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SEMI-ANNUAL REPORT

A FUNDAMENTAL APPROACH TO ADHESION: SYNTHESIS, SURFACE ANALYSIS, THERMODYNAMICS AND MECHANICS

by

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The research done during the period December 1, 1979 to May 31, 1980 covered the following areas:

I. Analysis and summary of a number of the samples received in two separate shipments from the Boeing Co. Specifically, the following analyses or summaries, have been made:

A. The results of the scanning electron microscopy (SEM) and electron spectroscopy for chemical analysis (ESCA) studies of the unprimed Ti 6-4 coupons supplied by the Boeing Co. as shipment #1 are summarized in a SAMPE paper. A copy of that paper submitted for presentation at the SAMPE meeting in Seattle in October, 1980 is included as a part of this report.

B. Scanning electron microscopy (SEM) of some of the fractured samples of adhesively bonded Ti 6-4 specimens supplied by the Boeing Co. as shipment #2. [see Table I.]

C. Electron spectroscopy for chemical analysis (ESCA) of some of the fractured samples of adhesively bonded Ti 6-4 specimens supplied by the Boeing Co. as shipment #2. [see Table I.]

II. The oxide layer present on the surface of Ti 6-4 is believed to play a major role in determining the strength and durability of adhesively bonded structures. It is not clear from the literature in what crystalline phase this surface oxide layer exists. This surface oxide layer in situ is amenable to analysis by some surface analytical techniques such as SEM, ESCA and reflectance infrared spectroscopy. On the other hand, because of the low surface area of the Ti 6-4 coupons, a number of surface measurements are precluded such as surface areas and heat of immersion. In order to more fully characterize this oxide layer, four TiO_2 powders in both the rutile and anatase forms have been studied. The following measurements have been obtained on these powders:

D. SEM photomicrographs and ESCA spectra of four TiO_2 powders have been obtained.

E. Determination of the surface area and surface acidity of the four TiO_2 powders.

F. Determination of the heats of immersion of the four TiO_2 in water, in m-cresol/xylene and in dilute solutions of poly(phenylquinoxaline) in m-cresol/xylene.

The results of the above analyses of the four TiO_2 powders are summarized in Table II.

TABLE I

ANALYSIS OF FRACTURED Ti 6-4 SAMPLES FROM BOEING SHIPMENT #2

Sample Description	SEM	ESCA
CAA[a]-PPQ[b]-RT[c]	X	
450[c]	X	
CAA-PPQM1[b]-RT	X	
450	X	
PF_B[a]-PPQ-RT	X	X
450	X	X
PF_B-PPQM1-RT	X	
450	X	

[a]CAA - chromium acid anodize
PF_B - phosphate-fluoride (Boeing)

[b]PPQ - poly(phenylquinoxaline)
PPQM1 - poly(phenylquinoxline) Modification

[c]lap shear test at room temperature (RT) or 450°F

TABLE II

SUMMARY OF THE CHARACTERIZATION OF TiO_2 POWDERS

Sample	Supplier	Crystalline Phase[a]	SEM[b]	ESCA	Surface Area(m^2/g)	Surface Acidity	Heats of immersion (mJ/m^2) Water	m-cresol/ xylene	PPQ m-cresol/xylene
A	Glidden	Rutile	X	Ti,O,Al,Cl,Na	7.04	–	– 293. 462.	282.	271.
B	Glidden	Anatase	X	Ti,O,Cl,K,P,S	10.5	> 7.6	74.[c] 247.[d] 334.[e]	252.	382.
C	duPont	Rutile	X	Ti,O,Al,Na	7.82	> 7.6	– 212. 336.		
D	Cabot	Mixed	X	Ti,O	51.0	> 7.6	109. 325. 422.	273.	

[a] according to supplier.

[b] SEM photomicrographs showed secondary particles consisting of a large number of very small sized particles.

[c] Sample not evacuated

[d] Sample evacuated overnight at room temperature.

