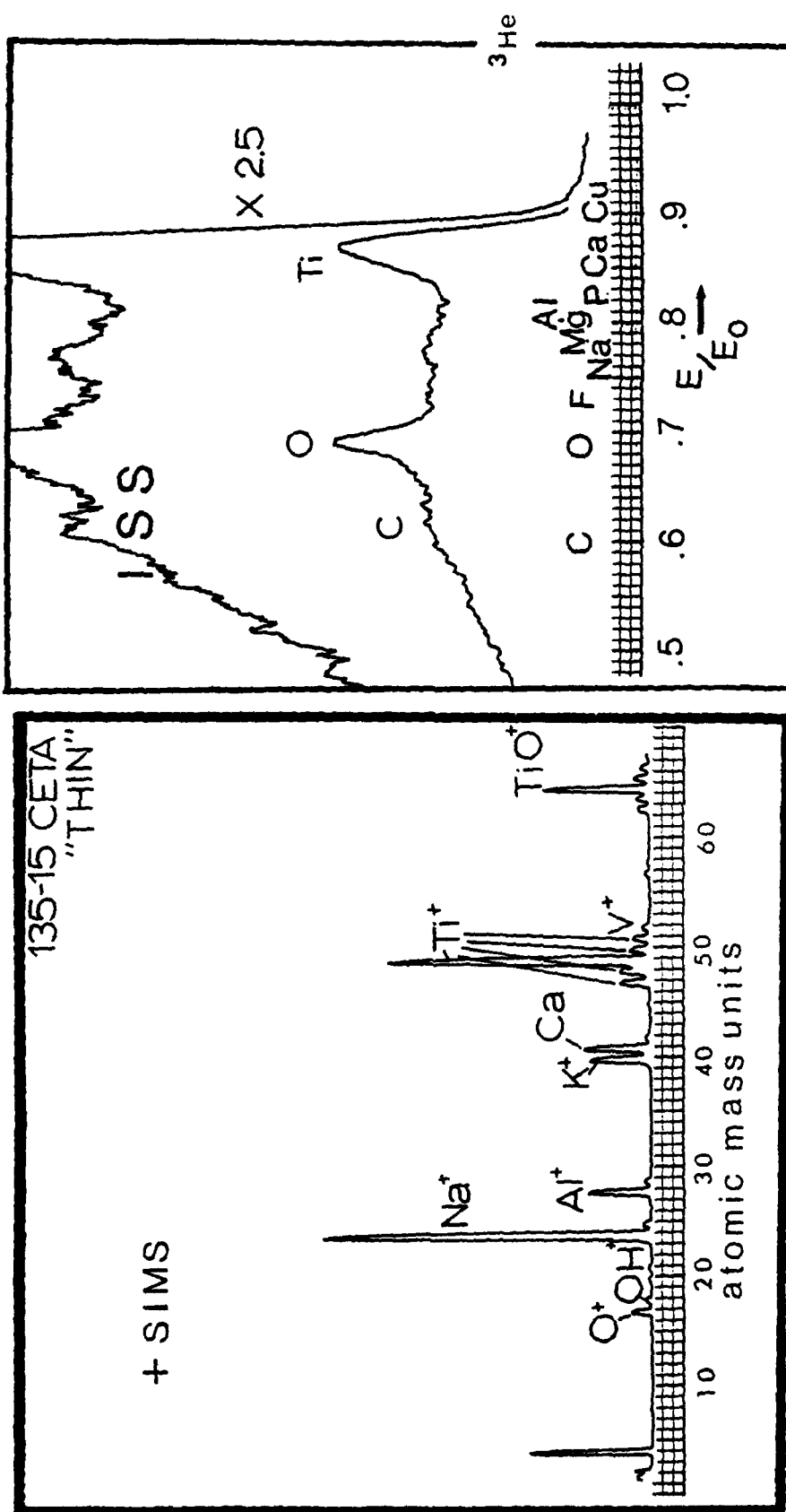


Figure 10. ISS/SIMS Data for "Thin" Specimen in Thick-Thin Crack Extension Test. Sample Cleaned, Etched in 15% Hydrofluosilicic Acid and Anodized at 60V in 0.05M NaOH.

