Novel Bonding Methodologies Toward the Attainment of Primary Bonded Aircraft Structure

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ARMD Seedling Project
Phase I Project Review June 5, 2012

Innovation

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- The innovation is in the creation of surface topography on the order of 5-10 microns deep into the surface of the Ti (Ti-6Al-4V alloy) while simultaneously changing the surface chemistry in a manner that enhances adhesive bonding.
- A Nd:YAG frequency tripled (355 nm) laser is used that is rapid, creates high precision topography in a very reproducible manner.
- The use of a laser to conduct the surface treatment can eliminate some chemical-dip steps involving high concentrations of carcinogenic chromium(VI), strong acids and bases, and negate the use of silicon carbide or aluminum oxide particles for grit blasting.

Technical Objective

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- **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.**
- **Develop a high precision, reproducible surface treatment process that is amenable to automation and scale-up that becomes part of an overall bonding process that leads to the certification of primary bonded structure on commercial aircraft**

Technical Approach

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- **Prepare laser treated Ti panels**
  - Investigate a range of laser parameters
    - Power, intensity, topographical pattern, feature dimensions
  - Characterize surface topography and chemistry
    - Ensure that the treatment maintains or improves properties relative to state-of-the-art grit blasting (i.e., is not detrimental in any way)
- **Fabricate laser treated Ti panels, fabricate adhesive specimens and conduct adhesive testing**
  - A test matrix was developed to investigate what steps in the state-of-the-art dip process could be eliminated
  - Approximately 50 Ti panels (8 in x 6 in) were surface treated, fabricated into adhesive specimens and are undergoing testing
  - Multiple single lap shear specimens (SLS) prepared and tested

Impact if Implemented

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- The SOA 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.
- The implementation of this process would reduce overall costs, eliminate toxic waste, and enable an automated surface treatment and bonding process.
- The precision and control associated with the automated surface treatment and bonding process would be part of a larger process leading to certification of adhesively bonded primary structure for commercial aircraft.

Distribution/Dissemination

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- U.S. Patent Application 20110086204 “Modification of Surface Energy Via Direct Laser Ablative Surface Patterning” April 14, 2011.
- Invention disclosures
- Palmieri, Frank P.; Wohl, Christopher J.; Morales, Guillermo; Williams, Thomas; Hicks, Robert; Connell, John W., “Laser Surface Preparation of Titanium Adherends”: Green Processing for Improved Bond Durability”, 57th International SAMPE Symposium and Exhibition, Baltimore, MD, May 21-24, 2012.
- Palmieri, Frank P.; Wohl, Christopher J.; Morales, Guillermo; Williams, Thomas; Hicks, Robert; Connell, John W., “Laser Surface Preparation of Titanium Adherends, will be submitted to ACS Journal of Applied Materials and Interfaces in June/July 2012.
- First Place NASA Langley Engineering Directorate Innovation Award, Sept. 2011.

Accomplishments

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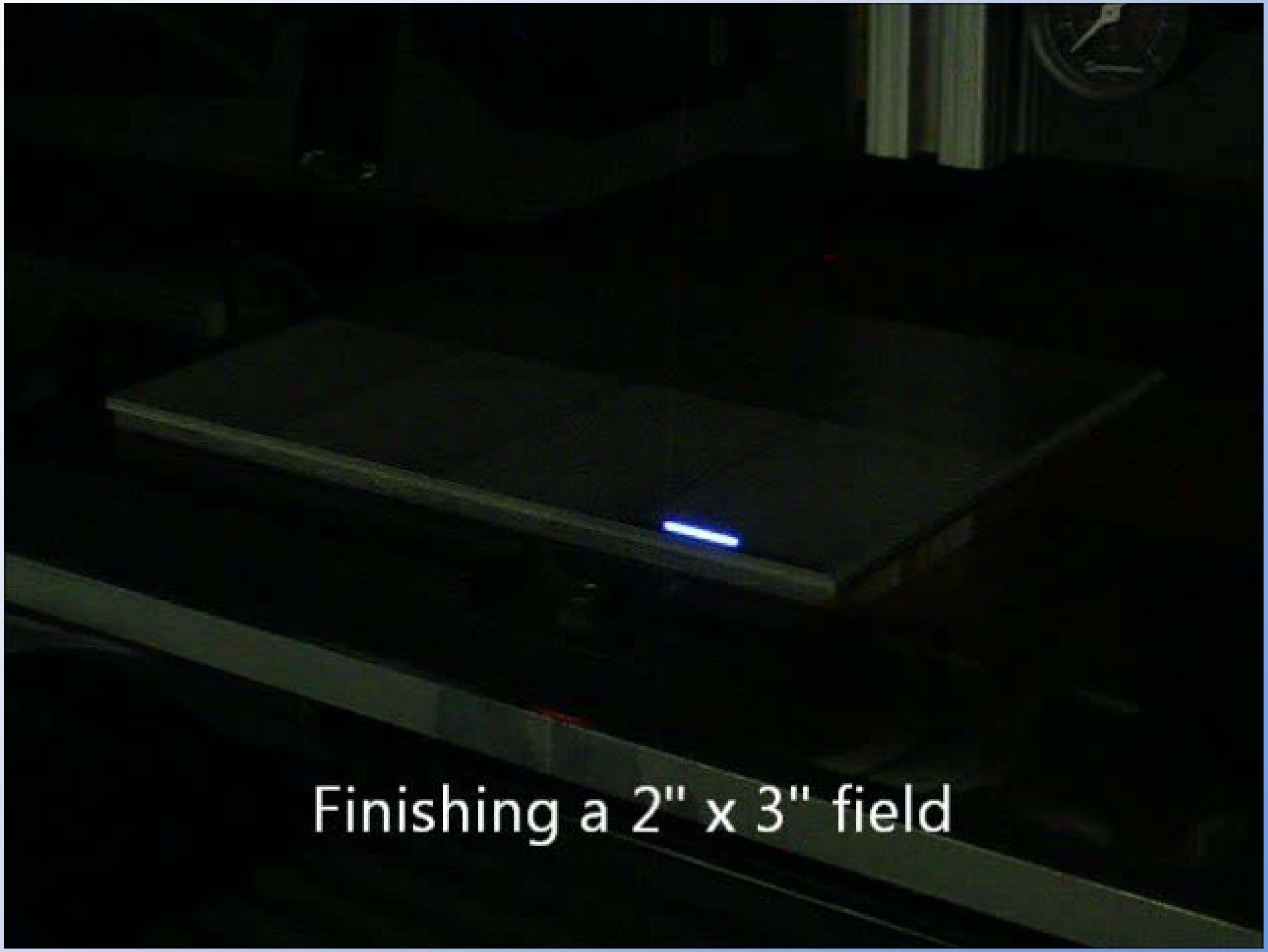

