Novel Bonding Methodologies Toward the Attainment of Primary Bonded Aircraft Structure

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Purpose

The focus of the work is to develop an environmentally friendly surface treatment for adhesive bonding of titanium alloys (Ti) using a Nd:YAG laser to create the desired surface chemistry and topography. The novelty lies in the creation of precise patterns on the order of 5-10 microns deep into the surface of the Ti while simultaneously producing chemical changes to the surface in a manner analogous to that of the state-of-the-art chemical etch surface treatments.

Background

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 (5-7). 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). As mentioned, the state-of-the-art for Ti surface preparation uses multi-step chemical-dip processes each of which is costly due to special handling and use requirements, facility maintenance, hazardous waste remediation, and quality control requirements. This surface treatment process for Ti is expensive to maintain, monitor and utilize in a production environment, and the chemicals involved are potentially hazardous to workers and the environment. There is presently a strong desire in the aircraft manufacturing industry to obtain Federal Aviation Administration (FAA) certification for adhesive bonding of primary aircraft structure. The industry and FAA believe that the path to certification of adhesive bonding for primary aircraft structure is strongly dependent on process control in manufacturing and shop environments. It is well known that controlled substrate surface treatment is fundamental for the initial and long-term performance of adhesively bonded joints. Non-standard techniques such as atmospheric pressure plasma, arc discharge, and laser irradiation have been demonstrated, but are still undergoing evaluation by the aerospace industry (8-10). An alternative approach, laser ablation, is a subtractive process which relies upon highly-focused laser radiation to remove and redistribute material on a surface (11-14). 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 contaminants and modification of surface chemistry (15, 16). To advance adhesive bonding towards FAA certification, there is clearly a need for an automated, reliable, scalable, repeatable, high precision and robust surface treatment process for Ti (as well as other structural airframe materials). The work discussed here utilizes laser ablation patterning as a surface preparatory treatment for Ti-to-Ti adhesive bonding that satisfies all of these requirements.

Approach

A Nd:YAG laser is being used for adherend surface preparation to generate nano- and micro-topographical features simultaneously with surface chemical activation. Novel surface topographies and patterns combined with desired surface chemistry generated via laser ablation provide a precision surface that is highly reproducible, and lends itself to automation. Quantitative analytical techniques are being used to characterize the chemical and topographical modifications. Ti-6Al-4V alloy PETI-5 (2500 g/mole) were used as substrate and adhesive, respectively. Adhesively bonded Ti single-lap shear and wedge test specimens with selected laser surface treatments as well as those using the state-of-the-art Ti surface treatment have been fabricated, and are being hygrothermally aged, mechanically tested and characterized. The results will provide a link between fundamental aspects of adherend surface topography/chemistry and adhesive bond performance. The laser surface treatment process is scalable, rapid and provides a high degree of reproducibility and flexibility. A number of different laser and patterning parameters can be easily and precisely controlled resulting in variation of the surface chemical and topographical modifications. In addition, the laser surface treatment process is amenable for use in production/manufacturing and repair depot type environments.

Status of Research

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 adhesive bonds. Laser ablation imparts both topographical and chemical changes to a surface which can lead to increased bond durability. Laser surface preparation 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. Surface roughness and surface chemical composition were characterized using interference microscopy and X-ray photoelectron spectroscopy (XPS), respectively. A technique for fluorescence visualization was developed which allowed for quantitative failure mode analysis. Wedge crack extension testing in a hot, humid environment indicated the relative effectiveness of various surface treatments. Increasing ablation duty cycle reduced crack propagation and adhesive failure. Single lap shear tests were conducted on bonded and aged specimens to observe bond strength retention and failure mode. An increase in strength and durability of lap shear specimens was observed as laser ablation duty cycle and power were increased. Chemical analyses showed trends for surface chemical species which correlated with those produced via state-of-the-art chemical etch methods along with improved bond strength and durability. These results suggest that laser ablation could be integrated into a titanium surface pretreatment process and replace one or more wet chemical processes. The following milestones were accomplished and are discussed in detail in the Accomplishments section.

1. Milestone-demonstrate that laser surface treatment did not introduce any undesirable microstructure (α-case).
2. Milestone-determine the surface chemistry that results from the laser ablation process.
3. An unplanned development was a novel fluorescence visualization inspection technique to aid in the near quantification of the failure mode.
4. Milestone-demonstrate comparable adhesive properties on lap shear and wedge crack test specimens comprised of laser ablated Ti adherends.

