LASER ABLATION SURFACE PREPARATION OF Ti-6Al-4V FOR ADHESIVE BONDING

F.L. Palmieri,[1,*] K.A. Watson,[1] G. Morales,[2] T. Williams,[3] R. Hicks,[3] C.J. Wohl,[4] J.W. Hopkins,[4] J.W. Connell[4]
[1]National Institute of Aerospace, Hampton, VA 23666
[2]NASA Langley Aerospace Research Summer Scholar (LARSS)
[3]University of California, Los Angeles, CA
[4]NASA Langley Research Center, Hampton, VA 23681

ABSTRACT

Adhesive bonding offers many advantages over mechanical fastening, but requires certification before it can be incorporated in primary structures for commercial aviation without disbond-arrestment features or redundant load paths. Surface preparation is widely recognized as the key step to producing robust and predictable bonds. Laser ablation imparts both topographical and chemical changes to a surface which can lead to increased bond durability. A laser based process provides an alternative to chemical-dip, manual abrasion and grit blast treatments which are expensive, hazardous, polluting, and less precise. This report documents preliminary testing of a surface preparation technique using laser ablation as a replacement for the chemical etch and abrasive processes currently applied to Ti-6Al-4V alloy adherends. Failure mode, surface roughness, and chemical makeup were analyzed using fluorescence enhanced visualization, microscopy, and X-ray photoelectron spectroscopy, respectively. Single lap shear tests were conducted on bonded and aged specimens to observe bond strength retention and failure mode. Some promising results showed increasing strength and durability of lap shear specimens as laser ablation coverage area and beam intensity increased. Chemical analyses showed trends for surface chemical species which correlated with improved bond strength and durability. Combined, these results suggest that laser ablation is a viable process for inclusion with or/and replacement of one or more currently used titanium surface treatments. On-going work will focus on additional mechanical tests to further demonstrate improved bond durability.

*To whom correspondence should be addressed: frank.l.palmieri@nasa.gov, (757) 864-8802

1. INTRODUCTION

Aircraft manufacturers rely increasingly on adhesive bonds to simplify airframe design and improve aircraft performance. Metal to composite bonds are becoming more common as the composite content of an aircraft is increased [1]. Replacing mechanically fastened joints with adhesive bonds can reduce weight, simplify manufacturing, and provide a stronger, more reliable joint, but solely bonded joints are rarely implemented in the primary structures of commercial aircraft due to predictability concerns and the inability to non-destructively assess bond strength. Restrictions on the application of adhesively bonded joints stem from a lack of control in current bonding methods [1] [2]. New surface preparation methods, which promise to improve

repeatability, minimize waste, and reduce costs, are becoming increasingly important to aircraft manufacturers.

The premature or unexpected failure of an adhesive bond can usually be traced to defects in the preparation of the faying surface [3] [4]. Current surface treatment techniques based on mechanical abrasion such as grit blasting or sanding have limited repeatability and can leave contamination that reduces bond performance. State-of-the-art methods for modifying the surface chemistry of titanium alloys depend on wet chemical etchants containing acids, caustics, and oxidizers, usually in combination [5] [6] [7]. Such processes are expensive to perform because they are dangerous, create large volumes of hazardous waste, and are difficult to automate. The automation of surface preparation, which increases reproducibility, may be necessary for the certification of bonded primary structures [1].

Non-standard techniques such as atmospheric pressure plasma, arc discharge, and laser ablation have been demonstrated, but are still undergoing evaluation by the aerospace industry [8] [9] [10]. Laser ablation is a subtractive process which relies upon highly-focused laser radiation to remove and redistribute material on a surface [11] [12] [13] [14]. Ultra-violet laser systems are commonly used for high precision work such as medical procedures, the machining of fine parts, and printing microelectronic circuit patterns. The ablation process has been demonstrated to generate high precision surface topography simultaneously with the removal of surface contaminates and modification of surface chemistry [15] [16].

This report presents the development of a laser ablation technique for the preparation of Ti-6Al-4V alloy faying surfaces. A neodymium doped yttrium aluminum garnet (Nd:YAG) laser that has been frequency tripled to a wavelength of 355 nm was used to clean/de-scale, create topographical patterns, and modify adherend surface chemistry prior to bonding with PETI-5 adhesive. The state-of-the-art processes that have been replaced include acid etching, caustic etching, grit blasting, and priming. Macroscopic bond properties for a variety of lasing conditions were surveyed using single-lap shear tests, and the results were correlated with surface roughness and surface chemistry based on X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL

2.1 Materials and Methods

Titanium alloy (Ti-6Al-4V, an alloy consisting of 90% titanium, 6% aluminum and 4% vanadium, 1.6 mm [0.063"] thick) was purchased from California Metal & Supply, Inc. and supplied in the configuration shown in Figure 1. This configuration is a modification of specimens called for in ASTM D1002-05, and allowed for the use of an existing bonding jig. Phenylethynyl terminated imide (PETI) high temperature adhesive, PETI-5 (2500 g/mole), was chosen for these experiments based on this laboratory’s extensive experience with polyimide adhesives. The synthesis of PETI-5 was conducted in-house, and is described elsewhere [17]. Optical micrographs were taken with a Zeiss Exciter microscope equipped with a Zeiss Axiocam digital camera. Roughness was measured using a New View 6000 optical surface profiler from the Zygo Corporation equipped with a 2.5 x objective and a 1 x zoom tube. XPS was performed on a ThermoFisher ESCAlab 250 X-ray photoelectron spectrometer.