Accomplishments

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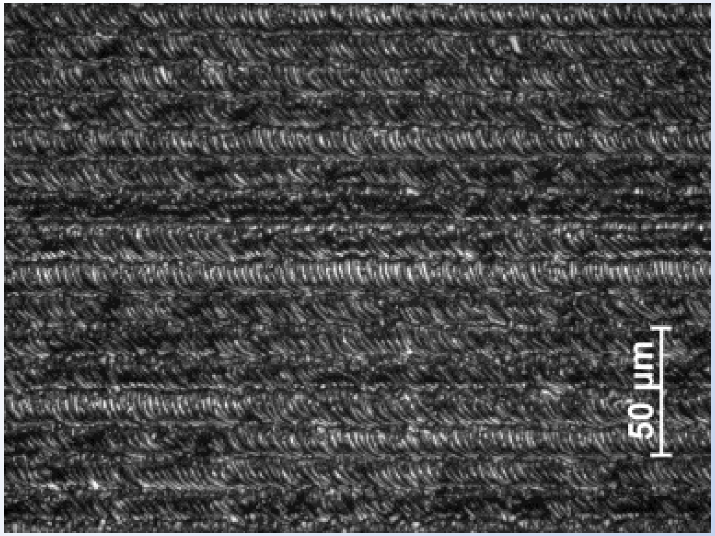
D = 200%



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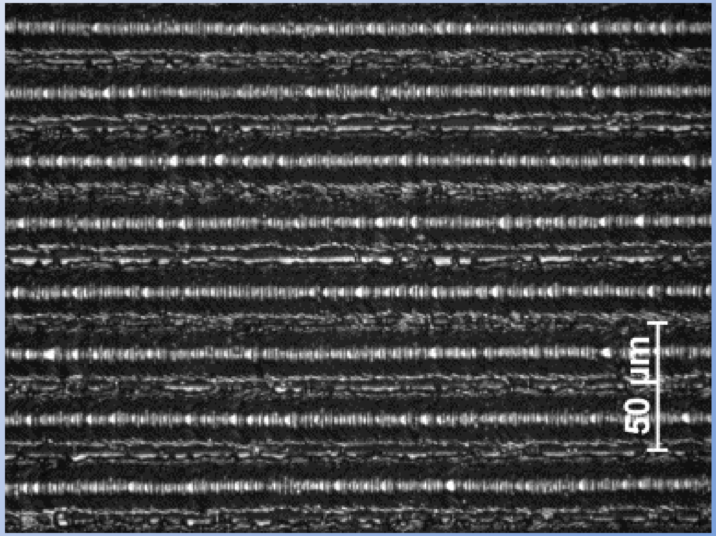
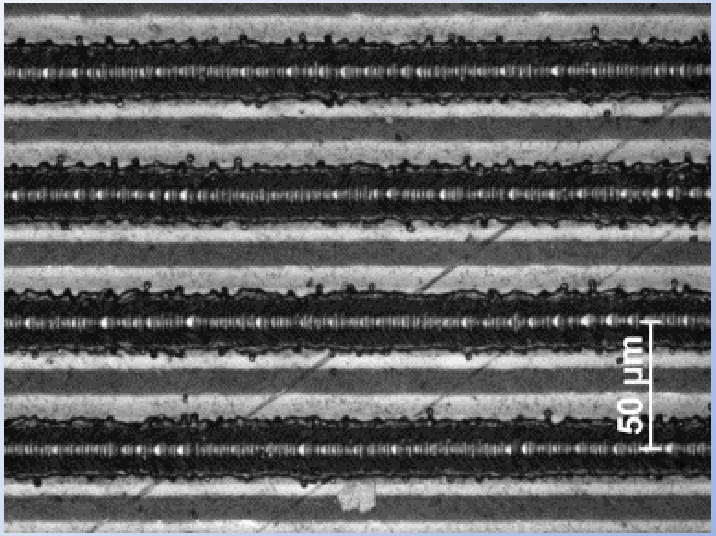
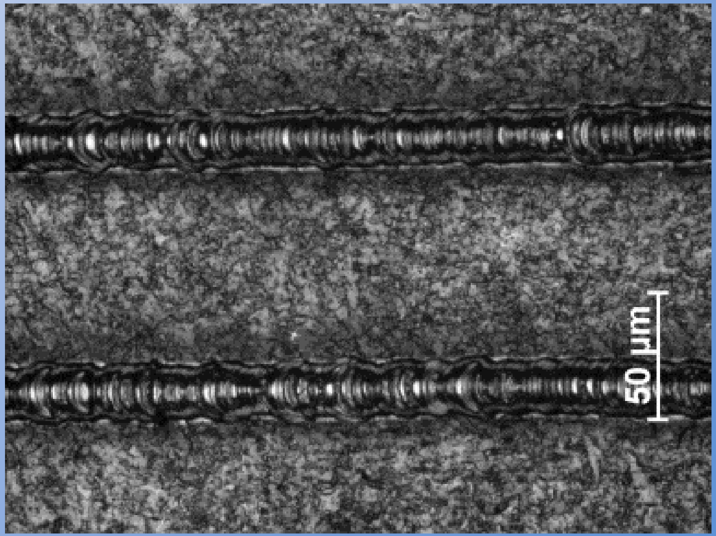