Accomplishments

Laser ablation resulted in highly reproducible topography in the Ti-6Al-4V surface, as shown in Figure 1. The ablated specimens in Figure 1 are all patterned with parallel lines of various center-to-center spacing (pitch). The fraction of the total surface area ablated by the beam is described by the ablation duty cycle. Duty cycle (d) is given by the ratio of the beam width (25.4 μm) to line pitch (p) such that d = 25.4 μm/p x 100%. A duty cycle of 100% indicates that the entire surface received laser ablation pretreatment.

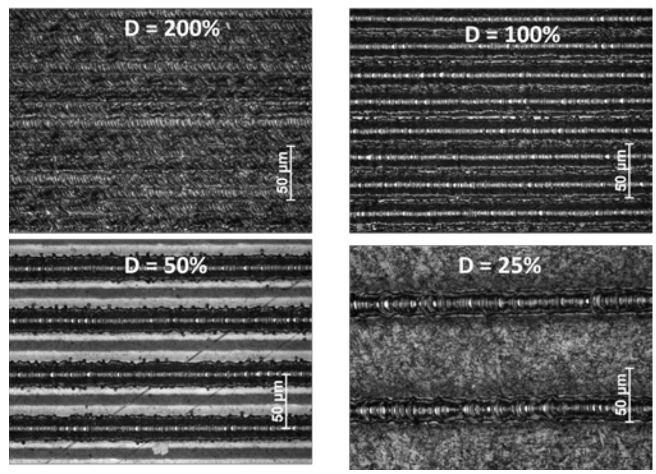

Figure 1: Parallel lines ablated into a Ti-6Al-4V surface with a pitch of: (upper left) 0.013 mm (0.0005 in), (upper right) 0.025 mm (0.001 in), (lower left) 0.051 mm (0.002 in) and (lower right) 0.102 mm (0.004 in).

It was of paramount importance to quickly demonstrate that the laser surface treatment process did not negatively affect the Ti alloy by introducing microstructures that caused reduction in adhesion, strength, toughness, durability, or corrosion resistance. Thus a key initial milestone was to show that the laser surface treatment process did not introduce any undesirable microstructure. One concern in particular was the formation of a microstructure known as α-case which diminishes the fatigue resistance of the alloy. Scanning electron microscopy (SEM) and micro-hardness experiments were conducted on laser etched coupons to determine if any α-case was observed. The α-case is sometimes visible in a polished and etched micro-section as a white layer in an optical metallurgical microscope or a dark layer in an SEM in back-scatter mode (Figure 2).

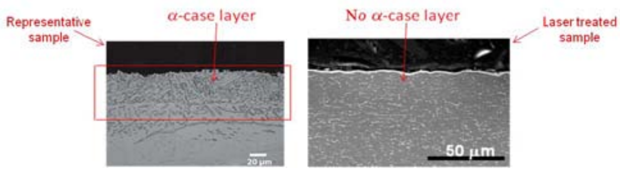

Figure 2. SEM images showing α-case layer in Ti alloy.

An α-case layer can also be detected by micro-hardness indentation of a section normal to the surface. The layer is caused by oxygen diffusion into the surface and in an α/β alloy like Ti-6Al-4V results in hardening, causing embrittlement of the Ti, which would adversely impact the performance of the bonded structure. It also stabilizes the α phase near the surface (which appears white in an optical micrograph in Figure 2). The thickness of the α-case depends on exposure time, atmosphere and temperature but for typical titanium forgings it is usually less than 20 microns. The α-case will only normally be a problem in high stress applications. The aerospace industry usually removes α-case by machining or chemical milling. A key finding was that, based on metallographic cross-section analysis and microhardness experiments, there was no indication of α-case formation as a result of laser ablation (Figure 3). The use of laser ablation may be useful in removing α-case from sensitive parts and faying surfaces.