2.2 Polishing of Titanium Adherends

A Buehler Ecomet III with an Automet head and 300 mm platen was used to polish a subset of samples to a RMS roughness of 0.050 ± 0.010 μm across the faying surface. The native RMS roughness found on the faying surface of titanium alloy lap shear substrates before polishing was 0.630 ± 0.030 μm. Polishing was performed in stages starting with 240 grit silicon carbide paper via wet-sanding and progressing through 320, 400, 600, 800, and 1200 grit papers. The final polish was performed on a velpol polishing cloth using slurry made from 0.05 μm colloidal alumina, water, and alkaline, liquid detergent in about equal parts. Lower platen polishing speeds were maintained between 100 and 150 rpm, and the downward force of the head was between 44.5 and 222 N (10 and 50 lbs).

2.4 Preparation of Adhesive Tape

PETI-5 (2500 g/mole) adhesive tape was prepared in-house and used for bonding all specimens. An E-glass scrim cloth (style 112, A-1100 finish, 2-ply twisted yarn in a 0º/90º plain weave, 0.09 mm thick, γ-aminopropyl silane treated) was stretched onto a 22.5 cm x 32.5 cm frame. The scrim cloth was impregnated with adhesive by brushing on a solution of PETI-5 poly(amic acid) adhesive in *N*-methyl-2-pyrrolidinone (NMP). Initial coats were made with an 8 wt. % solution of PETI-5 oligomer in NMP solvent, and were continued until a non-porous tape was formed (4 to 8 coats). Subsequent coats were applied at 20 and 30 wt. % to build the tape thickness to 0.13 mm (~5 mil; 10 to 15 coats). After each coat was applied, excess NMP was removed by heating the tape in stages to a final temperature of 230 °C.

2.5 Laser Ablation

Laser ablation of Ti-6Al-4V coupons was performed on a PhotoMachining, Inc. laser ablation system with a Coherent Avia® frequency tripled Nd:YAG laser (7-watt nominal pulsed output at 355 nm). Single lap shear specimens were ablated with parallel lines on the faying surface using a direct write process. The lines were oriented along the length of the specimen so that the ablation pattern was parallel to the tensile load during the mechanical test. The write speed (25.4 cm/s) and pulse frequency (80 kHz) were held constant for all experiments. The pattern density was varied by changing the pitch of the parallel lines and the laser power was varied and monitored after the final lens element using a thermopile sensor (model 3A-SH) and Nova II power meter from Ophir Spirocon LLC. Throughput of the laser system was not optimized in this study, but the experimental processing rate ranged from about 32 to 1.3 cm^2/min depending on pattern density.

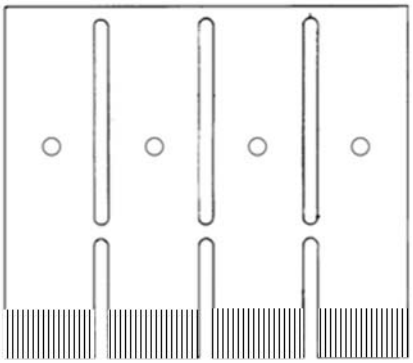

Figure 1: Modified adherend geometry indicating laser-etched portion.

2.6 Bonding

Mechanical test specimens were bonded in a 30 cm x 30 cm, heated Carver press for 1 h at 371 °C and 0.34-0.68 MPa (50-100 psi). Bonding configurations were shimmed to maintain a 0.13 ± 0.025 mm (0.005 ± 0.001 in) bondline thickness. Specimens were compressed and held at full load starting at room temperature and released after the press cooled below 150 °C. Compressed air was used to speed the cooling process.

2.7 Mechanical Testing

Single lap shear specimens were tested according to ASTM D1002-05 using a mechanically actuated test frame manufactured by Measurement Technology Inc. equipped with a 22.2 kN (5 kip) load cell and pin fixtures. Four specimens were tested for each set of experimental conditions. Additional lap shear specimens were subjected to a 72 h water boil according to ASTM D1151-00 immediately prior to testing. All specimens were tested at room temperature.

2.8 Fluorescence Failure Mode Analysis

The failure mode of each specimen was determined using a fluorescence visualization technique based on the fluorescent properties of the PETI-5 adhesive in contrast to the non-fluorescent metal adherends. Digital images of each adherend were collected using a Kodak DCS-760M camera with cold cathode detector and a LM2X-DM LED ultra violet light source from Innovative Science Solutions Inc. having a peak wavelength of 400 nm. An orange gelatin filter was used to prevent reflected light from reaching the camera detector. Example images of a failed lap shear specimen under visible and UV illumination, respectively, are shown in Figure 2. The contrast between adhesive-covered and adhesive-barren areas allows for the use of software to count the number of pixels in the bondline with no adhesive present. The percentage of surface area lacking adhesive was take as the percentage of adhesive failure.

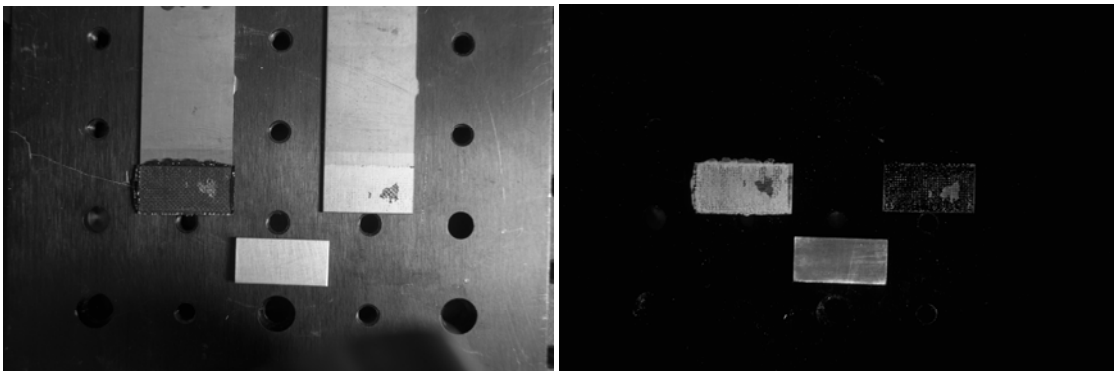

Figure 2: On the left is a visible light image of a failed lap-shear specimen showing mostly adhesive failure. On the right is a fluorescence image of the same specimen with clearly visible adhesive residues. A 12.7 x 25.4 mm (0.5” x 1”) reference standard with a fluorescent coating is visible at the bottom of each image.