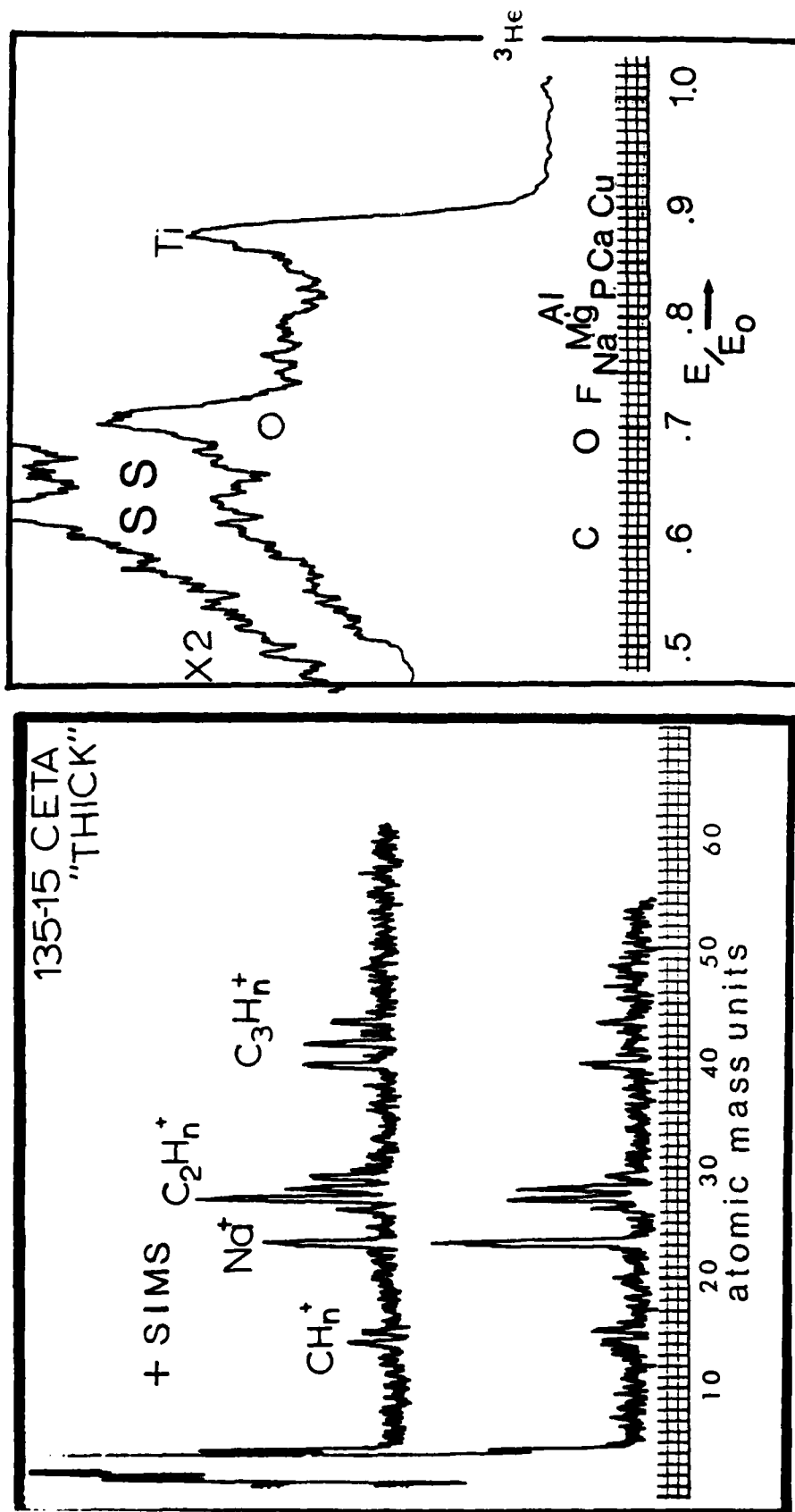


Figure 11. ISS/SIMS data for "Thick" Specimen in Thick-Thin Crack Extension Test. Sample Prepared as in Figure 10.

thick shows similar ISS spectrum, but it is not typical of the usual oxide (TiO_2). SIMS data is typical for an adhesive and really shows little impurity except for sodium. Carbon also is a major constituent of this surface. There appears to be too much oxygen for the amount of titanium present in the ISS spectrum. This data indicates that failure probably took place in a weak boundary layer within the oxide itself very close to the adhesive in an area that had been penetrated by the adhesive or low viscosity components of the adhesive. A much smaller amount of fluorine appears on these surfaces compared to the oxide/metal failures shown earlier.

