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SEMI-ANNUAL TECHNICAL REPORT
A CRITICAL STUDY OF THE ROLE OF THE SURFACE OXIDE LAYER IN TITANIUM BONDING

by

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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-Ⅳ 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 photopake. The metal failure surface contains a fair amount of adhesive since the predominant oxygen photopake occurs at 531.6 eV characteristic of the adhesive rather than the adherend. The O ls photopake 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

(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**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Surface Pretreatment</th>
<th>Time (hrs) [Temp]</th>
<th>Lap Shear Strength (psi)</th>
<th>Failure Mode</th>
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<td>L13-10-50</td>
<td>10V CAA</td>
<td>300 [450°F]</td>
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<td>L13-10-53</td>
<td>10V CAA</td>
<td>500 [120°F]</td>
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<td>10V CAA</td>
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<td>Mixed</td>
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<td>L13-P-25</td>
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<td>Pasa Jell</td>
<td>1200 [450°F]</td>
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<td>Pasa Jell</td>
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<td>056-P-37</td>
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### TABLE II

**SUMMARY OF WORK DONE ON BOEING Ti 6-4 FRACTURED LAP SHEAR SAMPLES**

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<th>Sample No.</th>
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### TABLE III

**XPS ANALYSIS OF FRACTURED BOEING TI 6-4 LAP SHEAR SAMPLES BONDED WITH L13**

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<td>B.E.</td>
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<td>NSP</td>
<td>NSP</td>
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<td>Cr</td>
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<tr>
<td>O</td>
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<td>531.6</td>
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<td>A.F.</td>
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## TABLE IV

**XPS ANALYSIS OF FRACTURED BOEING Ti 6-4 LAP SHEAR SAMPLES BONDED WITH PPQ**

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<th>Sample No.</th>
<th>PPQ-5-28B(MFS)</th>
<th>PPQ-10-46</th>
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<td>532.0</td>
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<td>Ti</td>
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**TABLE V**

XPS ANALYSIS OF FRACTURED BOEING Ti 6-4 LAP SHEAR SAMPLES BONDED WITH 056

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<th>056-P-55(AFS)</th>
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<tr>
<td>C</td>
<td>284.6 0.64</td>
</tr>
<tr>
<td>Al</td>
<td>73.4 0.012</td>
</tr>
</tbody>
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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.