3. RESULTS AND DISCUSSION

3.1 Ablated Surface Properties

Laser ablation resulted in highly reproducible topography in the Ti-6Al-4V surface, as shown in Figure 3. The ablation line density scales indirectly with the pitch. Because the beam width (w) is approximately 25.4 μm, a 101.6 μm pitch (p) results in a 25% duty cycle (D) while a 5.1 μm pitch produces a 500% duty cycle. The relationship between duty cycle and the parallel line pitch is given in equation 1. A duty cycle less than 100% indicates that some of the adherend surface did not receive laser processing and remains untreated.

$$D = \frac{w}{p} \times 100\% \qquad [1]$$

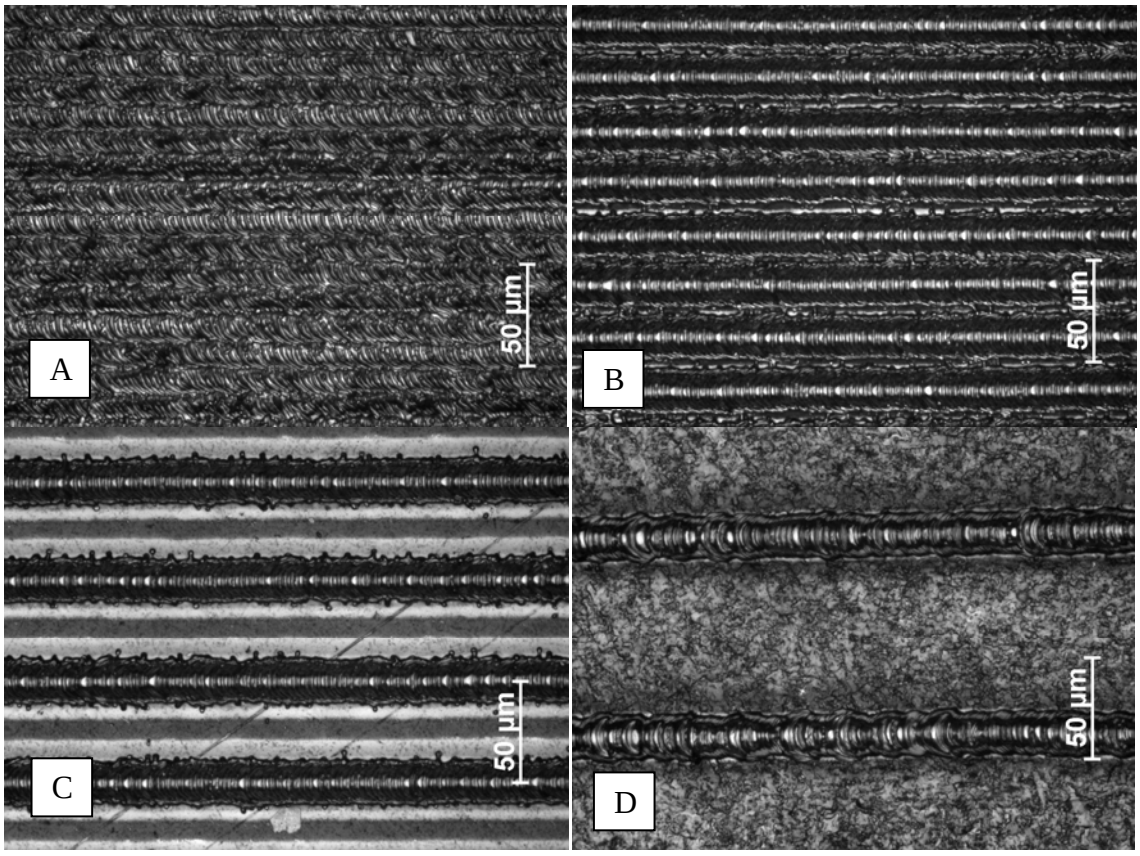

Figure 3: Parallel lines ablated into a polished Ti-6Al-4V surface with a pitch of: A. 0.013 mm (0.0005 in), B. 0.025 mm (0.001 in), C. 0.051 mm (0.002 in) and D. 0.102 mm (0.004 in)

Adherends were laser processed both as received and after polishing. RMS roughness of the surface, as measured on a white light interferometer, varied between 50 nm for highly polished surfaces, to 630 nm on the as-received surface, to about 1300 nm for heavily ablated surfaces. The effect of pattern density on roughness was observed by varying the pitch of the ablation pattern from 0.005 to 0.101 mm (0.2 to 4 mil), (500% to 25% duty cycle).

3.2 Single-Lap Shear Test Results

The mechanical test results for polished SLS specimens that were ablated at 1 W are shown in

Figure **4** along with roughness and failure mode statistics. Laser ablated specimens showed improvement in bond strength and predominantly cohesive failure mode in the adhesive as the pitch of the ablation pattern was reduced both before and after immersion in boiling water for 72 h. This supported the hypothesis that laser ablation improves the strength and durability of the titanium alloy/PETI-5 interface. The dashed lines in

Figure **4** show the highest apparent shear strength achieved for unpolished specimens with optimal laser ablation treatment both before and after 72 h of immersion in boiling water. Although polished and ablated specimens appear to be slightly stronger than unpolished and ablated specimens, SLS tests did not provide enough differentiation to indicate polishing as a practical means of surface preparation.