Still another type of failure appears to have occurred in this set of specimens as shown in Figures 12 and 13 for specimen 135-18, which was a nitric acid/hydrofluoric acid etch followed by a 30-volt 1 molar phosphoric acid anodize. Note in the data for the specimen labeled "thin" that the ISS spectrum is very atypical of an oxide film on titanium. Also the surface, as shown by both ISS and SIMS, contains an extremely large amount of sodium. This is typical of many adhesive failure surfaces, as will be reported separately¹⁰, which contain large amounts of alkali elements. Note that this surface also contains a fairly large amount of fluorine and, in addition, a molecular species corresponding to HF is observed. Just what this appearance of a molecular species of this nature means, is not known at this time, but perhaps it does indicate some hydrolysis at this interface containing a large amount of sodium to form a new interface which formed a weak boundary layer causing failure along that region. The data shown as the thick specimen is relatively typical of a clean adhesive containing appreciable amounts of sodium. Surface characterization methods such as ISS/SIMS are of great value in determining the mechanism of failure following such testing as outlined earlier¹².

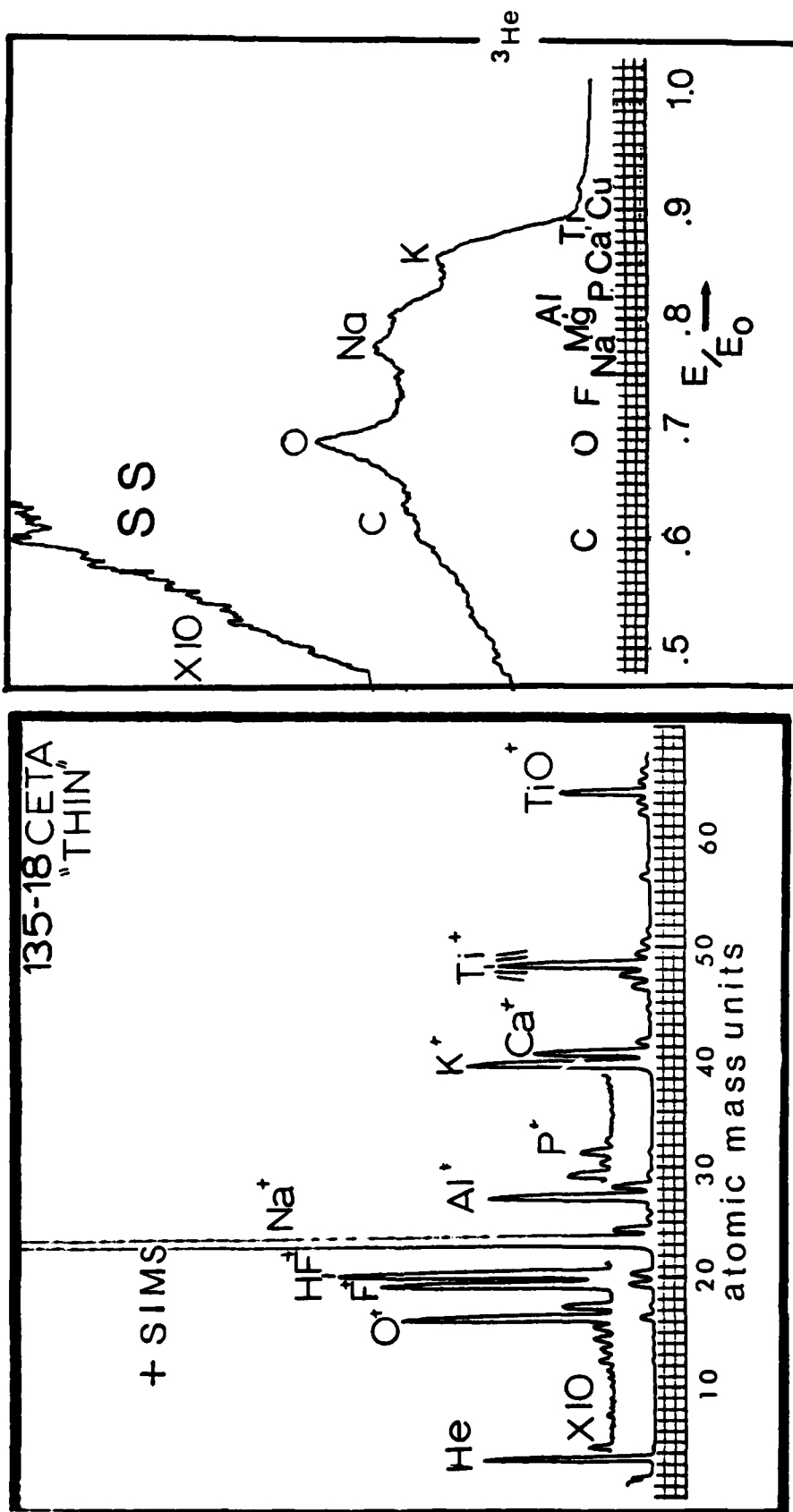


Figure 12. ISS/SIMS Data for Thin Specimen in Thick-Thin Crack Extension Test. Sample Prepared Originally by Cleaning, Etching in HF/HNO₃ Solution, and Anodized in 1M H₃PO₄ at 30 Volts.

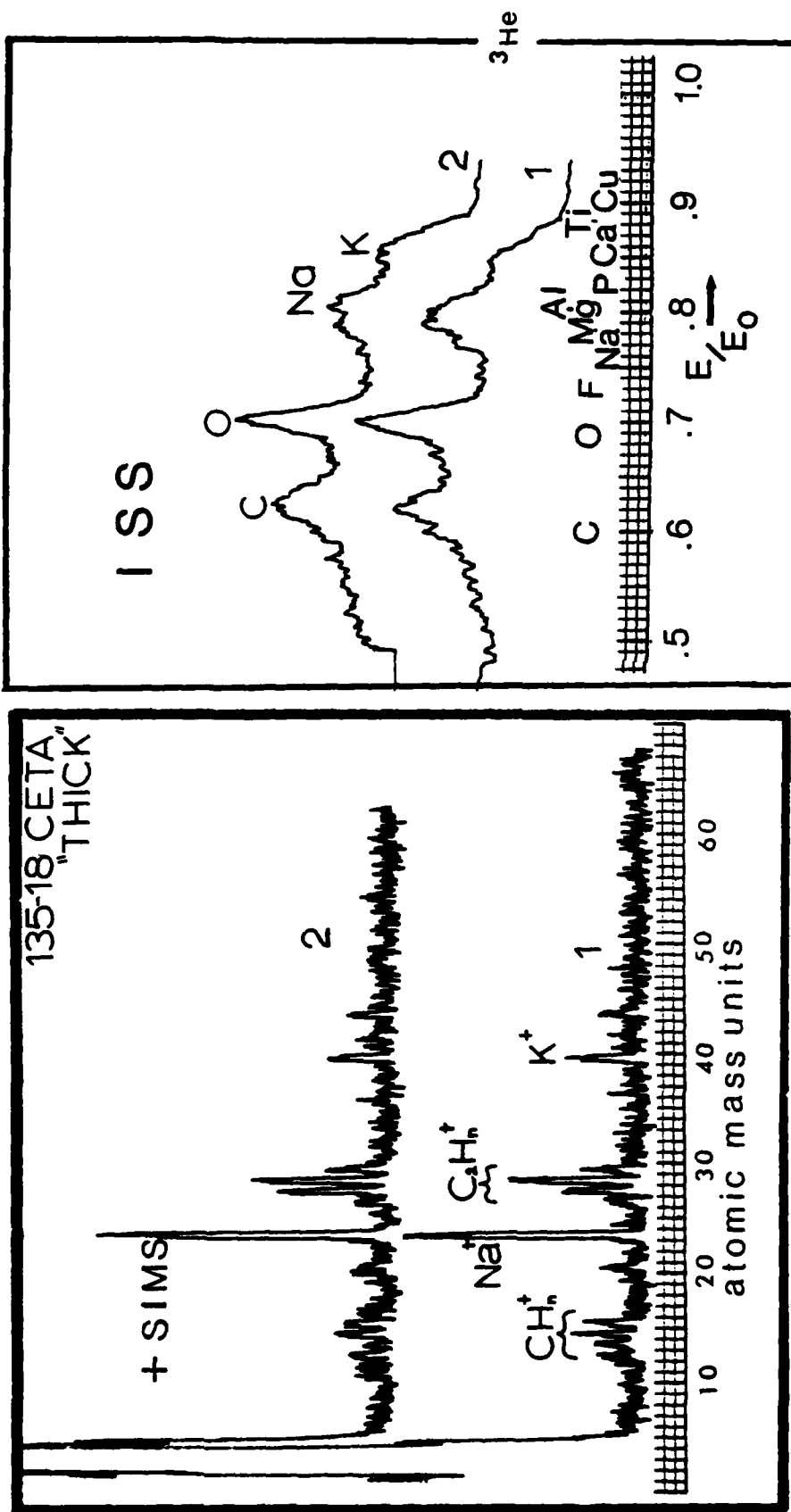


Figure 13. ISS/SIMS Data for Thick Adherend Which Matches Thin Side Shown in Figure 12.