D = 50%



D = 25%



Duty Cycle (D) = 0.001”/pitch x 100%

Accomplishments

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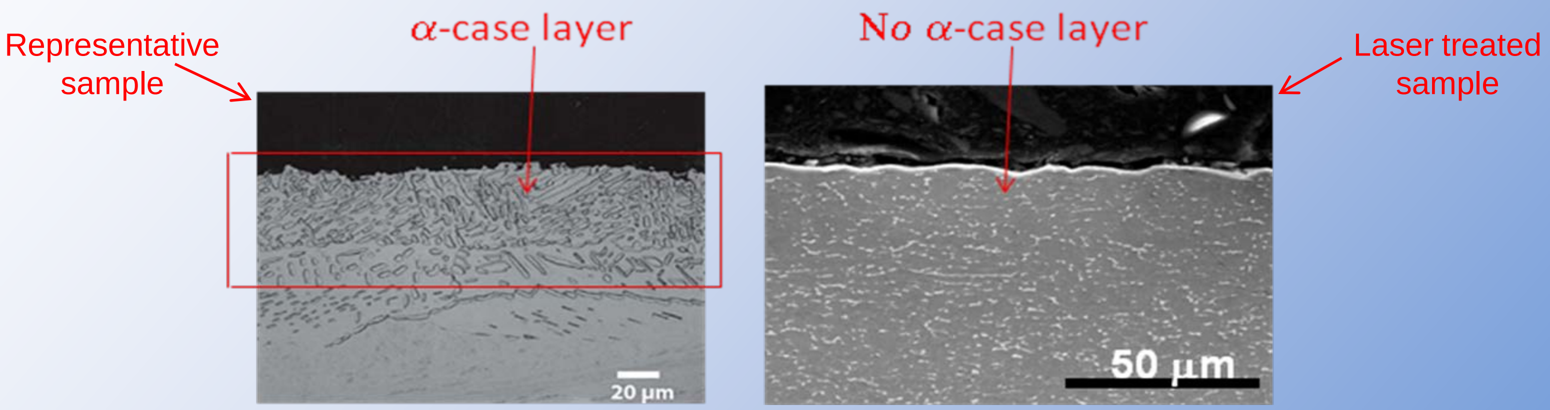
- **Milestone-demonstrate that laser surface treatment did not introduce any undesirable microstructure (α-case).**



- The α-case layer is caused by oxygen diffusion into the surface and in an α/β alloy like Ti-6Al-4V results in hardening causing embrittlement.
- Microscopic analysis and nanoindentation experiments were conducted on laser etched coupons to determine if any α-case was observed.
- No indication of α-case formation due to the laser ablation surface treatment process. Although laser ablation temperatures are high enough to form α-case, the duration of each pulse is much too short (nanoseconds) for the alloy transformation to occur.

Accomplishments Microhardness Profile

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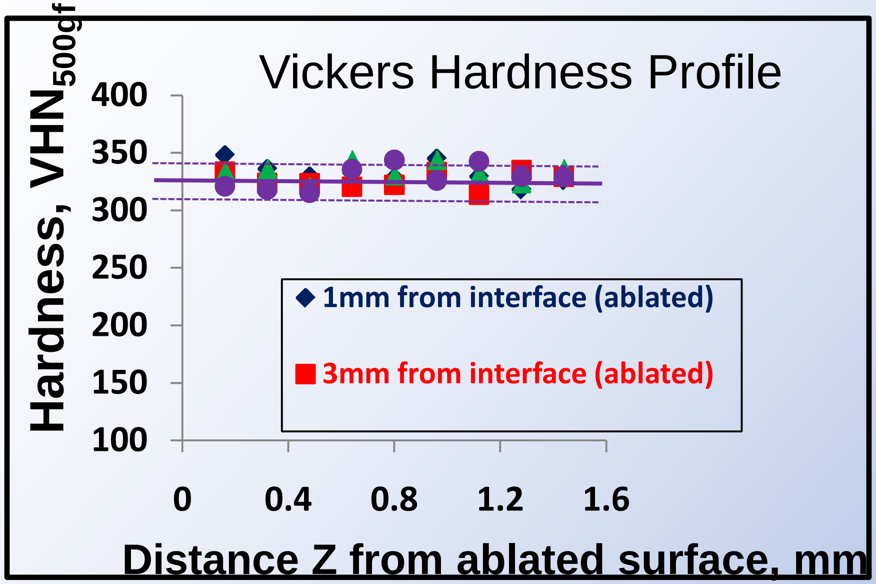

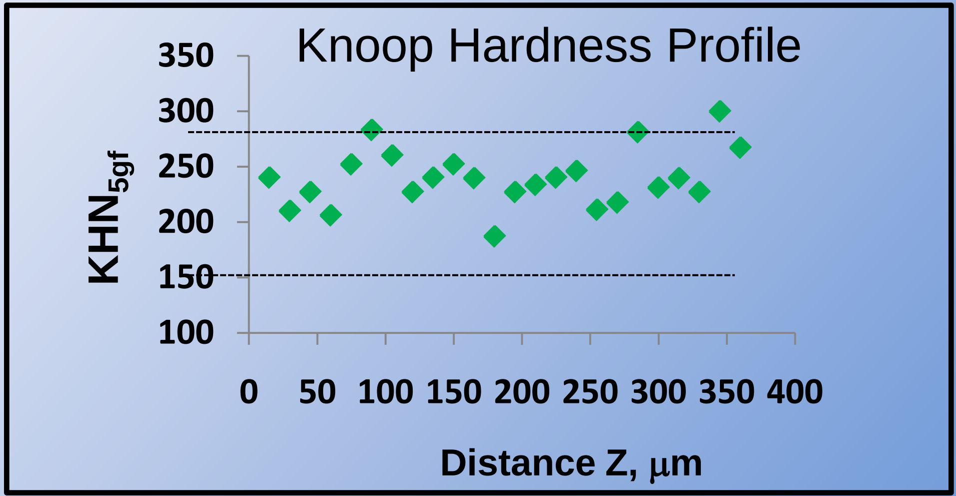

- Microhardness characterization results correlate with SEM data

Accomplishments

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- **Milestone -determine the surface chemistry that results from the laser ablation process.**
  - Certain chemical species (highly oxidized hydroxyl structures) on the Ti alloy surface are detrimental to the formation of robust and durable adhesive bonds.

- **No detrimental surface chemistries were detected by x-ray photoelectron spectroscopy**
  - This was the subject of a paper at the SAMPE Spring Conference in Baltimore Md in May 2012 (Palmieri, Frank P.; Wohl, Christopher J.; Morales, Guillermo; Williams, Thomas; Hicks, Robert; Connell, John W., "Laser Surface Preparation of Titanium Adherends: Green Processing for Improved Bond Durability", 57th International SAMPE Symposium and Exhibition, Baltimore, MD, May 21-24, 2012).

