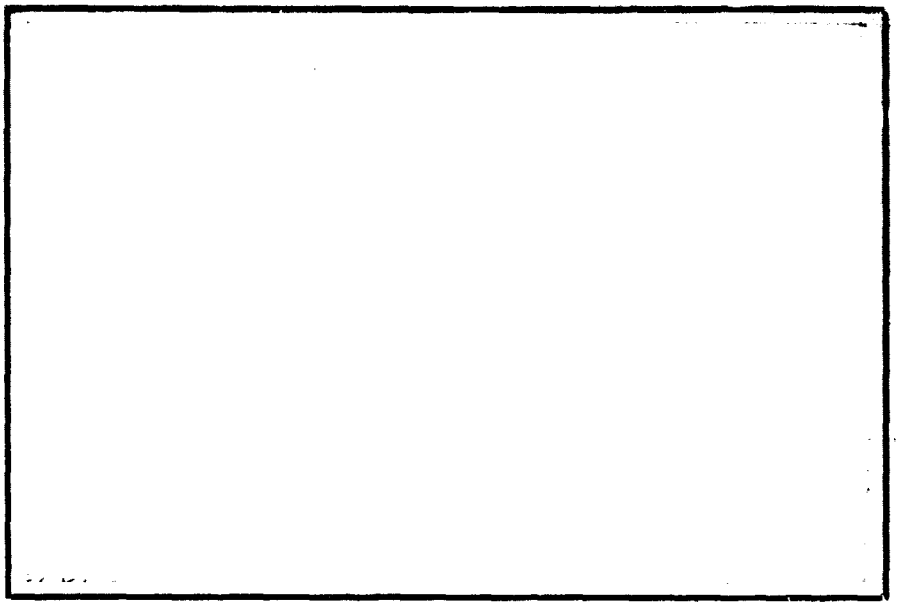
DEPARTMENT OF CHEMISTRY



Virginia Polytechnic Institute and State University

Blacksburg, Virginia 24061

SEMI-ANNUAL TECHNICAL REPORT

A CRITICAL STUDY OF THE ROLE OF THE SURFACE OXIDE LAYER IN TITANIUM BONDING

by

S. Dias and J. P. Wightman

Prepared for

National Aeronautics and Space Administration

October, 1982

Grant NAG-1-252

NASA-Langley Research Center
Hampton, Virginia 23665
Materials Division
Donald J. Progar

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

INTRODUCTION

There is a continuing and demonstrated need for a detailed molecular understanding of the role which the surface oxide layer of the adherend plays in titanium bonding. We have been involved in a long term research effort aimed at establishing the base line data necessary in such an understanding. The research has utilized pretreated Ti 6-4 adherends. The effects of adherend pretreatment, bonding conditions, and thermal aging of the lap shear specimens have been studied. Our primary emphasis has focused on the use of the SEM/EDAX and ESCA techniques to study surface morphology and surface composition. In addition, contact angles and both infrared and visible reflection spectroscopy have been used in ancillary studies. The results have been summarized recently (1).

One phase of our most recent work has focused on calorimetric studies using Ti 6-4 powders (2). The higher surface area of the powder compared to the standard lap shear coupon permits heats of immersion to be measured. The heats of immersion of Ti 6-4 have been measured in water, in PPQ and LARC-13 primer solutions and their respective solvents. The Ti 6-4 powder was heated to different temperatures in vacuum for varying time periods. The heats of immersion sharply increased between 200° and 300°C which was attributed to a chemical reaction of the liquid with elemental titanium. The results strongly support a model for thermal cracking of the surface oxide layer resulting in the interfacial failure associated with long term aging of bonded Ti 6-4 lap shear samples. There is a clear need then to pursue further research in this critical area.

The objective of this research is the characterization of the surface oxide layer on Ti 6-4 adherend with emphasis on SEM and XPS analysis of selected thermally aged Boeing samples (3).