[e] Sample evacuated for 2 hrs at 100°C

PREPRINT OF PAPER TO BE PRESENTED AT

SAMPE MEETING, SEATTLE, OCTOBER, 1980

SPECTROSCOPIC CHARACTERIZATION OF TITANIUM 6-4 SURFACES AFTER CHEMICAL PRETREATMENTS

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Abstract

Several techniques have been used to study pretreated Ti 6-4 surfaces including scanning electron microscopy (SEM), electron spectroscopy of chemical analysis (ESCA), and, reflectance visible spectroscopy. Each pretreatment type gives a characteristic surface morphology as seen by SEM. Elemental analysis of the Ti 6-4 surfaces was done using ESCA. Trace residual contaminants from particular chemical pretreatments are identified readily. Reflectance visible spectroscopy using indicator dyes placed on Ti 6-4 surfaces appears to be a feasible approach to establish surface acidity. Differences in surface acidity have been observed using bromthymol blue on Ti 6-4 surfaces pretreated by two different methods.

1. INTRODUCTION

Titanium 6-4 alloy is a highly stabilized, alpha-beta phase alloy, using aluminum as the alpha stabilizer and vanadium as the beta stabilizer[1]. These impart toughness and strength at temperatures up to 627 K (750°F). Superior in corrosion resistance to many metals, titanium and its alloys are protected by an inherent oxide film at low and moderate temperatures, but are subject to oxidation above 523 K (480°F)[2]. The nature of this oxide film has been the subject of a number of papers[3-10].

One of the most important considerations for joining of

titanium and its alloys by adhesive bonding is the pretreatment of the surface prior to bonding. A variety of specialized surface treatments[11] have been developed over the past decade, and increasingly sophisticated measurements are being used to characterize the surfaces involved. The use of secondary ion mass spectroscopy[6], Auger electron spectroscopy[4], ion scattering spectroscopy[12] and scanning transmission electron microscopy[13] is noted. Work has been reported [3,4,14,15] on the characterization of titanium 6-4 surfaces after phosphate-fluorice and alkaline pretreatments. In every case, an oxide film is formed. The role of this oxide film in determining bond strength and bond durability is not yet established as judged by the contradictory evidence in a number of recent papers[3-5, 7-10, 14,15].

Previous work[16-19] in our laboratory has been directed towards a fundamental study of adhesion with particular emphasis on analysis of the Ti 6-4 surface. The objective of the present work was to characterize Ti 6-4 surfaces after a variety of pretreatments with emphasis on scanning electron microscopy (SEM), electron spectroscopy for chemical analysis (ESCA), and, reflectance visible spectroscopy.

2. EXPERIMENTAL

2.1 MATERIALS

The Ti 6-4 coupons used in the SEM and ESCA studies were supplied by personnel at the Boeing Company after the following six chemical pretreatments:

(1) chromic acid anodize with fluoride,
(2) phosphoric acid anodize with fluoride,
(3) Pasa-Jell 107,
(4) phosphate-fluoride (Picatinny modified)
(5) Turco 5578 alkaline etch and,
(6) RAE process - an alkaline hydrogen peroxide etch.

Details of the process parameters for each of the above pretreatments are available on request. The Ti 6-4 coupons used in the reflectance visible spectroscopic studies were supplied by personnel at the NASA-Langley Research Center. These coupons were pretreated by the phosphate-fluoride and Turco 5578 methods.

2.2 PROCEDURES

SEM photomicrographs at various magnifications were obtained at 20 kV on an Advanced Metals Research Model 900 scanning electron microscope. Most SEM samples were run after ESCA analysis. A thin (~20 nm) film of Au-Pd alloy was vacuum evaporated onto the samples to enhance conductivity. ESCA data were collected on a duPont 650 electron spectrometer with a magnesium anode and an analog output on an x-y recorder. The carbon 1s photopeak taken at 284.0 ev was used to evaluate the work function of the spectrometer. Circular (6.4 mm or 32 mm^2) samples were punched from the Ti 6-4 coupons and mounted on copper sample probes. The atomic fraction (AF_i) of the i-th element contained in the surface was calculated according to equation (1)

$$AF_i = \frac{A_i/\sigma_i}{\Sigma A_i/\sigma_i} \qquad (1)$$

where A_i is the area of the i-th photoelectron peak and σ_i is the photoelectron cross-section.[20]