Accomplishments XPS Results

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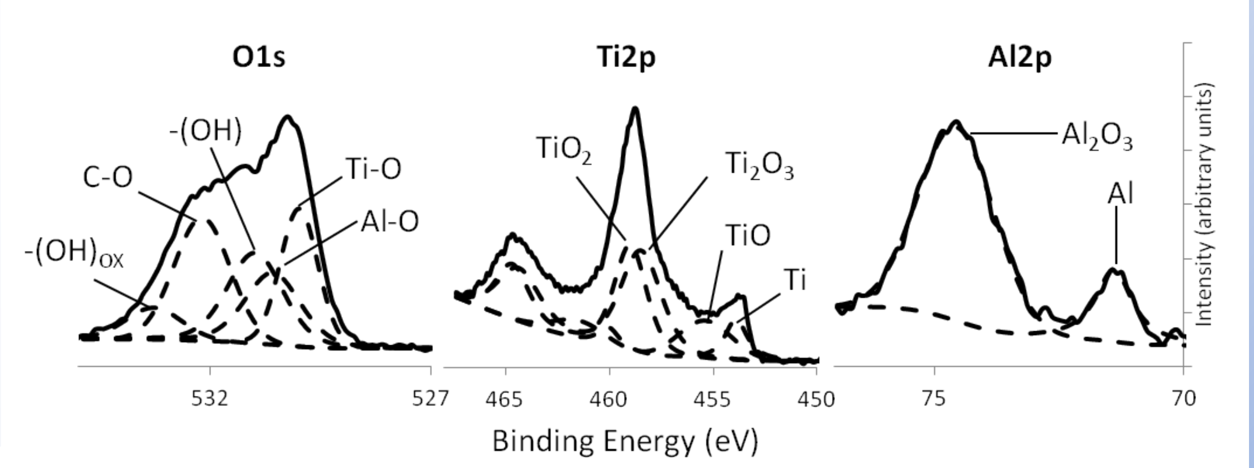
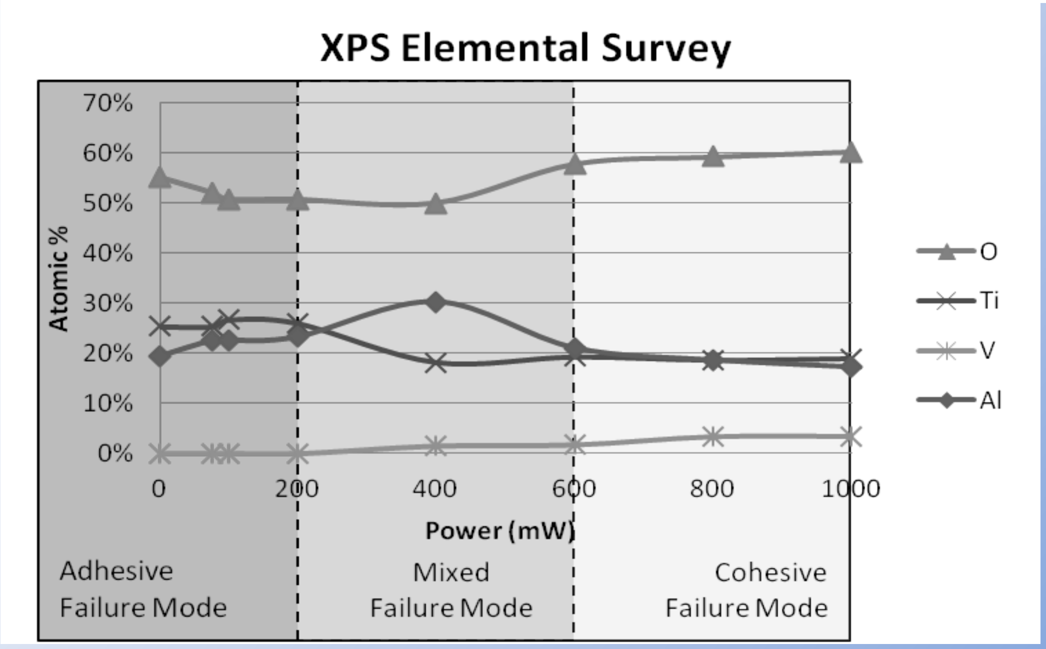


Peak Identification



- Al and Ti decrease with ablation
- O and V increase with ablation
  - Oxidation
  - Removal of surface material
- Higher power ablation provides desired failure mode