EXPERIMENTAL

A. Samples -Fractured lap shear samples were sent from the Boeing Aerospace Company and these panels were used as received. The samples are described in Table I. The Ti 6-4 panels were bonded with three different resin adhesives coded LARC-13 (polyimide), PPQ (polyphenylquinoxaline) and 056 (polyimide). The Ti 6-4 adherends were pretreated by 5V or 10V chromic acid anodize (CAA) or by the Pasa-Jell process. Two sets of representative samples were selected after examining the lap shear strength, exposure time and surface preparation for each sample. The fractured Ti 6-4 surfaces were categorized as cohesive, interfacial and mixed mode failure [see Table I]. A 3/8" diameter sample was punched after a close examination of both fracture surfaces. These punched samples were then assigned to the following groups: metal failure surface (MFS), metal substrate surface (MSS), adhesive failure surface (AFS) and adhesive substrate surface (ASS). These four different surfaces are depicted schematically in Figure 1. A Bausch and Lomb stereo-zoom optical microscope was used to photograph each sample at 20X.

B. Scanning Electron Microscope (SEM) - The samples were mounted with copper tape on an aluminum stub. The first set of samples were coated with a gold-palladium alloy and photomicrographs at various magnifications were obtained on an AMR (Advanced Metal Research Corporation: Model 900) scanning microscope. A second set of samples were gold-coated. Photomicrographs of these specimens were obtained using JEOL JFM 35c scanning electron microscope. The surface of some samples were examined by EDAX (Energy Dispersive Analysis of X-rays) in order to identify the elements present that particular surface. These selected samples were coated with carbon since carbon is not detected by EDAX.

C. X-ray Photoelectron Spectroscopy (XPS) -The XPS studies of the fractured samples were done using a Physical Electronics ESCA/SAM Model 550 electron spectrometer. Data acquisition was accomplished using a SAM 550 data system and a Digital PDP-1104 computer. The punched samples were mounted with double sided stick tape. A wide scan (0 to 2200 eV) spectrum was helpful to identify the major elements present on the surface of the samples. Samples were scanned repetitively to obtain the atomic fraction of elements present in the sample surface.

RESULTS AND DISCUSSION

Research accomplished during the report period is summarized in Table II.

A. Scanning Electron Microscopy (SEM) - The SEM photomicrographs in general supported the failure mode assignments based on optical microscopy. However, the detailed features of the Ti 6-4 adherend surfaces are clearly delineated in the SEM photomicrographs. Representative SEM photomicrographs will be included in the Final Technical Report.

B. X-ray Photoelectron Spectroscopy (XPS) - The XPS results are summarized in Tables III-V and are discussed below.

1) L13-10 and L13-P Series.-There were no detectable quantities of fluorine, chromium, calcium or phosphorus in the surface of any of these aged fracture samples. This result is in contrast to the results of XPS analysis of freshly pretreated Ti 6-4 adherends (1). Significant concentrations of Si were found on each fracture surface.

2) L13-10-21.-The adhesive failure surface contains a significant quantity of Ti suggesting oxide fracture. The metal failure surface gives a strong

Ti signal but also a doublet oxygen 1s photopeak showing that a significant amount of adhesive remains on the metal failure surface. This sample had a reduced lap shear strength of 1180 psi after 5000 hours at 450°F.

3) L13-20-50.-The results for the adhesive and metal failure surfaces parallel those for the L13-10-21 sample. This sample had a minimum lap shear strength of 300 psi after 10000 hours at 450°F. The conclusion drawn from these XPS results is that failure occurred within the surface oxide layer.

There is a second entry for the L13-10-50 (MFS) sample. These XPS results were obtained on a DuPont 650 electron spectrometer and the agreement between the binding energies is quite good. The atomic fractions are also in fair agreement.

4) L13-10-53.-This high strength (3000 psi) lap shear sample showed a minimal Ti signal.

5) L13-10-60.-This high strength (2200 psi) lap shear sample gave no detectable Ti photopeak.

6) L13-P-25.-The adhesive failure surface showed no significant Ti signal whereas the metal failure surface gave a significant Ti photopeak.

7) PPQ-10-36. The adhesive failure surface gave a minimal Ti signal which was not expected for this low strength sample (910 psi). The metal failure surface contained a fair amount of adhesive as evidenced by the doublet oxygen 1s photopeak. The XPS results for the adhesive substrate and metal substrate surfaces parallel those for the failure surfaces. A significant Pb photopeak is noted in all the PPQ samples. This result has been reported previously (1) but the source of the lead is not known.