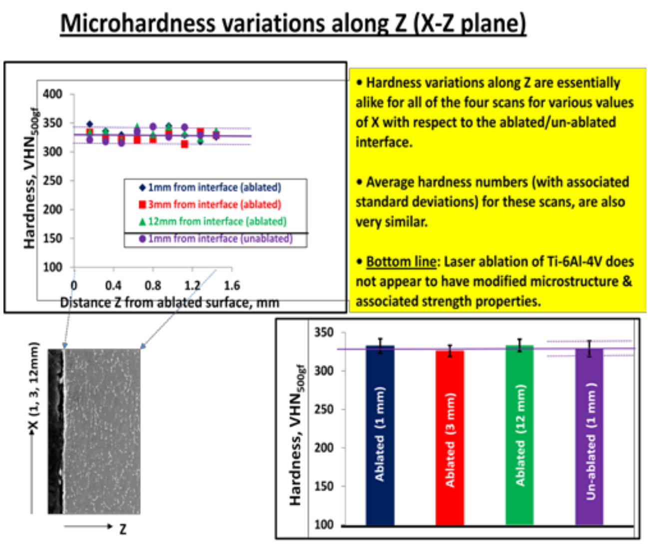

Figure 3. Microhardness characterization results from a laser ablated Ti-6Al-4V surface.

Another key accomplishment was the successful completion of a new Space Act Agreement with Boeing (SAA1-1155 Annex 2) as the previous one expired in September 2011. This agreement allows for the collaborative investigation of laser surface treatment for both metallic and composite surfaces. It facilitates the exchange of samples and information in a synergistic manner taking advantage of the unique capabilities and expertise within each organization. The inclusion of composite surface treatment is important because composite to metal bonding is often encountered in the construction of new aircraft (1). Also, the team already has considerable research experience with surface treatment of structural epoxy based composites using laser ablation techniques. Metal to composite bonding is an area that will be investigated in the Phase II of this effort, if this project is selected for continuation.

Another key accomplishment was establishment of an informal relationship with Professor Robert Hicks (UCLA) who has world-class expertise in XPS analyses of Ti, a particularly complex element to analyze, which was critical to understanding changes in surface chemistry. This interaction was key to our ability to elucidate and understand how the laser process affects surface chemistry of the Ti-6Al-4V specimens. A major accomplishment was the determination that the laser ablation process appears to eliminate any highly oxidized hydroxyl species on the Ti alloy surface, which have been shown to be detrimental to the formation of robust and durable adhesive bonds. In addition, under the proper conditions, laser surface treatment produces a fresh surface comprised mostly of TiO_2, which is what state-of-the-art chemical etch methods are designed to create. Laser processing is inherently high precision and capable of providing a repeatable surface preparation. In addition, laser ablation provides an alternative, “green” means of surface preparation on titanium adherends by avoiding the use of toxic chemical etchants and abrasive media.

Unpolished 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 4 for select elements. Shaded areas indicate the dominant failure modes observed during single lap shear (SLS) testing. 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 were introduced as surface contaminants after ablation but before XPS analysis. The survey scan data in Figure 4 indicate changes in elemental abundance at the adherend surface that correlate with changes in the observed failure mode in SLS specimens tested at room temperature. At low laser ablation powers, oxygen abundance decreases while aluminum and titanium abundances increase. This may indicate the removal of surface oxides and mill scale. At ablation powers greater than 400 mW, vanadium begins to appear at the surface and the abundance of oxygen increases. The appearance of vanadium on the surface is likely due to surface material ablation which exposes the underlying, bulk alloy. The increase in oxygen concentration is attributed to the oxidation of the surface metals and sub-oxides. At greater than 400 mW, the surface concentrations of titanium and aluminum decreased slightly due to dilution by vanadium and oxygen as the ablation power was raised.

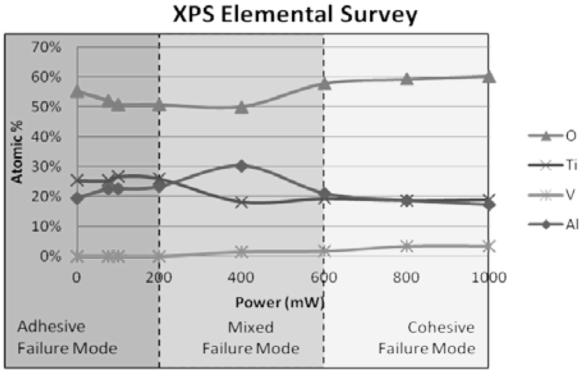

Figure 4. XPS survey scan data showing the atomic percent abundance of select elements found in survey scan spectra. Shading on the figure indicates the dominant failure mode seen in SLS test specimens.