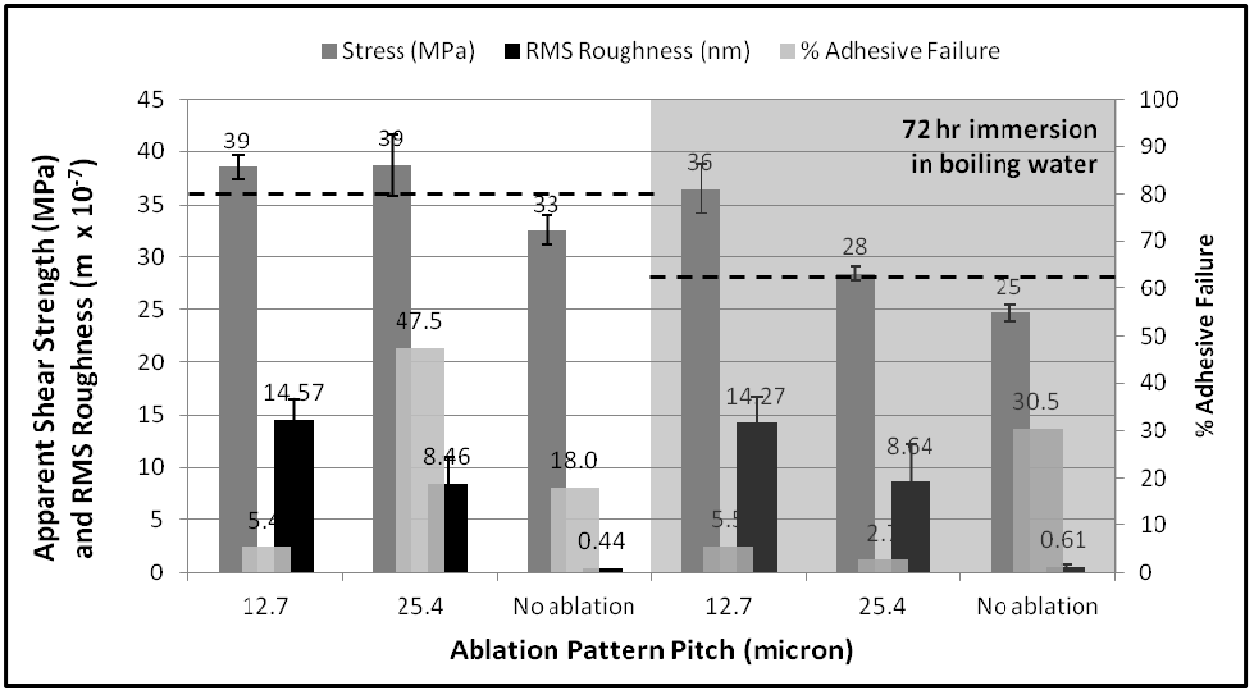

Figure 4: Results for SLS specimens prepared with polished adherends. Laser power was 1 W for all ablated specimens. Data in the shaded region was collected from specimens that underwent a 72 hr immersion in boiling water immediately prior to testing. Dashed lines indicate the apparent shear strength values achieved for unpolished SLS specimens. (1×10^{-7} m = 0.1 μm)

Faying surfaces of adherends were polished before laser processing to provide a smoother starting surface than the inherently rough surface of the unpolished adherends. The effects of laser generated topography on bond performance were to be isolated from the effects of native roughness by providing a smooth baseline (RMS roughness about 50 nm). Polished specimens without laser ablation were significantly stronger than the inherently rougher, untreated specimens (apparent shear strength: 16.5 MPa). These surprising results showed that the polishing process improved bond strength solely through surface chemistry modification. Thus,

the effects of changing surface topography could not be isolated from surface chemistry variation. Additionally, polishing is a slow, manual process which would be difficult to automate in a manufacturing environment; therefore, the polishing step was removed from subsequent experiments.

Lap shear test results for unpolished specimens ablated with varying pattern density are summarized in Figure 6 with apparent shear strength, failure mode, and RMS roughness Decreases in apparent shear strength corresponded well with increases in adhesive failure mode, as anticipated. Laser ablation appeared to play a key role in maintaining an adhesive bond and driving the specimen to a cohesive failure mode. As the ablation duty cycle fell below 100%, bond properties immediately began to decline in sample sets with and without immersion in boiling water. In all specimens, the 72 h immersion in boiling water resulted in about 25% loss in apparent shear strength although a cohesive failure mode was maintained. This indicated that immersion in boiling water for 72 h did not weaken the adhesive/metal interface, but degraded the properties of the cured PETI-5 adhesive. Capillary ingression of water along the glass fiber scrim cloth is suspected based on the speed and magnitude of the property loss.