Accomplishments

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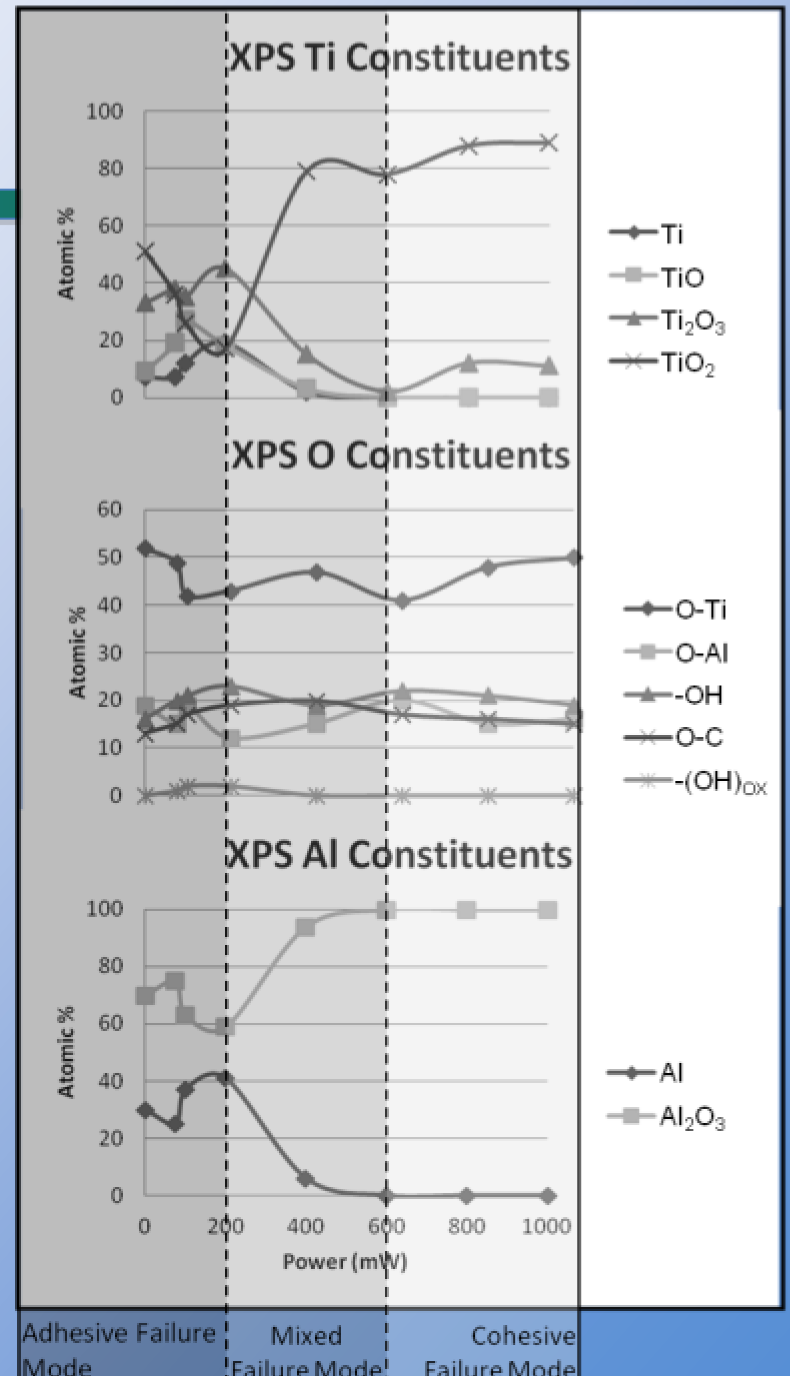
Surface Oxide Concentration Correlates with SLS Failure Mode

- Laser ablation removes TiO_2 at low power
- Fresh oxide formed only at higher power
- Similar trend observed with Al and Al_2O_3
- Oxidized hydroxyl species are removed at low power



Accomplishments

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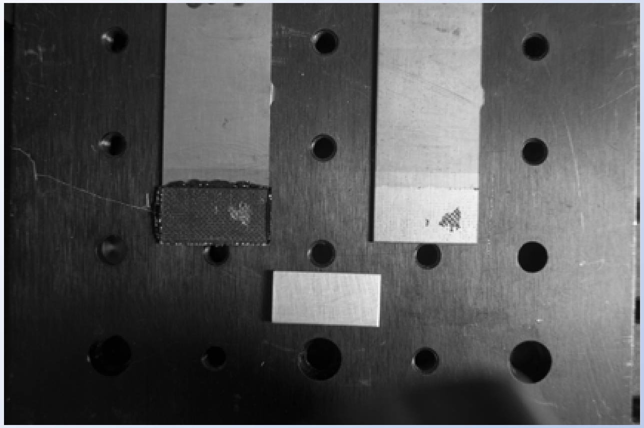
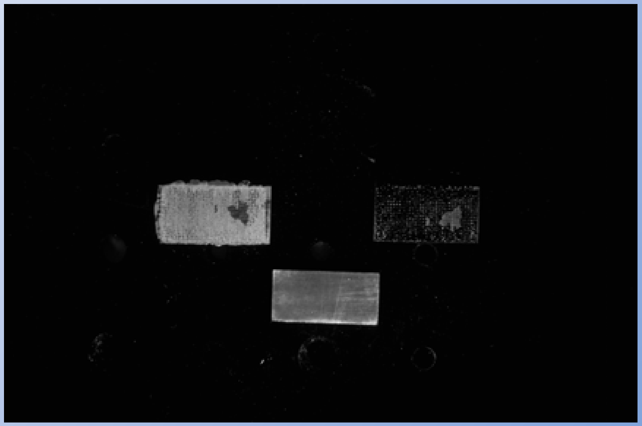
- An unplanned development was a novel fluorescence visualization inspection technique to aid in the near quantification of the failure mode.





- **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.**

- **Software is used to count pixels to quantify fluorescent area.**

Accomplishments

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- During the Phase I effort, a Space Act Agreement with Boeing (SAA1-1155 Annex 2) was finalized which includes collaborative research on laser-based surface treatments for both Ti and carbon fiber reinforced composites.
- A comprehensive test matrix was subsequently developed and is being executed.

	@Boeing		@NASA	@Boeing				@NASA
Test Number	Nitric/HF preclean	Thermal Age	Laser Prep	BAC5667 Class 1			Bond Primer	Bonding, Testing
				Nitric/HF	TiBoe	Sol-Gel		
1	X		A	X	X	X	X	X
2	X		A		X	X	X	X
3	X		A			X	X	X
4	X		A				X	X
1b	X		B	X	X	X	X	X
2b	X		B		X	X	X	X
3b	X		B			X	X	X
4b	X		B				X	X
3c	X		C			X	X	X
4c	X		C				X	X
3d	X		D			X	X	X
4d	X		D				X	X
3e	X		E			X	X	X
4e	X		E				X	X
5	X	X	A	X	X	X	X	X
6	X	X	A		X	X	X	X
7	X	X	A			X	X	X
8	X	X	A				X	X

Test Number	Nitric/HF preclean	Thermal Age	Laser Prep	BAC5667 Class 1			Bond Primer	Bonding, Testing
				Nitric/HF	TiBoe	Sol-Gel		
Control 1	X			X	X	X	X	X
Control 2	X	X		X	X	X	X	X

Nitric/HF Preclean	5 minute etch to remove mill scale in accordance with BAC5753 Method II.
Thermal Age	2 hours @ 500 °F.

Laser Labels	
A	4 mil crosshatch
B	16 mil crosshatch
C	1 mil linear*
D	0.5 mil linear*
E	1 mil crosshatch

*linear patterns parallel to 6" dimension (built in crack arrest?)