8) 056-P-55.-The adhesive failure surface showed no significant Ti photopaek. The metal failure surface contains a fair amount of adhesive since the predominant oxygen photopeak occurs at 531.6 eV characteristic of the adhesive rather than the adherend. The O 1s photopeak for Ti 6-4 occurs at 529.4 eV. A small tin signal was noted on each of the 056 samples.

A review of the XPS results suggests that for the 10 V chromic acid anodized samples, high Ti surface concentrations on the adhesive failure surfaces are associated with low lap shear strengths. This conclusion applies to both L13 and PPQ adhesives. The lap shear strengths are plotted as a function of the atomic fraction of Ti in the adhesive failure surface in Figure 2. It is proposed that long term thermal aging weakens the surface oxide layer. The high surface Ti concentrations observed on the adhesive failure surface following fracture after long term thermal aging result from fracture of the surface oxide layer.

REFERENCES

(1) J. P. Wightman, SAMPE Quarterly, 13, 1-8 (1981).

(2) R. V. Siriwardane and J. P. Wightman, submitted to J. Adhesion.

(3) Fractured lap-shear samples supplied to VPI & SU by Boeing.

TABLE I

DESCRIPTION OF BOEING Ti 6-4 FRACTURED LAP SHEAR SAMPLES

Sample No.	Surface Pretreatment	Time (hrs) [Temp]	Lap Shear Strength (psi)	Failure Mode
L13-10-21	10V CAA	5000[450°F]	1180	Interfacial
L13-10-50	10V CAA	10000[450°F]	300	Mixed
L13-10-53	10V CAA	500[120°F]	3000	Cohesive
L13-10-60	10V CAA	500[450°F]	2280	Mixed
L13-P-25	Pasa Jell	500[120°F]	2640	Mixed
L13-P-35	Pasa Jell	5000[450°F]	1200	Interfacial
L13-P-36	Pasa Jell	10000[450°F]	700	Interfacial
PPQ-5-28	5V CAA	5000[120°F]	1780	Interfacial
PPQ-10-14	10V CAA	5000[120°F]	2920	Cohesive
PPQ-10-36	10V CAA	10000[450°F]	910	Interfacial
PPQ-10-46	10V CAA	500[450°F]	2560	Interfacial
PPQ-10-67	10V CAA	500[450°F]	2850	Mixed
056-10-55	10V CAA	3000[120°F]	2340	Mixed
056-P-37	Pasa Jell	10000[450°F]	540	Mixed
056-P-55	Pasa Jell	3000[120°F]	740	Interfacial

TABLE II

SUMMARY OF WORK DONE ON BOEING Ti 6-4 FRACTURED

LAP SHEAR SAMPLES

	Technique			
Sample No.	XPS	SEM	EDAX	FT-IR
L13-10-21 (AFS)	X	X	X	X
L13-10-21 (MFS)	X	X	X	X
L13-10-50 (MFS)	X	X	X	
L13-10-50 (AFS)	X	X	X	
L13-10-53	X	X	X	
L13-10-60	X	X	X	
L13-P-25 (MFS)	X	X		
L13-P-25 (AFS)	X	X		
L13-P-35 (MFS)		X		
L13-P-35 (AFS)		X		
L13-P-36 (ASS)		X		
L13-P-36 (AFS)		X		
L13-P-36 (MFS)		X		
L13-P-36 (MSS)		X		
PPQ-5-28 (B) (MFS)	X			
PPQ-5-28 (AFS)		X		
PPQ-5-28 (MFS)		X		
PPQ-10-14		X		
PPQ-10-36 (MSS)	X	X	X	
PPQ-10-36 (MFS)	X	X	X	
PPQ-10-36 (AFS)	X	X	X	
PPQ-10-36 (ASS)	X			
PPQ-10-46	X	X	X	X
PPQ-10-67	X	X	X	X
056-10-55 (MSS)		X		
056-10-55 (AFS)		X		
056-P-37 (MFS)	X			
056-P-37 (ASS)		X		
056-P-37 (MSS)		X		
056-P-55 (AFS)	X	X		
056-P-55 (MFS)	X	X		
056-P-55 (ASS)	X	X		
055-P-55 (MSS)	X	X		