Little correlation was seen between the elemental composition of the surface, and the failure mode of the adhesive; however, the bonding states of each element must also be considered. De-convolution of the Ti2p$_{1/2}$, Ti2p$_{3/2}$, O1s, and Al2p multi-plex peaks was performed on high resolution XPS spectra and peak assignments were made as shown in Figure 5. Figure 6 summarizes the surface composition data for each of the metals and oxides found on the alloy surface after ablation. Shading on the figure indicates the dominant SLS failure mode observed in three power ranges identified. The concentration of titanium dioxide increased steeply between 200 and 400 mW of laser power while all other titanium constituents diminished in concentration. This is consistent with the increased atomic percentage of oxygen observed (Figure 4). It also indicates that more intense laser ablation causes oxidation reactions linked to improved bond performance.

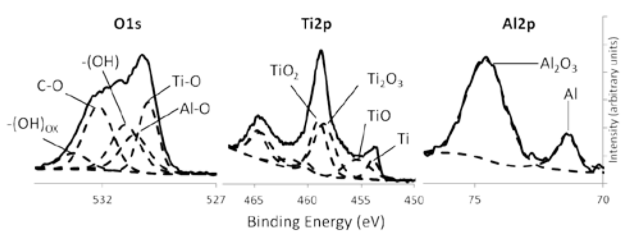

Figure 5. De-convolution of a high-resolution O1s, Ti2p, and Al2p spectra from different specimens showing peak assignments.

The de-convolution of the XPS spectra in Figure 5 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 (18). De-convolution of the aluminum multiplex revealed two components: aluminum metal and alumina (Al_2O_3). Between 200 and 400 mW of laser power, the aluminum metal was quickly oxidized to alumina which coincided with changes in bond performance. The correlation of these XPS results with SLS data (discussed later) indicated strongly that formation of new titanium and possibly aluminum oxide layers on the surface contributed significantly to bond performance. Based on the XPS and SLS results, parallel lines ablated at greater than 400 mW power and at about 25 μm pitch produced high surface concentrations of titania and alumina, which when bonded with the PETI-5 adhesive, formed robust bonds with apparent shear strengths comparable to those fabricated using current state-of-the-art surface preparation techniques (19).