In another set of treatments (140 series) the specimens were prepared by an abrasive pad plus detergent, followed by a pre-treatment of hydrofluosilicic acid and then followed by an anodization in several different electrolytes including phthalic acid which is considered to be non-aggressive to titanium. Crack extension data as seen in Figure 14 on these specimens seemed to be approximately the same as the earlier set, indicating a dependence on the pre-treatment, but very little dependence on the anodization that is given to the specimens. Here again only thin films as applied by 30 or 60 volts are used along with one porous film as provided by the addition of lithium nitrate to the phthalic acid electrolyte. Better initial bonding and less crack growth is seen on porous oxide specimens. The lithium nitrate was added to increase the current density and produce a porous film which showed better wetting characteristics than the dense oxide. The lithium nitrate was used in this particular case to provide a tracer since lithium has very high sensitivity and a high SIMS yield. The lithium does not appear in the oxide formed on titanium by this mixture. Similarly porosity may be induced by anodization at high voltages. Such increased porosity improves wetting as shown by H_2O contact angle data shown in Table II for three solutions.

Other series (147) prepared with hydrofluosilicic acid pre-treatment were prepared to determine the effect of the primer on the crack extension characteristics of the titanium pre-treatments. Data for this series was virtually the same as for the 140 series showing about the same crack extension and no particular dependence on whether the sample was or was not primed. The primer in this series was a solution (10 grams per liter) of the adhesive 729-3 in MEK. Failure sites were extremely similar with adhesive failure appearing to progress along a region high in sodium and weak boundary layers formed when appreciable amounts of fluorine were present in the