TABLE III

XPS ANALYSIS OF FRACTURED BOEING Ti 6-4 LAP SHEAR

SAMPLES BONDED WITH L13

Sample No.	L13-10-21(AFS)		L13-10-21(MFS)		L13-10-50(AFS)		L13-10-50(MFS)		L13-10-50(MFS)	
Photopeak	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.
F				NSP		NSP		NSP		NSP
Cr						NSP		NSP		NSP
							531.2		531.8	
O	532.0	0.19	531.6_D	0.24	531.8	0.24	529.8	0.33	530.0	0.38
Ti	458.8	0.004	458.2	0.036	458.2	0.009	458.0	0.08	458.6	0.049
N	400.4	0.046	400.0	0.037	399.8	0.032	399.6	0.018	399.9	0.024
Ca						NSP		NSP		NSP
C	284.6	0.72	284.6	0.67	284.6	0.70	284.6	0.54	284.6	0.53
P						NSP		NSP		NSP
Si	102.0	0.035	101.8	0.023	102.0	0.004	101.6	0.014	102.0	0.018

Sample No.	L13-10-53		L13-10-60		L13-P-25(AFS)		L13-P-25(MFS)	
Photopeak	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.
F				NSP		NSP		NSP
Cr				NSP		NSP		NSP
O	531.9	0.17	531.8	0.22	531.8	0.020	531.6	0.21
Ti	458.2	0.001		NSP		NSP	458.4	0.008
N	400.2	0.020	399.8	0.041	399.8	0.027	399.8	0.020
Ca				NSP		NSP		NSP
C	284.6	0.77	284.6	0.70	284.6	0.73	284.6	0.72
P				NSP		NSP		NSP
Si	102.6	0.036	102.6	0.020	102.6	0.027	102.2	0.009

TABLE IV

XPS ANALYSIS OF FRACTURED BOEING Ti 6-4

LAP SHEAR SAMPLES BONDED WITH PPQ

#PPQ-10-36	AFS		MFS		ASS		MSS	
F 1s		NSP		NSP		NSP		NSP
Cr 2p		NSP		NSP		NSP		NSP
O 1s	532.2	0.15	531.8 (529.9)	0.33	532.4	0.14	531.9 (530.0)	0.27
Ti 2p	458.6	trace	465.9	0.028		NSP		R
N 1s	398.8	0.028	399.2	0.02	398.8	0.021	399.2	0.016
Ca 2p		NSP		NSP		NSP		
C 1s	284.6	0.73	284.6	0.59	284.6	0.74	284.6	0.71
Pb 4f	138.6	0.005	138.1	0.017	138.8	0.005	138.4	0.02
P 2p								NSP
Si 2p	102.0	0.005	102.0	0.014	102.2	0.011		NSP

Sample No.	PPQ-5-28B(MFS)		PPQ-10-46		PPQ-10-67	
Photopeak	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.
F	689.0	trace		NS		NS
Cr		NSP		NS		NS
O	532.0$_D$	0.18	532.4	0.18	532.4	0.13
Ti	457.8	0.017	458.4	0.001	458.6	0.001
N	399.0	0.031	399.0	0.02	399.0	0.030
Ca		NSP		NS		NS
C	284.6	0.76	284.6	0.75	284.6	0.80
Pb	138.4	0.006		NS		NS
Si	102.6	trace	102.8	0.046	102.4	0.040

TABLE V

XPS ANALYSIS OF FRACTURED BOEING Ti 6-4 LAP SHEAR

SAMPLES BONDED WITH 056

Sample No.	056-P-55(AFS)		056-P-55(MFS)		056-P-55(ASS)		056-P-55(MSS)	
Photopeak	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.
F	687.8	0.065	688.0	0.065	687.8	0.096	687.8	0.10
Cr						NSP		
O	531.6	0.18	531.6	0.14	531.4	0.13	531.4 529.4	0.18
Sn	483.8	0.001	483.8	0.001	483.6	0.001		
Ti		NSP	457.4	0.005		NSP	457.8	0.022
N	399.8	0.034	400.0	0.019	399.8	0.033	400.0	0.031
Ca						NSP		
C	284.6	0.67	284.6	0.75	284.6	0.70	284.6	0.65
Si					101.6	0.01		
Al	74.6	0.049	74.4	0.021	74.4	0.02	74.6	0.018