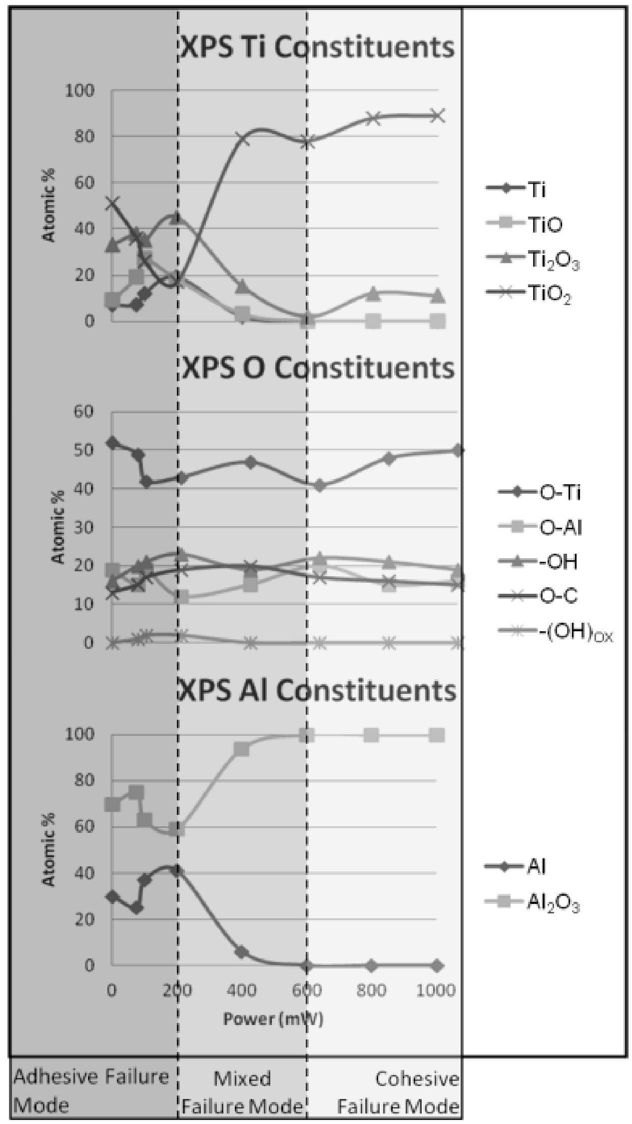

Figure 6. Atomic percent abundance of surface constituents based on the deconvolution of the Ti2p1/2 and Ti2p3/2 mulitplex (top), O1s peak (center), and Al2p peak (bottom). Shading on the figure indicates the dominant failure mode seen in SLS test specimens.

Combined, these two technical accomplishments (i.e, no α-case formation, and generation of desirable surface chemistry) demonstrated that the laser ablation process can achieve the objectives stated in the original proposal. The potential shortcomings of the process initially raised by metallurgists were addressed first. Once these were satisfactorily addressed, the focus of the work shifted towards generation of sufficient mechanical property data on laser treated Ti adhesive specimens tested under a variety of conditions. Ultimately, it must be demonstrated that the laser ablation surface treatment process can meet or exceed performance specifications as compared to that of the state-of-the-art process.

The mechanical test results for polished SLS specimens that were ablated at 1 W are shown in Figure 7 along with roughness and failure mode statistics. Laser ablated specimens showed improvement in bond strength and exhibited 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 7 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.

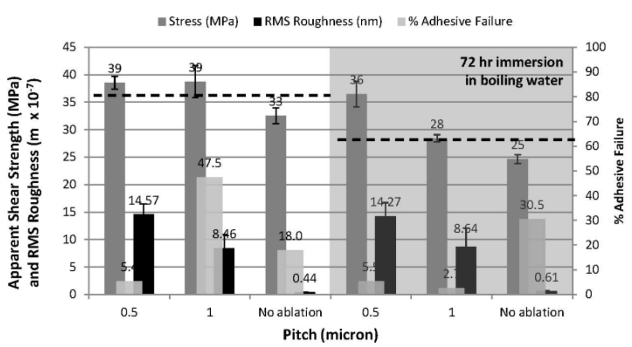

Figure 7. Results for PETI-5 SLS specimens prepared with polished adherends. Laser power was 1 W for all ablated specimens. Data in the shaded region was collected from specimens that underwent a 72 h immersion in boiling water immediately prior to testing. Dashed lines indicate the apparent shear strength values achieved for unpolished SLS specimens. ($1x10^{-7}$ 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 as-received adherends. The intention was to isolate the effects of laser generated topography on bond performance from the effects of native surface roughness by providing a smooth baseline (RMS roughness of 50 nm). The surface roughness and apparent shear strength of the specimens in Figure 7 show a strong, direct correlation which demonstrates the benefit of a roughened surface for bonding. Even though RMS roughness increased by more than two orders of magnitude, the apparent shear strength increased by less than 50% for samples immersed in boiling water and less than 20% for un-aged samples. In addition, polished specimens without laser ablation were significantly stronger than specimens receiving neither polishing nor laser ablation processing (data not shown, apparent shear strength: 16.5 MPa). These surprising results indicated that the polishing process increased bond strength primarily through surface chemistry modification, removal of contamination and stripping of weakly bonded oxide layers. Thus, the effects of changing surface topography could not be isolated from surface chemistry variation through a polishing technique. 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 that received laser surface preparation are summarized in Figure 8, showing trends for apparent shear strength, failure mode, and RMS roughness as the ablation line pitch was varied. Decreases in apparent shear strength correspond well with increases in adhesive failure mode, as anticipated. Laser ablation pitch appears 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 likely via a plasticization process. Capillary ingression of water along the glass fiber scrim cloth is suspected based on the speed and magnitude of the property loss. This may be an additional topic of investigation in Phase II.