Color changes of acid-base indicators spread from solution onto freshly pretreated Ti 6-4 coupons were detected using diffuse reflectance visible spectroscopy. Dilute aqueous solutions of bromthymol blue, thymol blue, bromphenol blue, and, bromcresol green were used as indicators having a range of pK_a values. The reflectance spectra were obtained on a Cary 14 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 SEM/ESCA OF ANODIZED Ti 6-4

A representative SEM photomicrograph of chromic acid anodized Ti 6-4 is shown in Figure 1. On the substrate, there appears to be a surface layer containing minute cracks or fissures of irregular shape. At the highest magnification (X 10,000), the whole surface layer appears to be sponge-like presumably due to the presence of small diameter pores not resolved in the SEM. The ESCA results for this sample are listed in Table I. The binding energy (BE) in ev of each photopeak and the atomic fraction (AF) for each element calculated using equation (1) are tabulated. In addition to the photopeaks for ubiquitous carbon and for titanium and oxygen, significant quantities of nitrogen and fluorine were detected. The binding

energy of nitrogen suggests the presence of a nitride. It is worthwhile to note that the same nitrogen photopeak was observed on the Ti 6-4 surface following all six pretreatments. The fluorine peak appeared as a doublet with the higher binding energy peak at 687.6 ev being the larger. This result suggests two different bonding states of fluorine in the surface. A representative SEM photomicrograph of phosphoric acid was anodized Ti 6-4 as shown in Figure 2. The surface features are similar to those described for the chromic acid anodized Ti 6-4. The ESCA results in Table I for both of these anodized surfaces are similar except that a small phosphorus photopeak is observed and the fluorine photopeak appears as a singlet for the phosphoric acid anodized Ti 6-4.

3.2 SEM/ESCA OF ACID ETCHED Ti 6-4

A representative SEM photomicrograph of the phosphate-fluoride treated Ti 6-4 is shown in Figure 3. There appear fairly well defined alpha (gray) and beta (white) phases. These surface features are in contrast to those observed for the anodized surfaces. At higher magnification, the beta phase crystals are poorly defined but the alpha phase shows regularly-spaced edges about 100 nm apart. The ESCA results in Table I indicate the presence of trace calcium and phosphorus on the surface. A representative SEM photomicrograph of the Pasa-Jell treated Ti 6-4 is shown in Figure 4. The surface features are similar to those observed for the phosphate-fluoride treatment. Closer inspection of Figure 4 or of photomicrographs obtained at higher magnification show that the surface is littered with "popcorn" particles whose identity was not established. The ESCA results in Table I for both of these acid etched surfaces are similar except a chromium photopeak is observed for the Pasa-Jell etch instead of a phosphorus photopeak.

3.3 SEM/ESCA OF ALKALINE ETCHED Ti 6-4

A representative SEM photomicrograph of the Turco treated Ti 6-4 is shown in Figure 5. The surface features for this alkaline etch are in sharp contrast to those following the acidic pretreatments. The beta phase appears to have grown at the expense of the alpha

phase and exists as highly fragmented structures. The ESCA results in Table I indicate the absence of fluorine in the surface. Further ESCA work[21] has demonstrated the presence of significant quantities of sodium in the surface. A representative SEM photomicrograph of RAE alkaline hydrogen peroxide treated Ti 6-4 is shown in Figure 6. The surface features here are unlike any of the preceding ones. A mottled surface is obtained containing no distinct features. The ESCA results in Table I for both of the alkaline etched surfaces show that trace quantities of calcium and aluminum are seen following the RAE process.

3.4 SURFACE ACIDITY OF Ti 6-4

The surface acidity results are shown in Table II for Ti 6-4 pretreated by the Turco and phosphate-fluoride processes. Only thymol blue changes color (blue to yellow) from the base form to the conjugate acid form on the Turco etched Ti 6-4 surface. The λ_{max} value at 476 nm is characteristic of the acid form. Thus the Turco etched surface is basic and the basicity lies between 7.3 and 9.2, the pK_a values of the bracketing indicators. Results from Table II demonstrate that the phosphate-fluoride surface is acidic and the acidity lies between 4.9 and 7.3.