Sample No.	056-P-37(MFS)	
Photopeak	B.E.	A.F.
F 1s	687.6	0.13
O	531.2 529.2	0.17
Ti	457.6	0.017
N	399.8	0.029
C	284.6	0.64
Al	73.4	0.012

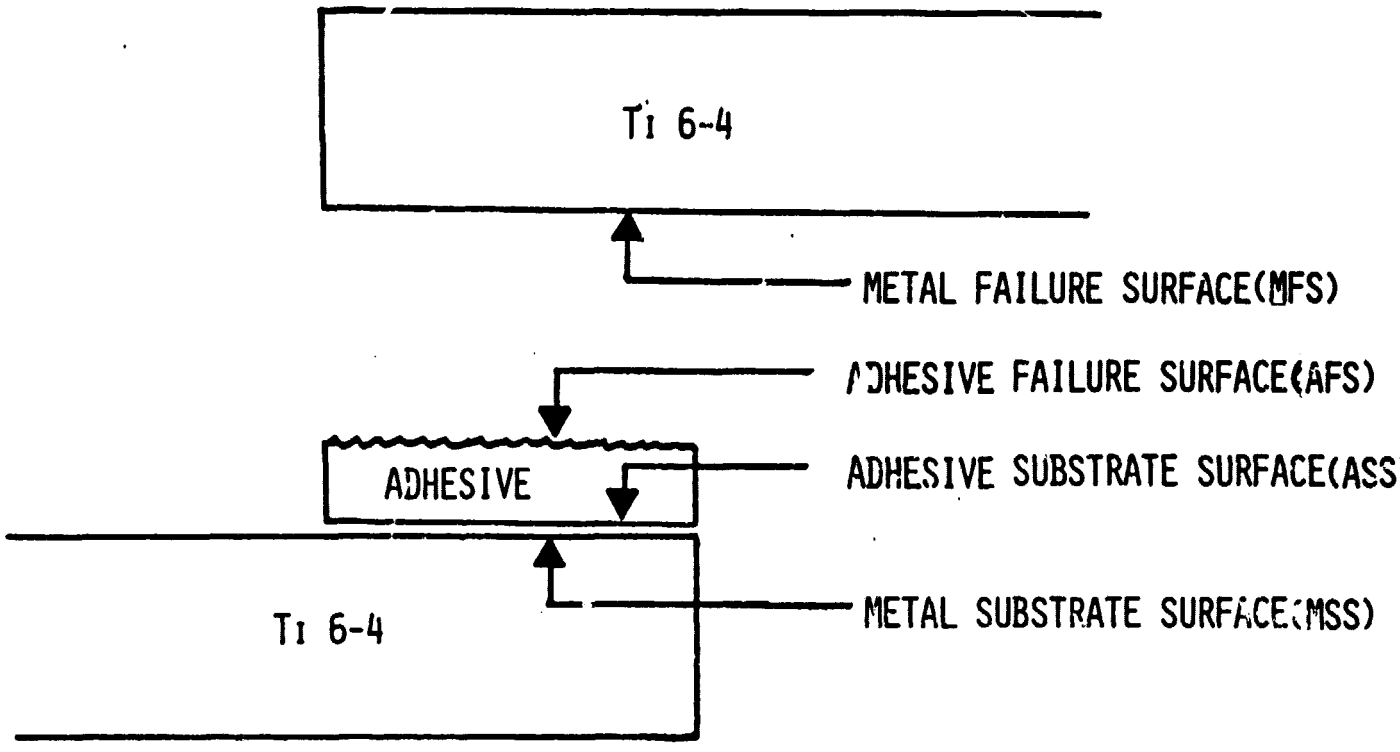


Figure 1. Schematic of fractured lap shear specimen