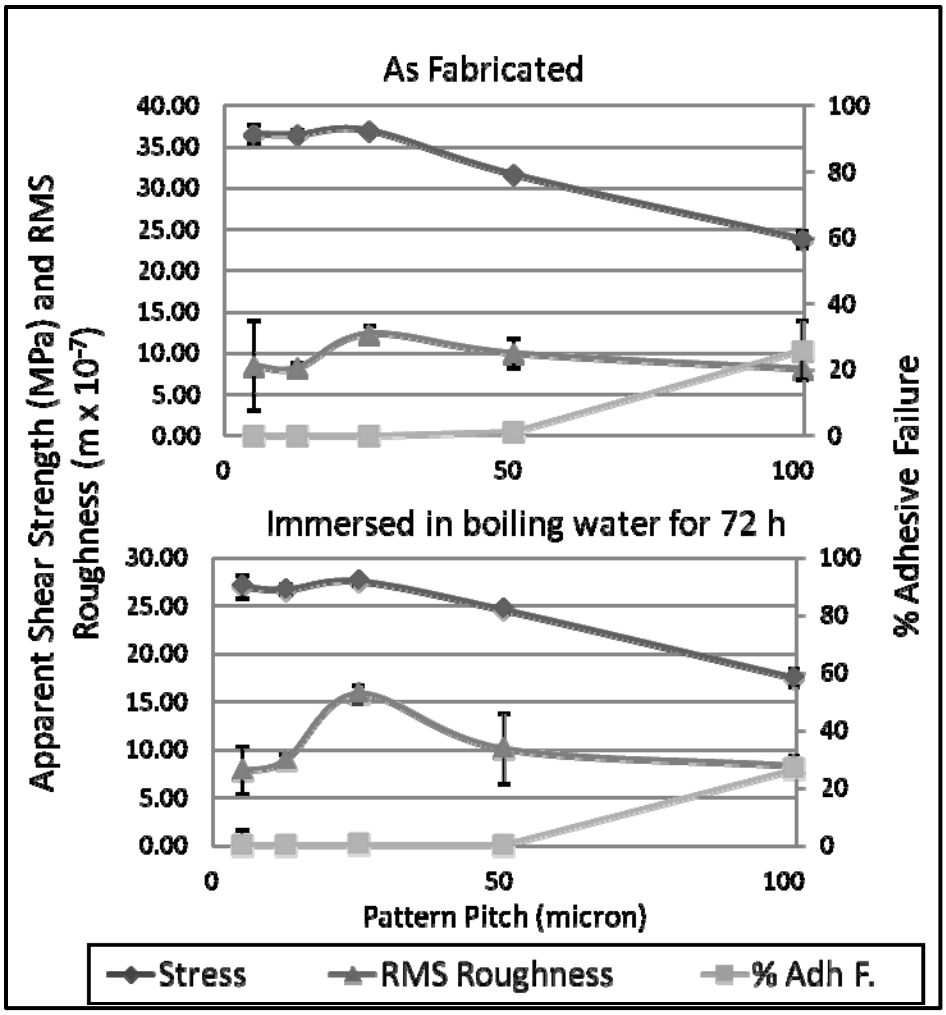

Figure 5: Roughness and lap shear data for non-polished adherends are shown for two data sets: line pitch variation without (top) and with (bottom) immersion in boiling water. (1 x 10^{-7} m = 0.1 μm)

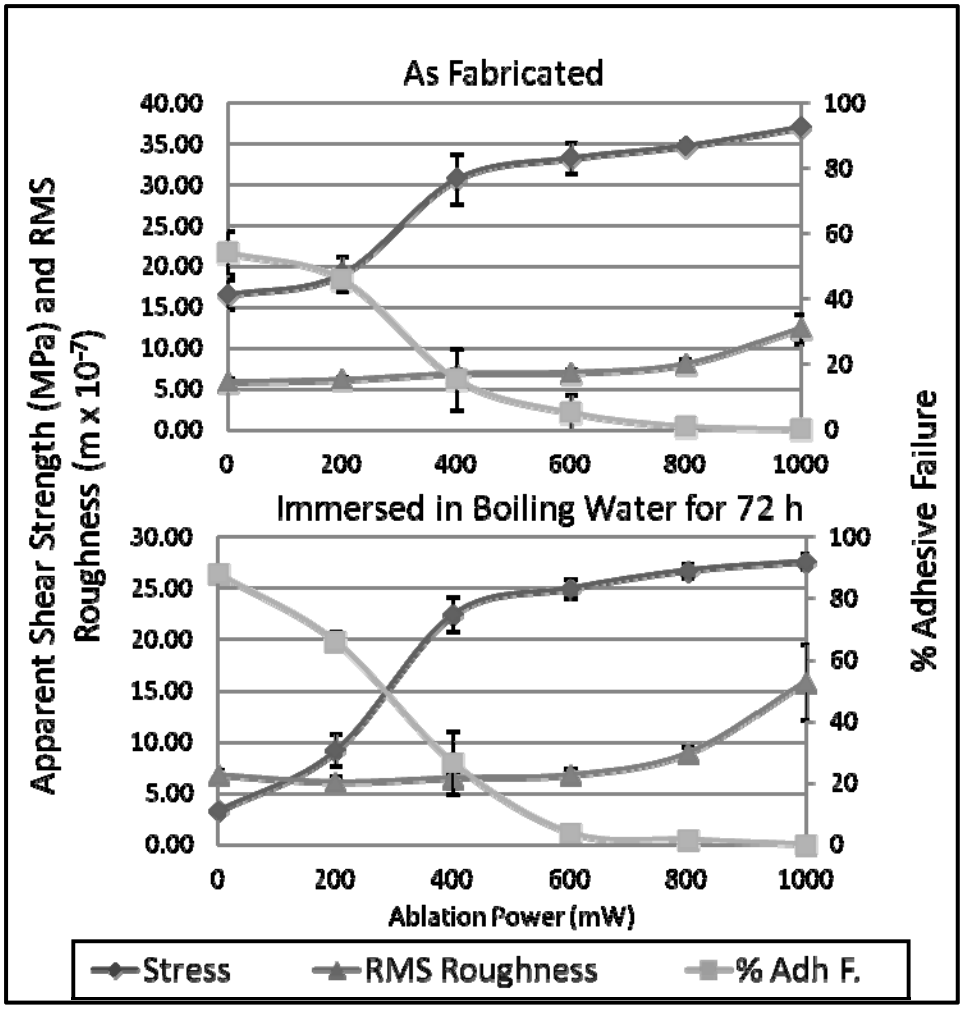

Figure 6: Roughness and lap shear data for non-polished, laser ablated adherends are shown for two data sets: laser power variation without (top) and with (bottom) immersion in boiling water. (1 x 10^{-7} m = 0.1 μm). Ablation pitch was 25.4 μm for all specimens.