A marked decrease in the surface acidity of phosphate-fluoride etched Ti 6-4 occurred between 5 and 10 hours as noted by the appearance of a second peak at 630 nm in the reflectance spectrum of bromthymol blue characteristic of the base form. This result is a quite significant one since it establishes a surface chemistry basis for priming a freshly pretreated metal adherend prior to adhesive bonding.

4. SUMMARY

Different surface features are seen in the SEM photomicrographs for the anodized, acid, and, alkaline etched Ti 6-4 surfaces. However both of the anodized and both of the acid etched surfaces have similar surface features in contrast to the SEM photomicrographs for the two alkaline etched Ti 6-4 surfaces. The binding energies of the O 1s, Ti $2p_{3/2}$ and N 1s photopeaks at 529.6 $\pm$ 0.2, 457.9 $\pm$ 0.2 and 399.3 $\pm$ 0.2 ev, respectively, were constant following all six surface pretreat-

ments. Each pretreatment gave rise to a unique ESCA "fingerprint" analysis of Ti 6-4. The chromic acid anodized Ti 6-4 gave a fluorine doublet photopeak. The phosphoric acid anodized and phosphate-fluoride etched Ti 6-4 both gave phosphorus photopeaks but a calcium photopeak was only observed for the latter process. A chromium photopeak was only observed for the Pasa-Jell treated Ti 6-4. No fluorine photopeak was observed following the alkaline etch processes. But, sodium and aluminum photopeaks were observed for the Turco and RAE processes, respectively.

5. ACKNOWLEDGEMENT

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7. BIOGRAPHIES

Wen Chen is a native of Taiwan and received his B.S. and M.S. degrees in Chemistry from Chung Yuan College and Marquette University, resp. He was a graduate research assistant at VPI&SU from 1977

in 1979 working on the characterization of adherend surfaces.

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James P. Wightman is Professor of Chemistry at VPI&SU. He received his B.S. degree from Randolph-Macon College and his Ph.D. degree in Chemistry from Lehigh University. He was a Research Associate at Penn State prior to joining the faculty at Virginia Tech in 1962 and was a Visiting Professor (1975-76) at the University of Bristol (U.K.). He is co-author of 50 publications and is a member of the Advisory Board of the Journal of Colloid and Interface Science. His research interests include the adsorption of gases and liquids on solids and the characterization of solid surfaces.

TABLE I

ESCA ANALYSIS OF Ti 6-4 SURFACES AFTER CHEMICAL PRETREATMENT

	Chromic Acid Anodize		Phosphoric Acid Anodize		Pasa-Jell		Phosphate-Fluoride		Turco		RAE	
Photopeak	BE	AF	BE	AF	BE	AF	BE	AF	BE	AF	BE	AF
F 1s	687.6 684.4	0.03 -	684.4	0.02	684.2	0.01	683.8	0.01				
Cr $2p_{3/2}$					577.0	0.01						
O 1s	529.4	0.19	529.6	0.24	529.8	0.44	529.2	0.29	530.0	0.30	529.4	0.48
Ti $2p_{3/2}$	457.8	0.08	458.2	0.10	457.8	0.15	457.6	0.10	458.0	0.09	458.0	0.18
N 1s	399.2	0.03	399.4	0.01	399.4	0.01	399.0	0.02	399.5	0.01	399.4	0.01
Ca $2p_{3/2}$					346.8	0.01	348.0	0.02			346.4	0.04
C 1s	(284.0)	0.67	(284.0)	0.60	(284.0)	0.38	(284.0)	0.53	(284.0)	0.60	(284.0)	0.26
P $2p_{3/2}$			133.0	0.02			132.4	0.02				
Al 2s											118.2	0.03

TABLE II

λ_{max} VALUES OF THE INDICATORS ON PRETREATED Ti 6-4 SURFACE

Indicator	pKa	λ_{max}(nm) value after drying	λ_{max} (nm) value after drying
Bromphenol blue	4.1	635	636
Bromeresol green	4.9	644	610
Bromthymol blue	7.3	604	464
Thymol blue	9.2	476	478