Lines 5/9/19 test if laser patterning augments 3 steps
Lines 6/10/20 test if laser patterning can replace 1 step
Lines 7/11/13/15/17/21 test if laser patterning can replace 2 steps
Lines 8/12/14/16/18/22 test if laser patterning can replace 3 steps

Laser Parameters	
Power (W)	1.5
Freq. (kHz)	100
Speed (in/s)	20
Therma Track	optimized

Lines 5-8 "fully" test one laser pattern; lines 9-12 another.
Lines 19-22 test if laser patterning does anything to heat scale.

Sol-Gel and Primer steps can be performed at NASA as capabilities are verified (0.15-0.40 is acceptable; 0.20-0.25 mil thick primer is most preferred).

Accomplishments

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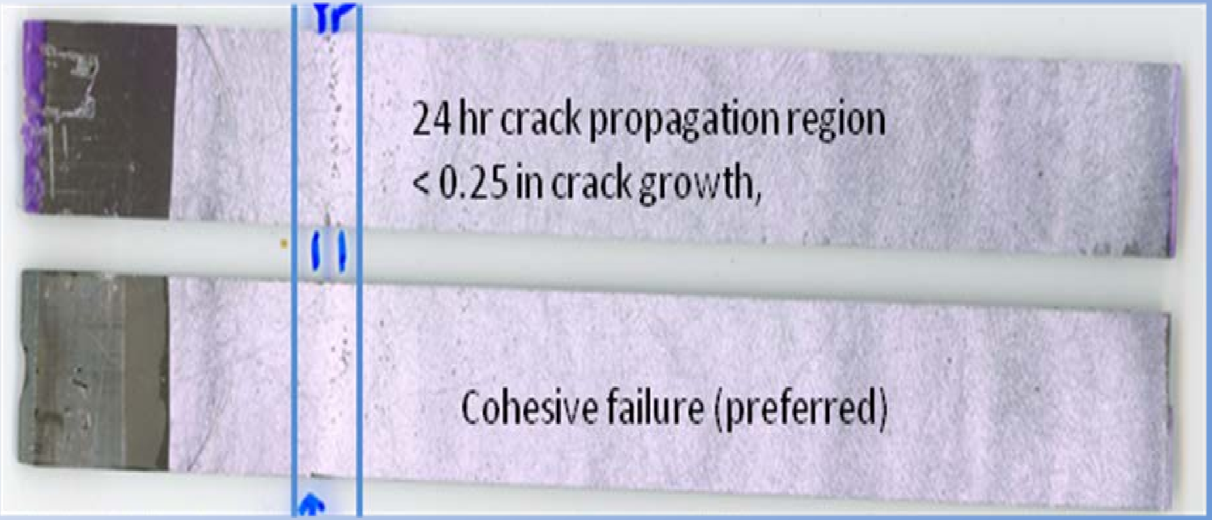
- A significant milestone was the results from wedge testing of laser ablated Ti adherends.
  - The adherends were treated with the laser ablation process as received to remove mill scale and prepare the surface for bonding. Sub-sets of the ablated adherends were treated with a sol-gel coating and or an adhesive primer which are used commonly in assembly of aircraft joints.
- The industry standard of less than 0.25 inch of crack extension with predominantly cohesive failure mode during the first 24 hours of exposure to 140°F and 99% RH was achieved.



Fractured laser treated Ti-6Al-4V wedge crack specimens

Accomplishments

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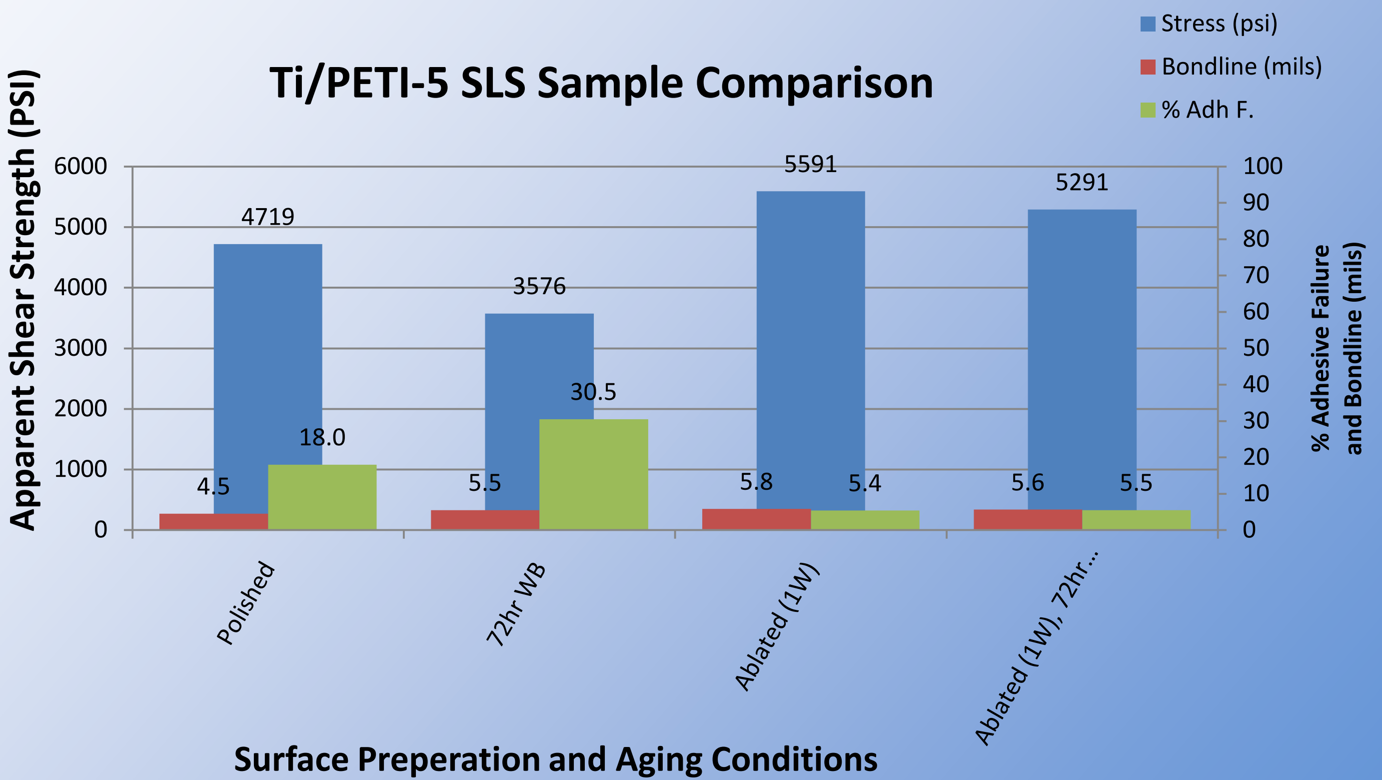
- Laser surface treatments were performed on SLS specimens and compared to control samples that were polished.
  – The results indicate that the laser treated specimens performed better than the control specimens.