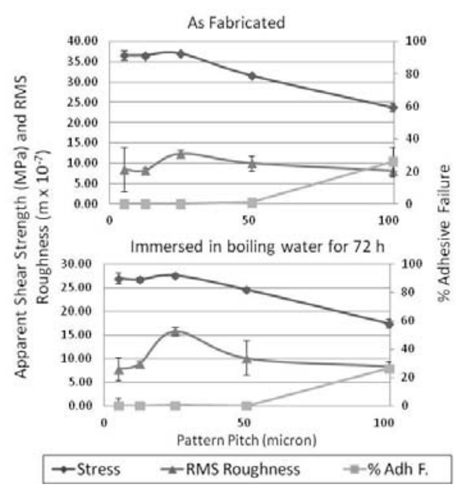

Figure 8. Apparent shear strength, failure mode and roughness results for non-polished adherends are shown for two data sets: variation of ablation line pitch without (top) and with (bottom) immersion in boiling water. ($1x10^{-7}$ m = 0.1 μm).

In Figure 8, RMS roughness is a maximum for a pitch of 25 μm (1 mil) which corresponds to a duty cycle of about 100%. The increase in roughness as the pitch decreases from 200 to 25 μm was attributed to reduced space between the ablation trenches. At a pitch of 25 μm the ablation trenches were separated by a narrow line of unablated material as seen in Figure 1. This "sawtooth-like" pattern has greater roughness than any parallel line array with greater pitch. As the pitch was further reduced, the trenches overlapped one another to form a single ablation field which removed the large topographical variations from between trenches. The apparent shear strength had a maximum value corresponding to the peak in RMS roughness, which indicated that increasing roughness improved strength. As observed for polished specimens, the large changes in RMS roughness (100%) manifested as small changes in apparent shear strength (5%).

The data shown in Figure 9 presented a strong correlation between bond performance and laser power. Apparent shear strength increased dramatically and the failure mode switched to cohesive failure as ablation power was increased. The same trend was also observed for specimens immersed in boiling water for 72 h. Bond improvement appeared to plateau at about 800 mW of laser power, which coincided with the adhesive failure mode reaching nearly 0%. RMS roughness of the ablated surface did not significantly increase relative to the roughness of the native titanium alloy surface for laser powers less than 800mW.

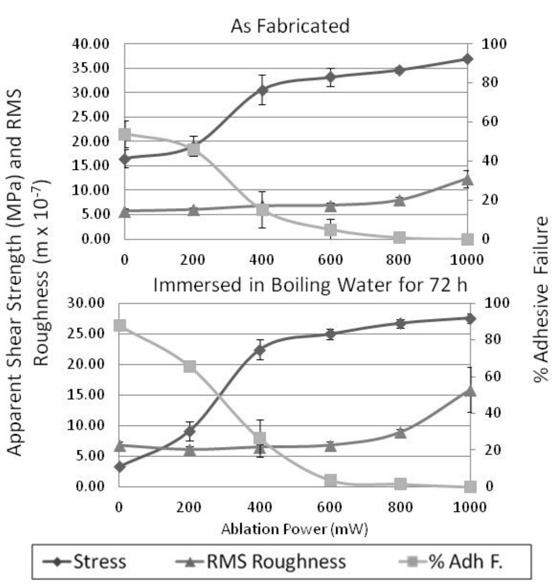

Figure 9. Roughness and lap shear data for non-polished, laser ablated adherends are shown for two data sets: laser power variation without (top) and with (bottom) immersion in boiling water. ($1x10^{-7}$ m = 0.1 μm). Ablation pitch was 25.4 μm for all specimens.

Apparent shear strength increased dramatically between 200 and 400 mW of ablation power while the apparent shear strength above 400 mW of laser power increased slowly. Taken together, these two observations, indicate that laser ablation at relatively low power has a profound effect on surface chemistry with minor effect on surface topography. Surface chemical changes significantly improved the apparent shear strength and failure mode observed below 400 mW ablation power. As surface roughness increased steeply between 600 and 1000 mW laser power, improvements in bond properties were less significant. These findings supported previous observations that surface roughness was 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 (17).

Wedge tests provided an excellent, semi-quantitative comparison of surface preparations by applying a mode I opening stress in a hot wet environment. Unlike other mode I mechanical tests, such as the double cantilever beam test, wedge tests are relatively inexpensive to prepare and conduct. Combination of the wedge test method with a precision failure mode inspection technique such as the fluorescence visualization technique presented here provided a quantitative means for failure analysis. Thus, accurate characterization and distinction of different surface preparations was possible using these techniques.