The data shown in Figure 6 present strong correlation between bond performance and laser power. The apparent shear strength increases dramatically and the failure mode switches to cohesive failure as the ablation power is increased. The same trend is also observed for specimens immersed in boiling water for 72 h. Bond improvement appears to plateau at about 800 mW of laser power, which coincides with the adhesive failure mode reaching nearly 0%.

Figure 5 and 6 show how the roughness of the non-polished specimen surfaces varied with pitch of the ablation pattern and laser power. The RMS roughness of the ablated surface was not significantly increased over that of the native surface for laser powers less than 800 mW. Mostly minor variations in roughness are observed for both the power variation and pitch variation experiments. The bond properties reach a maximum without increasing the roughness more than

35%, which indicates that roughness may be a secondary factor influencing the bond strength of a lap shear specimen prepared by laser ablation. Similar results have been observed by others using alumina grit blasting to roughen titanium alloys [18].

3.3 XPS Analysis

Polished titanium adherends were ablated at a 25.4 µm pitch with power variation between 0 and 1000 mW before interrogating the surface using XPS. Survey scan data are presented in Figure 7 for select elements with shaded areas indicating the failure mode observed in SLS specimens. Constituents such as carbon, nitrogen and silicon appeared in the XPS spectra, but were removed from the data analysis. It is believed that these elements played no role in bonding, and they were introduced as surface contaminates after ablation but before XPS inspection.

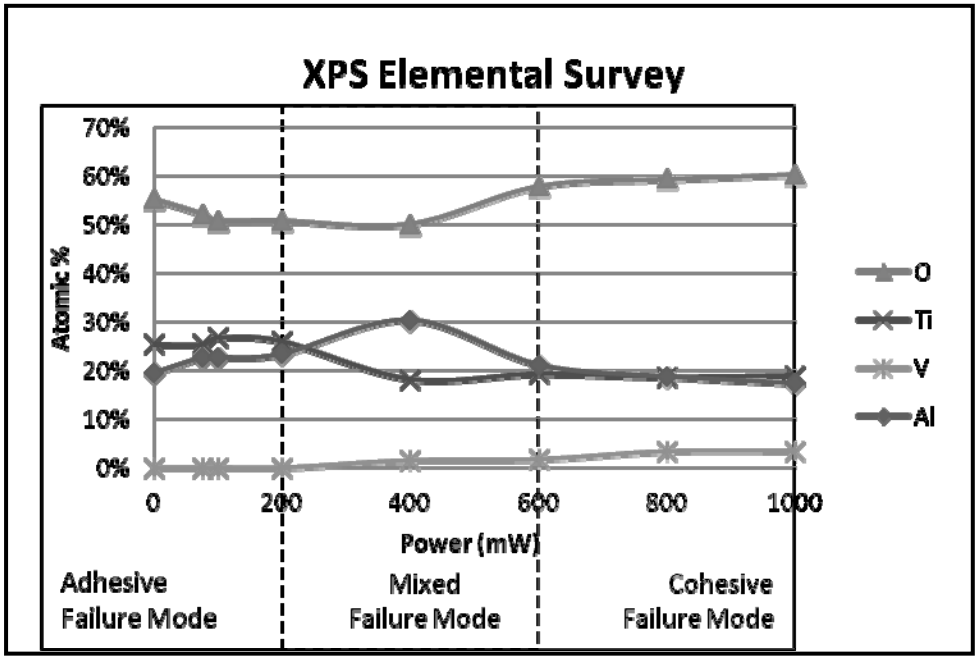

Figure 7: XPS survey scan data showing the atomic percent abundance of select elements found in survey scan spectra. Shading on the figure indicates the dominant failure mode seen in SLS test specimens.

The survey scan data (Figure 7) do not indicate major changes in elemental abundance at the adherend surface to correlate with changes in the observed failure mode. The most significant changes seen include the appearance of vanadium at the surface and an increase in the oxygen concentration. Vanadium tends to segregate to the bulk of the alloy; therefore, its presence at the surface was probably the result of surface material ablation and the exposure of underlying, bulk material. The increase in oxygen concentration was attributed to the oxidation of the surface metals and sub-oxides during the ablation process. The surface concentrations of titanium and aluminum decreased nominally due to dilution by vanadium and oxygen as the ablation power was raised.

Little correlation was seen between the atomic composition of the surface, and the failure mode of the adhesive. However, the bonding states of each element must also be considered. The de-

convolution of the $Ti2p_{1/2}$, $Ti2p_{3/2}$, O1s, and Al2p high-resolution XPS spectra showed variation in surface chemistry as laser ablation power was increased (Figure 8). Figure 9 summarizes the surface composition data for each of the metals and oxides found on the alloy surface after ablation. The shading on the figure indicates the dominant failure mode observed in three power ranges based on the SLS failure mode results. The concentration of titanium dioxide increased steeply across the power range for mixed failure mode while all other titanium constituents diminished in concentration. This is consistent with the increased atomic percentage of oxygen observed in Figure 7. It also indicates that more intense laser ablation causes oxidation which has been linked to improved bond performance.

The de-convolution of the XPS spectra in Figure 8 shows that oxygen was found in five different chemical species on the adherend surface though none of them appeared to change dramatically across the range of laser power explored. The removal of the more highly oxidized hydroxyl species ($-(OH)_{OX}$) is thought to improve bond performance based on previous work [19]. De-convolution of the aluminum multiplex revealed two components: aluminum metal and alumina (Al_2O_3). Above 200 mW of laser power, the aluminum metal was quickly oxidized to alumina which coincided with changes in bond performance. These results suggest that alumina at the surface may enhance adhesive bonding of Ti-6Al-4V substrates with PETI-5 adhesive.