Next Steps (Phase II Proposal)

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- Initiate fatigue testing on laser treated Ti coupons, continue characterization and analysis associated with test matrix
- Conduct fatigue test, complete test matrix and associated analyses
- Initiate Ti/CFRP surface treatments, characterize Ti fatigue specimens and analyze fatigue test results
- Fabricate Ti/CFRP specimens and conduct mechanical tests
- Complete characterization and analysis of all test results
- Analysis of all characterization and test results provided in a final report, recommendations for any future work needed that may lead to ARMD directed funding, or to next steps required to implement the technology into production processes
- Boeing to commit $100K in-kind funding if the project advances to Phase II

Fatigue Test Details

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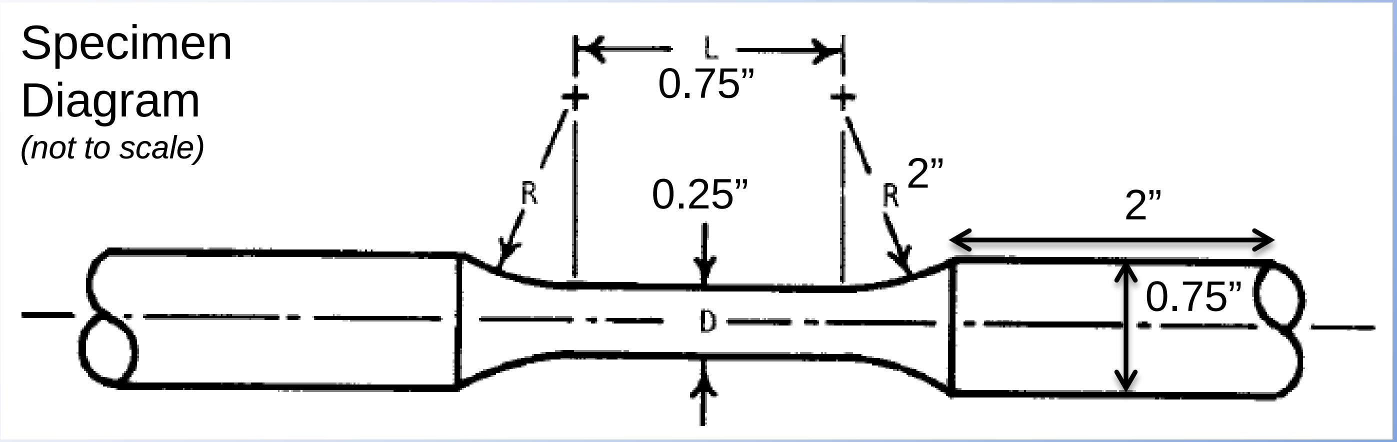
- ASTM E466-07: Conducting Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials



- Fatigue test matrix @ 15 Hz cyclic loading
  - Test: parent material, SOA process, and laser ablation surface treatment
  - Load range: 700 – 1000 MPa
  - Expected cycle range: 10^4 to $2x10^7$
  - Test duration: 5 months on two test stands (estimated cost $60-85K)

Composite Ablation & Bonding

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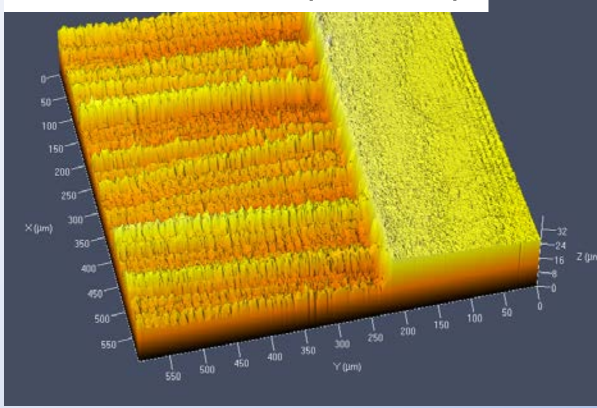
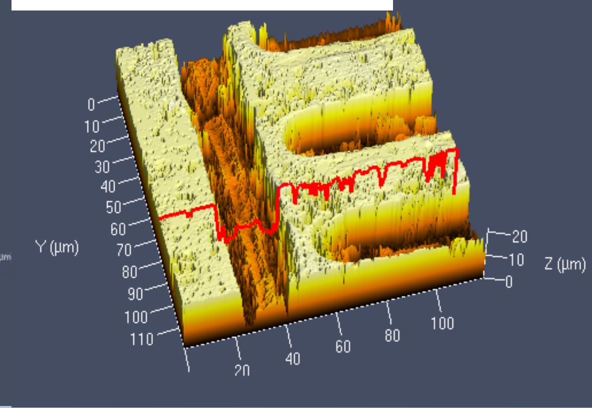
- Ablation of T800H/3900-2 composites previously performed for bonding applications
- Single-lap joints have been prepared with ablated composite panels and tested for bond durability in hot/wet environments
- Our team already has significant experience with laser ablation of composites, several publications and talks presented at technical conferences

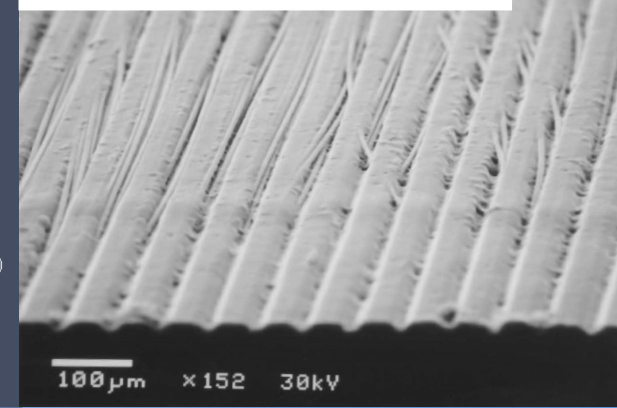
Blanket Ablation (confocal)