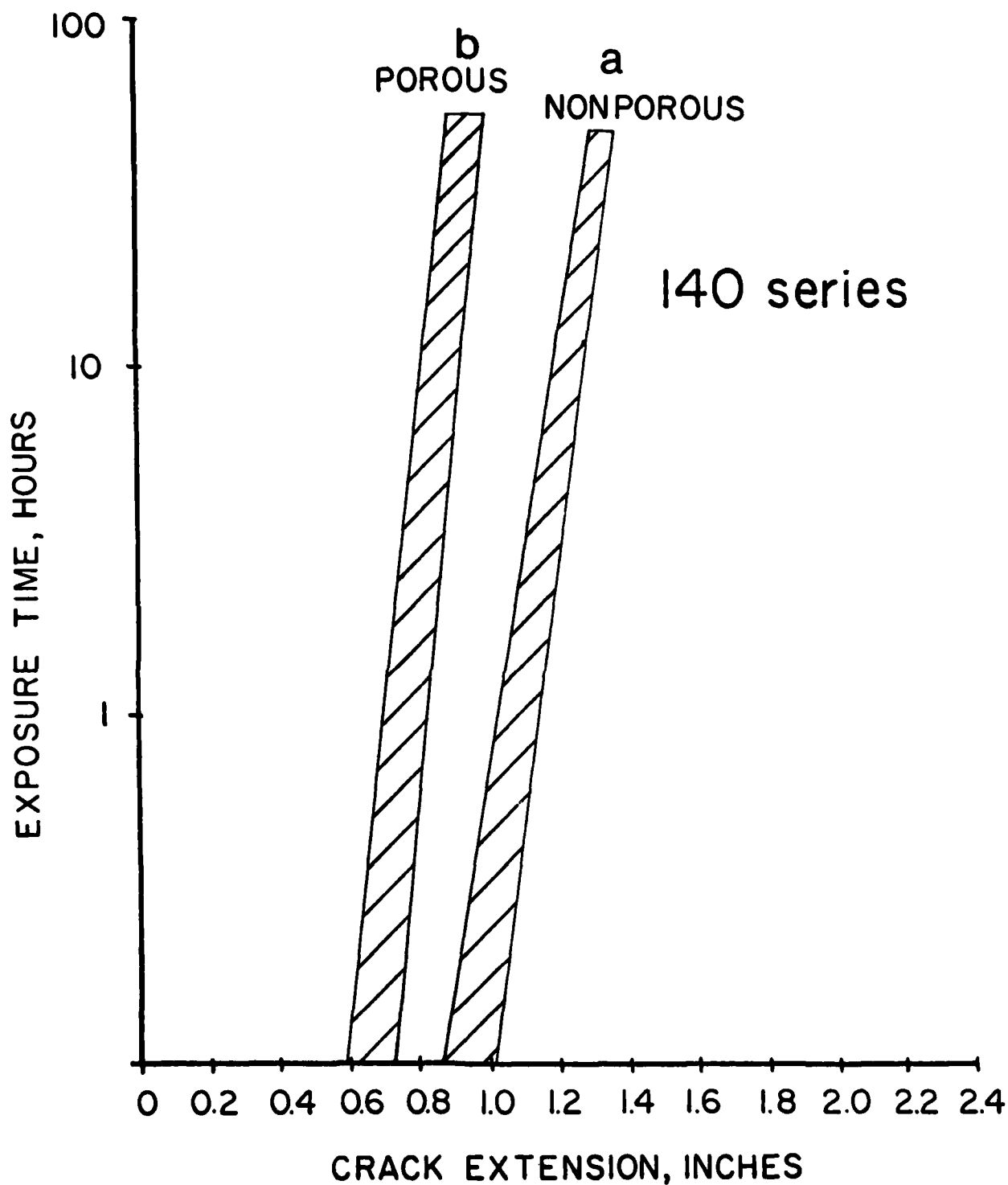


Figure 14. Crack Extension Data for Samples Pretreated with Hydrofluosilicic Acid and Anodized to Form Dense Oxide (A) and Porous Oxide (B).

TABLE II
EFFECT OF INCREASING OXIDE POROSITY
ON H₂O CONTACT ANGLE
ON TITANIUM 6 ALUMINUM 4 VANADIUM

Sample	Electrolyte	Voltage	H ₂ O Contact Angle
197-1	Na ₂ HPO ₄ + H ₃ PO ₄ 0.5M pH = 7	20V	74°
		50V	57°
		100VS*	14°
197-3	NaOH 0.1M pH = 12.4	20V	72°
		50V	58°
		200VS*	53°
197-4	H ₃ PO ₄ 0.1M pH = 1.80	20V	60°
		50V	54°
		250VS*	36°

*Sparking or hissing

anodizing or pre-treatment solutions. The importance of using the correct test was brought out with these samples. It was found that good initial bondability and low crack extension was achieved in samples anodized in baths containing fluorine such as hydrofluosilicic acid. However when the samples were peeled open following crack extension, the mode of failure was interfacial between the oxide and metal along a very weak boundary layer. Experiments have shown that the fluorine layer as deposited by the pre-treatments such as the nitric/hydrofluoric acid or by the hydrofluosilicic acid may be removed by treatment with a dilute solution of sulfuric acid. The morphology of the surface appears to remain the same, but the chemistry changes. ISS and SIMS data for a surface treated initially with hydrofluosilicic acid and then with dilute sulfuric acid is shown in Figure 15. Fluorine has been removed from the surface. No failure at the oxide/alloy interface has been observed in any of the specimens using this surface treatment. Other useful techniques may be to wash the fluoride treated surfaces with wash or rinse waters which contain ions which combine with fluorine to provide high thermal and hydrolytic stability at the interface. Such experiments show calcium ions have a high affinity for fluorine at the surface and provide a stable surface for bonding.