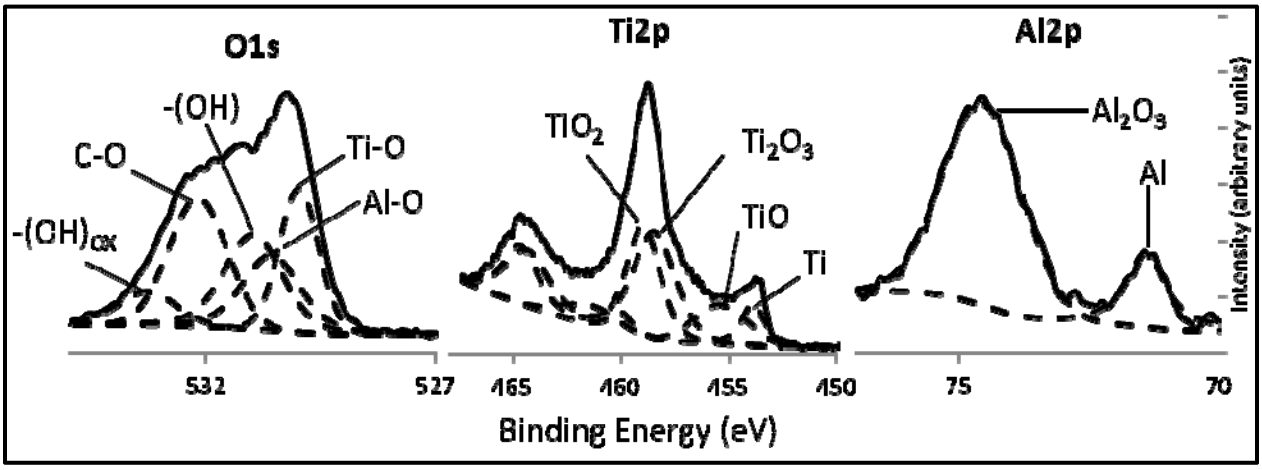

Figure 8: De-convolution of a high-resolution O1s, Ti2p, and Al2p spectra from different specimens showing peak assignments

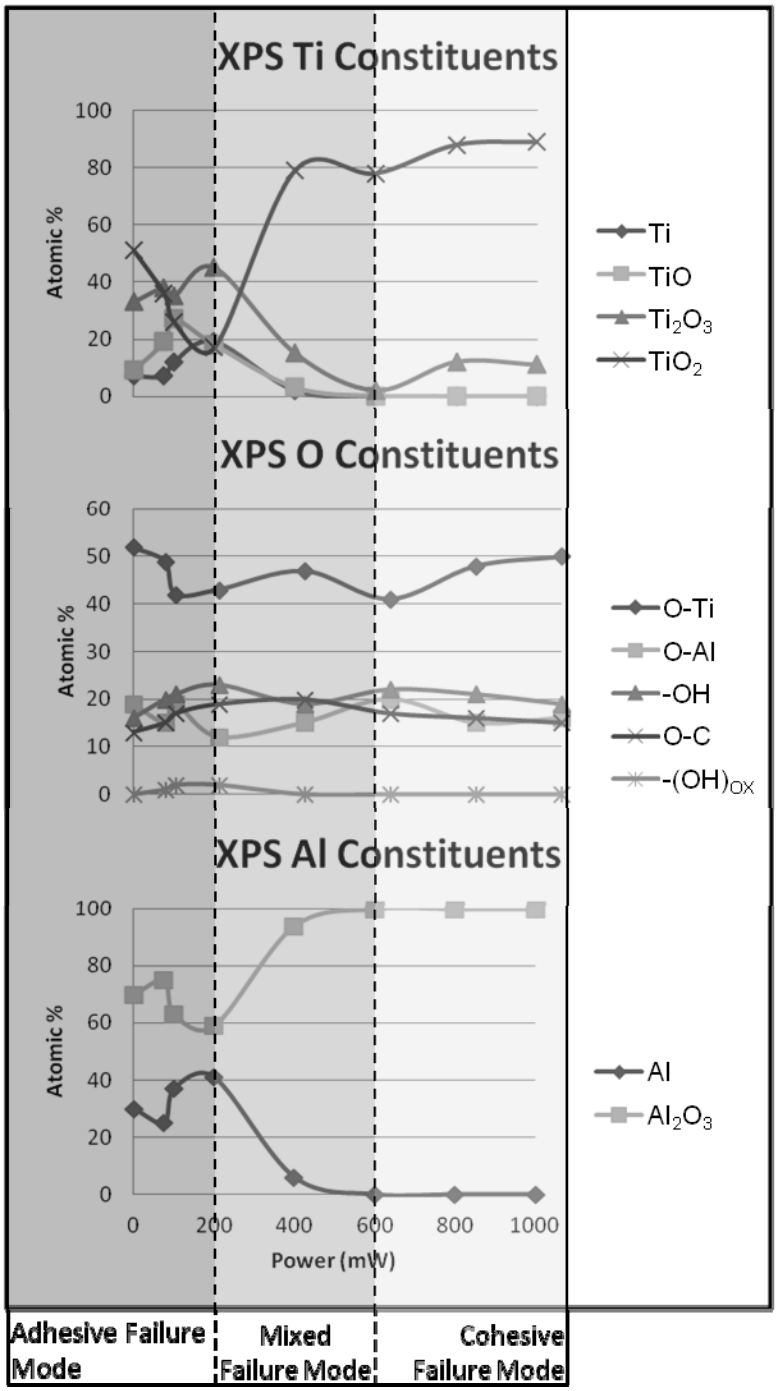

Figure 9: Atomic percent abundance of surface constituents based on the deconvolution of the $Ti2p_{1/2}$ and $Ti2p_{3/2}$ mulitplex (top), O1s peak (center), and Al2p peak (bottom). Shading on the figure indicates the dominant failure mode seen in SLS test specimens.