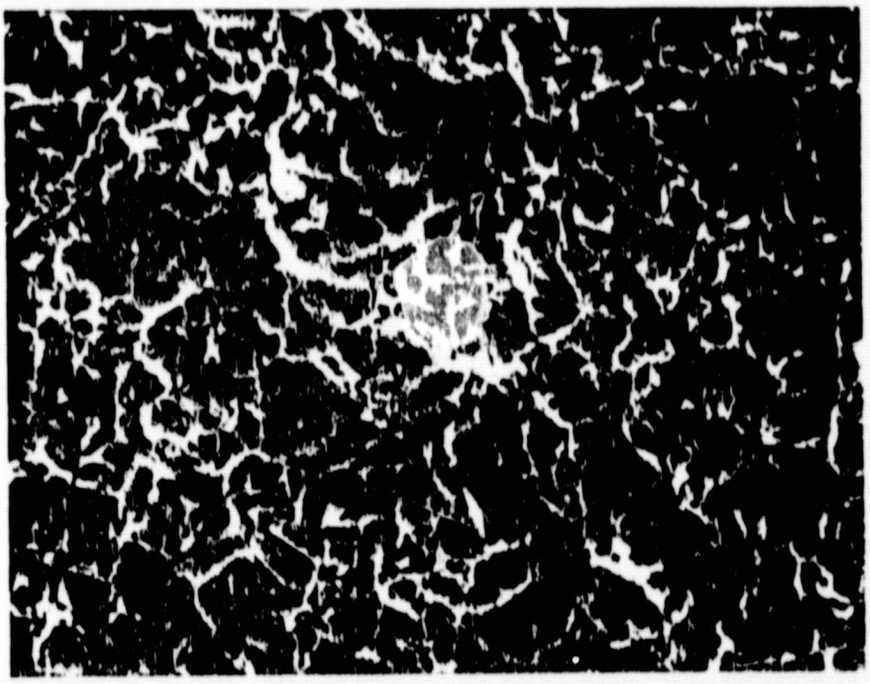

Figure 1. SEM PHOTOMICROGRAPH (X2000) OF CHROMIC ACID ANODIZED Ti 6-4.

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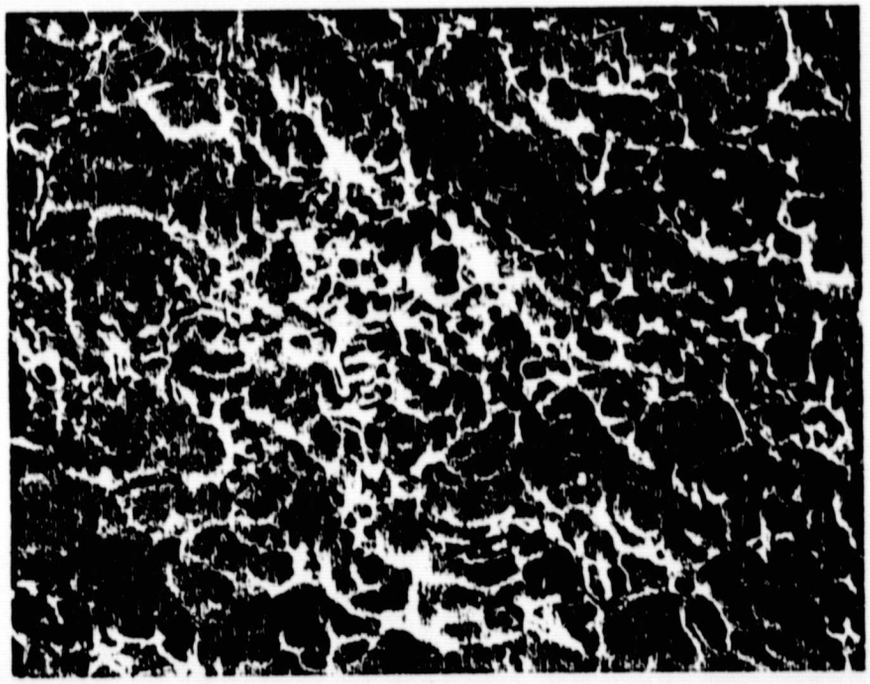