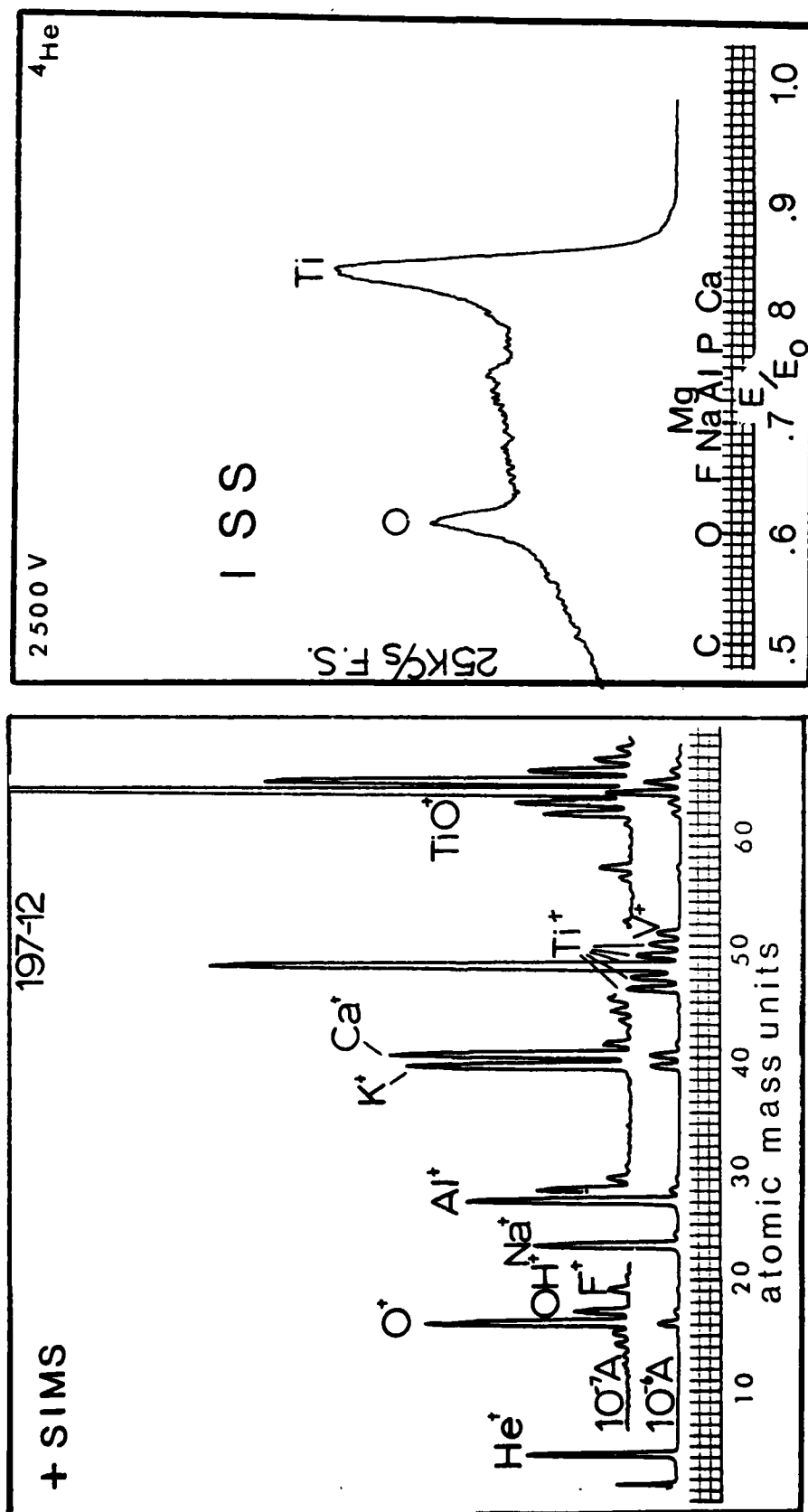


Figure 15. ISS/SIMS Data for Ti6Al4V Treated with Hydrofluosilicic Acid Followed by Rinse with Dilute H₂SO₄.

SECTION IV

CONCLUSIONS

The experiments described herein on Ti6Al4V indicate that thin anodized films in a dense form do not contribute to bondability or durability of adhesive bonds. In only one set of experiments (anodization in alkaline electrolyte) did anodization provide any apparent improvement in either bondability or durability. Generally, it appeared that anodization on top of surface active pre-treatments had little effect on the adhesive bond. Sometimes anodization actually proved detrimental to the adhesive bond. Colored anodized films do, however, provide an aid to inspectability and other non-destructive applications and provide galvanic corrosion resistance to other metals in contact with titanium alloys. Fluorine present in the anodization bath or remaining on the surface from pre-treatments can lead to oxide/metal failure. Fluorine ions should be avoided, removed, or neutralized by chemical combination before adhesive bonding.