Based on the XPS and SLS results, parallel lines ablated at greater than 600 mW power and at less than 50.8 µm pitch resulted in roughened surfaces with increased titania and alumina content which, when bonded with the PETI-5 adhesive, formed robust bonds with apparent shear strengths comparable to current state-of-the-art surface preparation techniques [20].

4. SUMMARY

A 355 nm laser was used to ablate patterns conducive to adhesive bonding onto Ti-6Al-4V surfaces. Microscopic inspection, mechanical testing, and chemical analysis of the ablated surfaces were performed. The ablation process was studied by varying two parameters independently: laser power (0 - 1000 mW, 25.4 µm pitch) and ablation duty cycle (5.1 – 101.6 µm pitch, 1000 mW power). Lap shear testing showed that laser ablation improved bond performance dramatically for ablation duty cycles greater than 50% and ablation power greater than 400 mW. XPS analysis of the laser ablated surfaces indicated the formation of titanium and aluminum oxides as the laser ablation power increased above 200 mW up to 1000 mW. More highly oxidized hydroxyl species were removed completely at ablation powers greater than 400 mW. Also above 400 mW and at duty cycles greater than 50%, essentially 100% cohesive failure modes were observed, and bond strengths were comparable to those produced by state-of-the-art surface preparation techniques. Improved precision and more reproducible surface preparation are inherent traits of laser processing. In addition, laser ablation provides an alternative, "greener" means of surface preparation on titanium adherends by avoiding the use of toxic chemical etchants and grit blast media.

5. ACKNOWLEDGEMENTS

The Authors thank Drs. Tony Belcher and Kay Blohowiak of The Boeing Company for their insightful technical discussions, recommendations and review of this manuscript. Dmitry Pestov and Everett Carpenter at Virginia Commonwealth University are acknowledged for providing XPS services and related technical advice. Finally, thanks are due to Thomas Jones from the NASA Langley Research Center for constructing the apparatus used for fluorescence visualization of failed mechanical specimens.

6. REFERENCES

[1] R. Bossi and M. Piehl, *Manufacturing Engineering*, pp. 101-109, March 2011.

[2] M. Perton, *Journal of Physics D: Applied Physics*, vol. 44, pp. 1-12, 2011.

[3] G. Davis, *Surface and Interface Analysis*, vol. 20, pp. 368-372, 1993.

[4] M. Davis and D. Bond, *International Journal of Adhesion and Adhesives*, vol. 19, pp. 91-105, 1999.

[5] H. Lui, C. Simone, P. Katiyar and D. Scola, *International Journal of Adhesion and Adhesives*, vol. 25, pp. 219-226, 2005.

[6] G. W. Critchlow and D. M. Brewis, *International Journal of Adhesion and Adhesives*, vol. 15, pp. 161-172, 1995.

[7] J. Cotter and A. Mahoon, *International Journal of Adhesion and Adhesives*, vol. 2, pp. 47-52, 1982.

[8] R. Rechner, I. Jansen and E. Beyer, *International Journal of Adhesion and Adhesives*, vol. 30, pp. 595-601, 2010.

[9] R. Broad, J. French and J. Sauer, *International Journal of Adhesion and Adhesives*, vol. 19, pp. 193-198, 1999.

[10] P. Molitor, V. Barron and T. Young, *International Journal of Adhesion and Adhesives*, vol. 21, pp. 129-136, 2001.

[11] E. Baburaj, D. Starikov, S. Evans, G. Shafeev and A. Bensaoula, *International Journal of Adhesion and Adhesives,* vol. 27, pp. 268-276, 2007.

[12] M. Rotel, J. Zahavi, S. Tamir, A. Buchman and H. Dodiuk, *Applied Surface Science,* pp. 154-155, 610-616, 2000.

[13] Q. Benard, M. G. M. Fois and P. Lauren, *International Journal of Adhesion and Adhesives,* vol. 26, pp. 543-549, 2006.

[14] Q. Benard, M. Fois, M. Grisel, P. Laurens and F. Joubert, *Journal of Thermoplastic Composite Materials,* vol. 22, pp. 51-61, 2009.

[15] M. Belcher, C. Wohl, J. Hopkins and J. Connell, "Laser Surface Preparation and Bonding of Aerospace Structural Composites," in *55th International SAMPE Symposium and Exhibition,* Seattle, WA, USA, 2010.

[16] M. Belcher, C. Wohl and J. Connell, "Surface Preparation and Bonding of Composite Aircraft," in *32nd Annual Meeting of the Adhesion Society,* Savannah, GA, USA, 2009.

[17] P. Hergenrother, J. Connell and J. Smith, *Polymer,* vol. 41, pp. 5073-5081, 2000.

[18] A. Harris and A. Beevers, *International Journal of Adhesion and Adhesives,* vol. 19, pp. 445-452, 1999.

[19] E. W. Harris, J. T. Massey, D. Chen, T. Williams and R. F. Hicks, in *SAMPE Symposium and Exhibition,* Long Beach, CA, USA, 2011.

[20] J. G. Smith, J. W. Connell and P. M. Hergenrother, "The Effect of Phenylethynyl Terminated Imide Oligomer Molecular Weight on the Properties of Composites," *Journal of Composite Materials,* vol. 34, pp. 614-628, 2000.