The polishing process was not performed for the preparation of wedge test samples. Based on lap shear test results, a reduced set of laser parameters were selected for wedge test experiments as shown in Table 1. Specimen A received optimum laser power and line pitch for maximum bond performance. Specimen B received optimum power for maximum bond performance, but the pitch was increased to reduce the duty cycle. Specimen C received the optimal line pitch but at a reduced power expected to give good surface chemistry but only minimally effect surface roughness. In Table 1, fluence (laser energy per unit area of substrate) is presented as a means of comparing surface treatments.

Table 1. Surface preparation of Wedge Test Specimens

Sample	A	B	C
Power (mW)	1000	1000	400
Pitch (μm)	25	100	25
Duty Cycle (%)	100	25	100
Fluence J/cm^2	20	5	8

Crack extension after 24 h of aging and the percent adhesive failure data for the samples are shown in Figure 10. Wedge tests supported the conclusions drawn from lap shear testing regarding identification of the optimum laser ablation surface preparation. Specimen A exhibited no adhesive failure mode and minimal crack growth over 24 h. Based on lap shear results, specimen C was expected to be similar to specimen A as moderate laser power at 100% duty cycle produces the necessary chemical modification over the entire surface for good bond performance. Crack extension was extremely low like that of specimen A, and adhesive failure mode was moderate which matched lap shear results. Specimen B was expected to perform poorly based on comparisons with lap shear data with the same duty cycle. A 25% duty cycle leaves about 75% of the faying surface untreated and therefore a poor bond resulted even though laser power was optimized at 1 W. Crack extension for B was greater than that for specimens A and C. The appearance of adhesive failure in B also supported this hypothesis. This result reinforced the observation that a high duty cycle was most important for good bonding, and best results were achieved when power was high enough to achieve full chemical modification of the surface and increase surface roughness. The large error bars for failure mode data in Figure 10 were attributed to sample fabrication issues where adhesive did not flow well and differences in bondline thicknesses of specimens cut from the edges of 6” by 8” panels compared to those cut from the center.

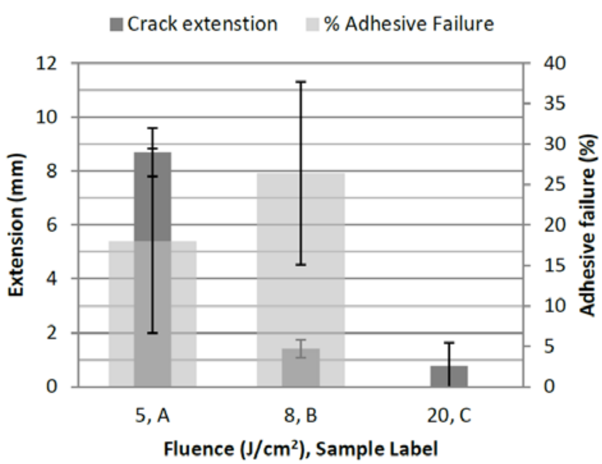

Figure 10. Crack extension and failure mode data for wedge test specimens ablated with three different laser fluence levels.

Experimental

Materials and Methods

Titanium alloy for single-lap shear testing [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 11. This configuration is a modification of specimens called for in ASTM D1002-05, and allowed for the use of an existing bonding jig. Titanium alloy for wedge test specimens was purchased from the same vendor with a thickness of 3.18 mm (0.125”) in a configuration specified by ASTM D3762-03. Phenylethynyl terminated imide (PETI) high temperature adhesive, PETI-5 (2500 g/mole), was also 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 (20). 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.

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).

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 0/90 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 0.30 mm (12 mil; 15 to 20 coats). After each coat was applied, excess NMP was removed by stage-heating the tape to a final temperature of 230 °C.

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 as indicated in Figure 11. 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 about 1.3 cm^2/min depending on pattern density.

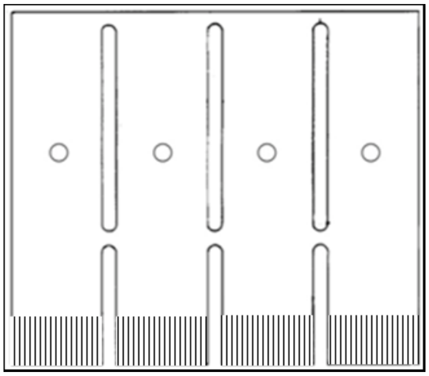

Figure 11. Modified single-lap shear adherend geometry indicating laser-etched portion.