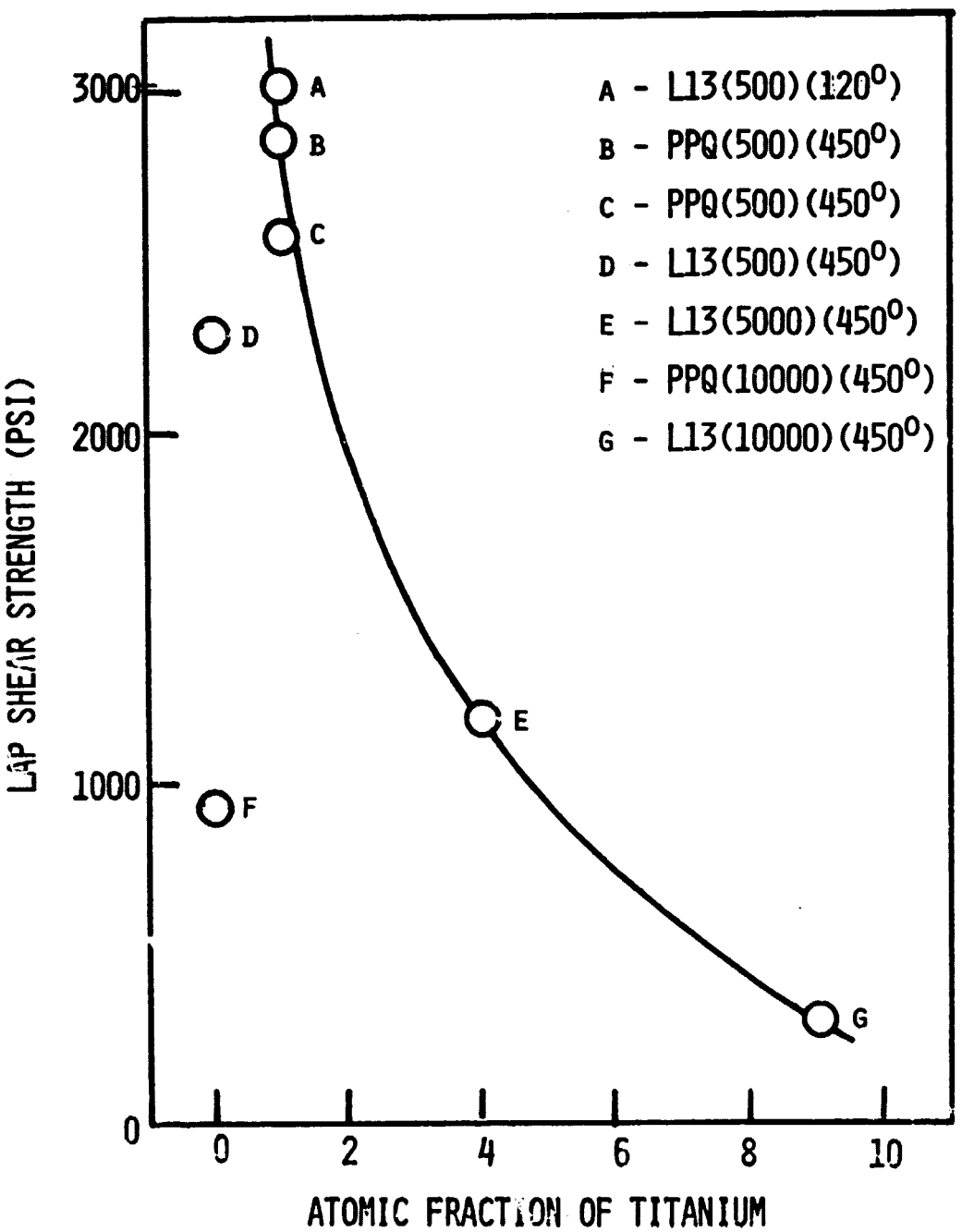


Figure 2. Lap shear strengths of fractured 10V CAA Ti 6-4 adherends bonded with LARC-13 and PPQ as a function of the atomic fraction of titanium on the adhesive failure surface as measured by XPS.