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APPENDIX A
ION SCATTERING DATA 90° SCATTERING

ELEMENT			E/E ₀ (at $\theta = 90^\circ$)			
Z	A		³ He	⁴ He	²⁰ Ne	⁴⁰ Ar
1	1.0	H		---		
2	4.0	He	.143	0	---	---
3	6.9	Li	.393	.266	---	---
4	9.0	Be	.500	.385	---	---
5	10.8	B	.565	.459	---	---
6	12.0	C	.600	.500	---	---
7	14.0	N	.647	.555	---	---
8	16.0	O	.684	.600	---	---
9	19.0	F	.727	.652	---	---
10	20.2	Ne	.741	.669	.005	---
11	23.0	Na	.769	.704	.070	---
12	24.3	Mg	.780	.717	.097	---
13	27.0	Al	.800	.742	.149	---
14	28.1	Si	.807	.751	.168	---
15	31.0	P	.824	.771	.216	---
16	32.1	S	.829	.778	.232	---
17	35.5	Cl	.844	.797	.279	---
18	39.9	Ar	.860	.818	.332	---
19	39.1	K	.857	.814	.323	---
20	40.1	Ca	.861	.819	.334	.001
21	45.0	Sc	.875	.837	.385	.059
22	47.9	Ti	.882	.846	.411	.090
23	50.9	V	.889	.854	.436	.120
24	52.0	Cr	.891	.857	.444	.130
25	54.9	Mn	.896	.864	.466	.157
26	55.8	Fe	.898	.866	.472	.165
27	58.9	Co	.903	.873	.493	.191
28	58.7	Ni	.903	.872	.492	.189
29	63.5	Cu	.910	.881	.521	.227
30	65.4	Zn	.912	.885	.532	.241
31	69.7	Ga	.917	.891	.554	.271
32	72.6	Ge	.921	.896	.568	.290
33	74.9	As	.923	.899	.578	.304
34	79.0	Se	.926	.904	.596	.328
35	79.9	Br	.928	.905	.600	.333
36	83.8	Kr	.931	.909	.615	.354
37	85.5	Rb	.932	.911	.621	.363
38	87.6	Sr	.934	.913	.628	.373
39	88.9	Y	.935	.914	.633	.379
40	91.2	Zr	.936	.916	.640	.390
41	92.9	Nb	.937	.917	.646	.398
42	95.9	Mo	.939	.920	.655	.411
43	99	Tc	.941	.922	.664	.424
44	101.1	Ru	.942	.924	.670	.433
45	102.9	Rh	.943	.925	.675	.440
46	106.4	Pd	.945	.928	.684	.454
47	107.9	Ag	.946	.929	.687	.459
48	112.4	Cd	.948	.931	.698	.475
49	114.8	In	.949	.933	.703	.483
50	118.7	Sn	.951	.935	.712	.496

APPENDIX B

RELATIVE ABUNDANCES OF
NATURALLY OCCURRING ISOTOPES

RELATIVE ABUNDANCES OF NATURALLY OCCURRING ISOTOPES

Z _i	A	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	H	99.9	0.1																		
2	He				100																
3	Li					7.4	92.6														
4	Be								100												
5	B									18.3	81.7										
6	C												98.9	1.1							
7	N														99.6	0.4					
8	O																99.8	0.04	0.20		
9	F																			100	
10	Ne																				90.5
Z _i	A	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
10	(Ne)	0.3	8.8																		
11	Na			100																	
12	Mg				78.6	10.1	11.3														
13	Al							100													
14	Si								92.2	4.7	3.1										
15	P											100									
16	S												95.0	0.8	4.2						
17	Cl															75.5		24.5			
18	Ar																0.34		0.06		99.6
19	K																			93.1	0.01
20	Ca																				97.0
Z _i	A	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
19	K	6.9																			
20	Ca		0.6	0.1	2.1		0.03		0.2												
21	Sc					100															
22	Ti						8.0	7.3	74.0	5.5	5.2										
23	V										0.3	99.7									
24	Cr										4.3		83.8	9.6	2.3						
25	Mn															100					
26	Fe																5.8	91.7	2.2	0.3	
27	Co																			100	
28	Ni																		67.8		26.2
Z _i	A	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
28	(Ni)	1.2	3.6		1.2																
29	Cu			69.1		30.9															
30	Zn				48.9		27.8	4.1	18.6		0.6										
31	Ga									60.5		39.5									
32	Ge										20.5		27.4	7.7	36.7		7.7				
33	As															100					
34	Se														0.9		9.0	7.6	23.5		49.8
35	Br																			50.6	
36	Kr																		0.4		2.3
Z _i	A	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
34	(Se)		9.2																		
35	(Br)	49.4																			
36	(Kr)		11.5	11.5	56.9		17.4														
37	Rb					72.2		27.8													
38	Sr				0.6		9.9	7.0	82.5												
39	Y									100											
40	Zr										51.5	11.2	17.1		17.4		2.8				
41	Nb													100							
42	Mo														15.9	9.1	15.7	18.5	9.5	23.7	9.6
43	Tc	DOES NOT OCCUR NATURALLY																			
44	Ru																5.6		1.9	12.7	12.6