Figure 2. SEM PHOTOMICROGRAPH (X2000) OF PHOSPHORIC ACID ANODIZED Ti 6-4

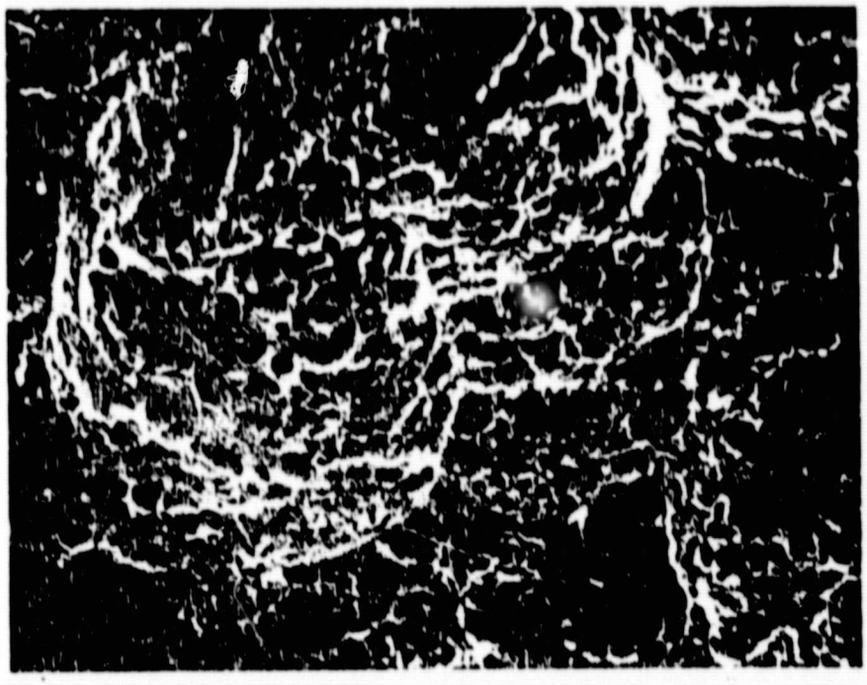

Figure 3. SEM PHOTOMICROGRAPH (X2000) OF PHOSPHATE-FLUORIDE TREATED Ti 6-4.

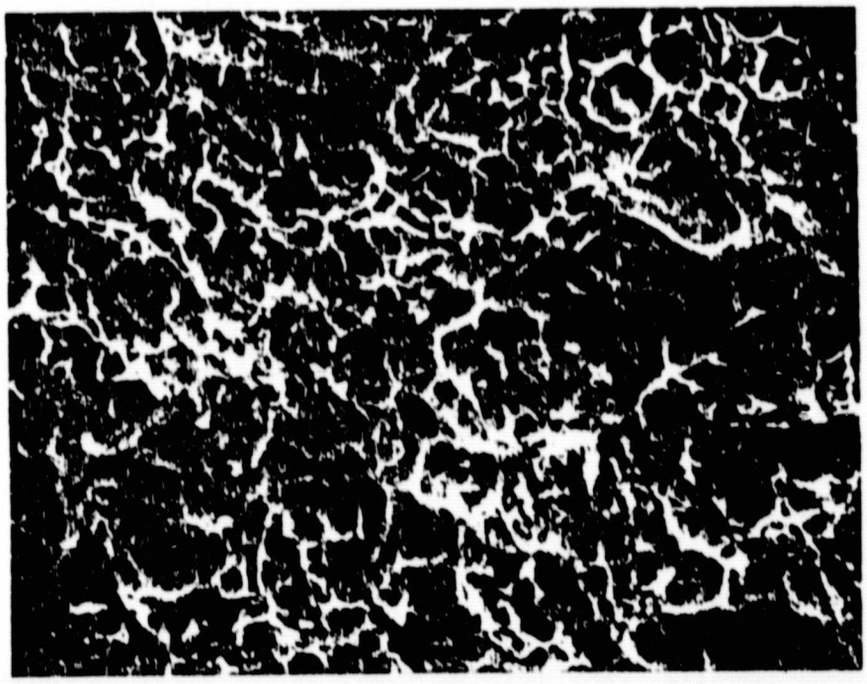

Figure 4. SEM PHOTOMICROGRAPH (X2000) OF PASA JELL TREATED Ti 6-4.