Bonding
Mechanical test specimens were bonded in a 30 cm x 30 cm heated Carver press for 1 h at 371 ^{o}C and 0.34 - 0.68 MPa (50-100 psi). For single-lap shear specimens, bonding configurations were shimmed to maintain a 0.13 +/- 0.025 mm (0.005 +/- 0.001 in) bondline thickness. Wedge test samples were bonded by aligning two 15 cm x 20 cm titanium alloy plates in an jig with a 15 cm x 17.5 cm adhesive film and a 15 cm x 2.5 cm precrack film placed between them. Shims were not required to maintain the minimum bondline thickness for wedge test specimens. Samples were compressed and held at full load beginning at room temperature until after the press cooled below 150 ^{o}C. Compressed air was used to speed the cooling process.

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. After bonding, wedge test samples were machined into 25.4 mm wide specimens using an abrasive water jet cutting tool to avoid heating. Bondline thickness was measured optically by viewing the cross-section of each specimen on both sides. Wedge specimens were opened by forcing an aluminum wedge into the pre-crack end according to ASTM D3762-03. The initial crack length was marked immediately before specimens were introduced to the aging chamber one hour after wedge insertion. Aging conditions were 60 ^{o}C and 100% relative humidity which were maintained by placing a closed vessel partially filled with water into an oven. Specimens were placed on a shelf in the vessel in the head space over the water. Specimens were removed to mark the crack tip position after 1 h, 8 h, 24 h, 48 h, 1 week, 2 weeks and 4 weeks.

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 ultraviolet light source from Innovative Science Solutions Inc. having a peak output 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 12. 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 taken as the percentage of adhesive failure.

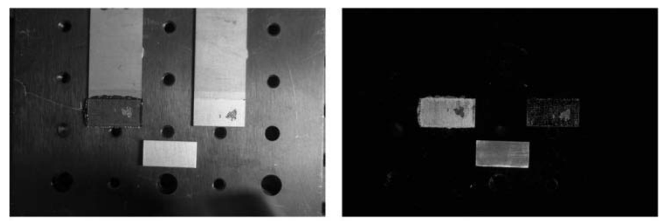

Figure 12. On the left is a visible light image of a failed lap-shear specimen showing mostly adhesive failure. On the right is a fluorescence image of the same specimen with clearly visible adhesive residues. A 12.7 x 25.4 mm (0.5 in x 1 in) reference standard with a fluorescent coating is visible at the bottom of each image.

Current TRL
The TRL is estimated to be at a level of 3 based on the experimental characterization and test results to date.

Applicable NASA Programs/Projects
Relevant NASA programs are Vehicle Systems Safety Technologies and Fundamental Aeronautics (Fixed Wing). Informal discussions with PI and PM from each indicate some interest. However, these individuals indicated that there is no budget for the introduction of new, unplanned work, and were reluctant to reduce or stop planned work to make resources available for something new due to obligatory milestone objectives. In general, it is difficult to find support for materials related technology development within NASA programs. This is presumably due to the long lead time needed to develop the data necessary to qualify a material or process for aerospace applications.

Publications and Patent Applications
Conference paper: "Laser Surface Preparation for Adhesive Bonding of Ti-6Al-4V" by F.L. Palmieri, K.A. Watson, G. Morales, C.J. Wohl, T. Williams, J.W. Hopkins, R. Hicks, and J.W. Connell. SAMPE Electronic

Proceedings, Spring Meeting, Baltimore, MD, May 21-24, 2012.

Patent application: Modifying Surface Energy Via Laser Ablative Surface Patterning, LAR-17769-1.

Invention Disclosure: LAR-18215-1, "Fluorescence Visualization Technique for Quantitative Analysis of Failure Mode in Adhesively Bonded Test Specimens", submitted May 2012.

Journal Article: "Laser Ablative Surface Treatment for Enhanced Bonding of Ti-6Al-4V Alloy" by Frank L. Palmieri, Kent A. Watson, Guillermo Morales, Thomas Williams, Robert Hicks, Christopher J. Wohl, John W. Hopkins and John W. Connell. Under internal review at Langley Research Center.

Awards & Honors

NASA Langley Engineering Directorate Innovation Award "Surface Treatment for Adhesive Bonding Via Laser Ablative Surface Patterning" Sept., 2011.

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