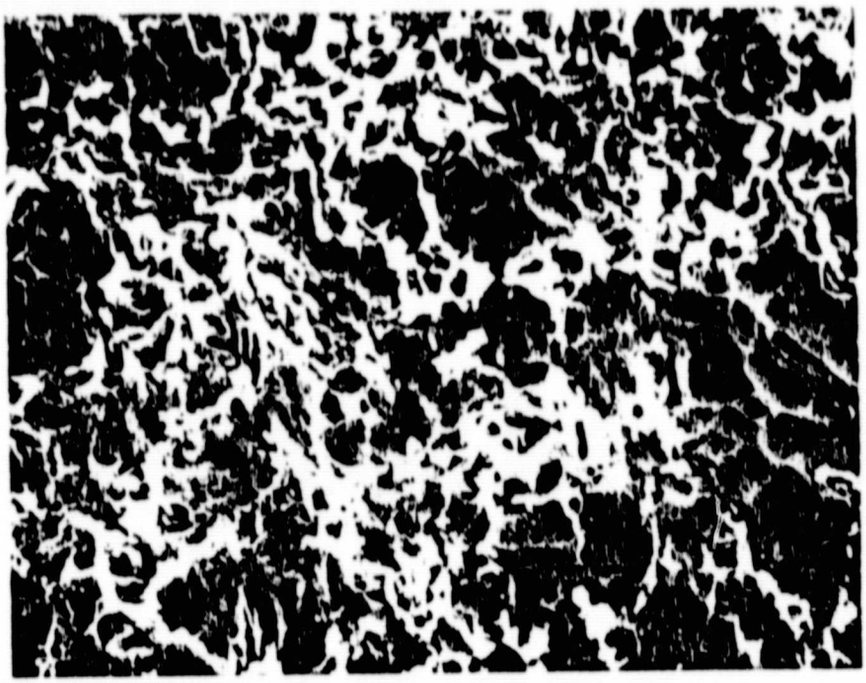

Figure 5. SEM PHOTOMICROGRAPH (X2000) OF TURCO TREATED Ti 6-4.

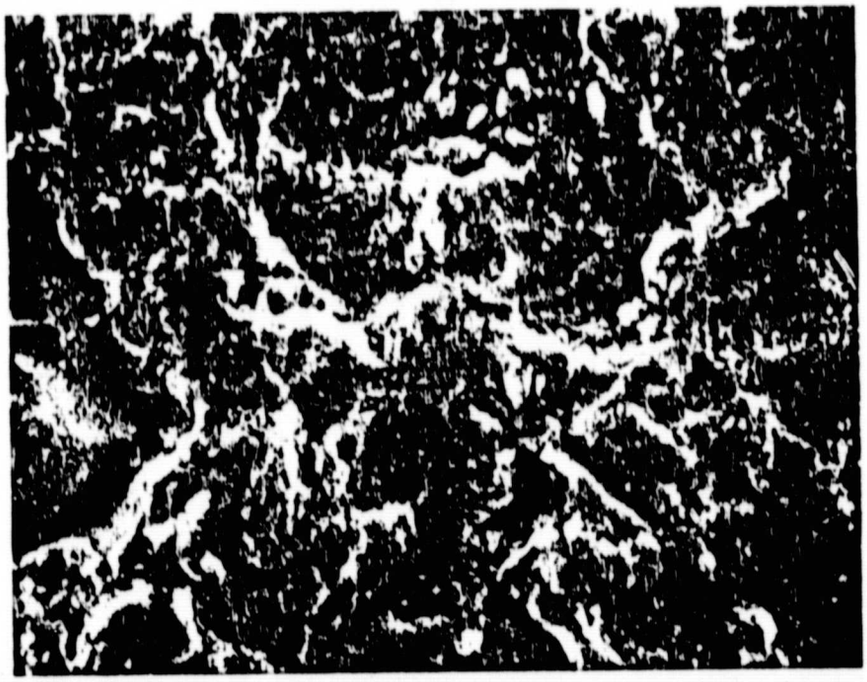

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Figure 6. SEM PHOTOMICROGRAPH (X2000) OF RAE TREATED Ti 6-4.