Line Ends (confocal)



Tilt view of x-section (SEM)



Summary of Phase I Results

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- The potential formation of α-case that was initially raised by metallurgists has been addressed at the micron scale. Mechanical fatigue testing is needed in the Phase II to demonstrate durability.
- XPS characterization indicated that detrimental hydroxyl species are removed by laser ablation, mil scale is efficiently stripped, and fresh (beneficial) oxides are readily formed at higher laser ablation energies.
- XPS has established that no detrimental chemistry is being produced by the laser treatment.
- A technique was developed to aid in failure mode analysis.
- Adhesion studies conducted with two test methods and two adhesives have indicated that a stable interface is formed.
- 1 patent application filed, 2 invention disclosures submitted, 1 conference presentation given, 1 journal article nearly complete, NASA Langley Engineering Directorate Innovation Award (9/2011).
- Boeing's (partner and end user) interest in the technology was validated by their commitment ($50k in-kind).

Appendix

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Backup Charts

Motivation for Bonding

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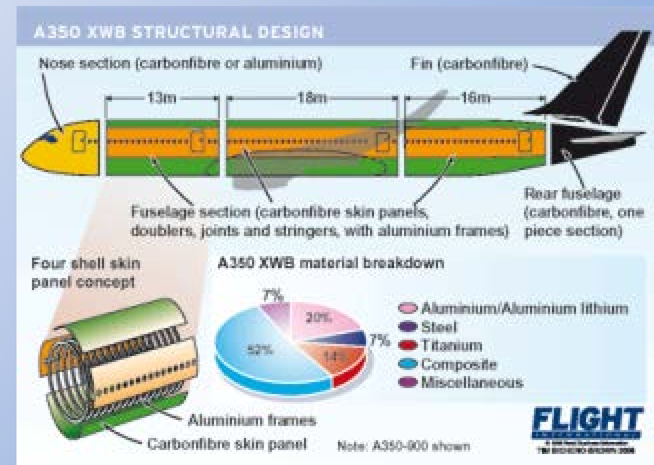
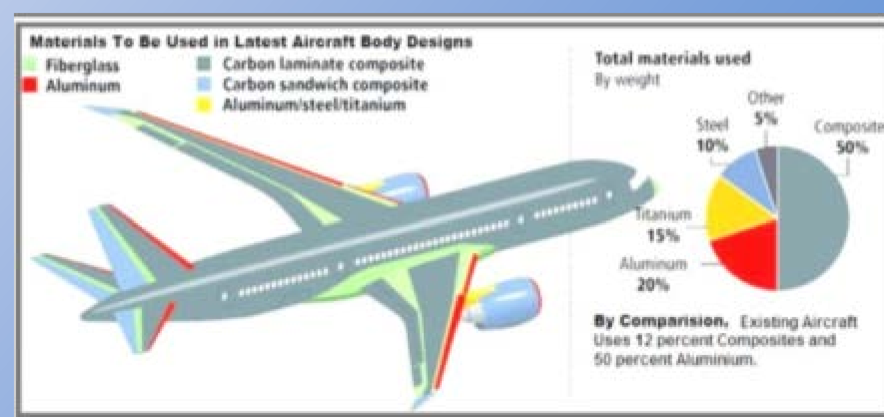
- Use of bonded joints is increasing.
  - Titanium ~ 15%
  - Composites ~ 50%
- Removing mechanical fasteners
  - Reduces weight and manufacturing cost
  - Improves design flexibility



Boeing 787 and Airbus A350



Images publicly available on the web.

Chemical Surface Preparation

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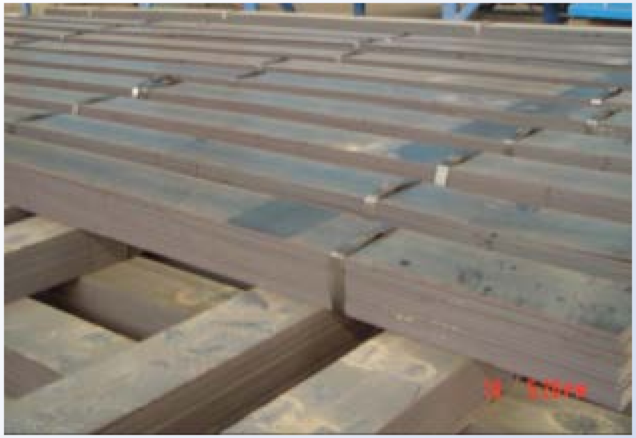

Corrosive/Caustic Stripping Processes

- Processes are polluting, dangerous, and difficult to automate & monitor
  - Acid etching: mill scale removal
  - Pasa-Jell treatment: contains HF

Cleaner, Cheaper, Safer is Needed!

Mechanical Surface Preparation

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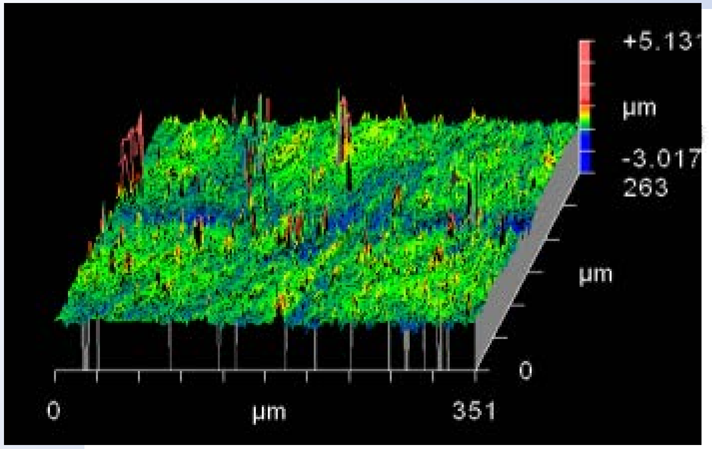
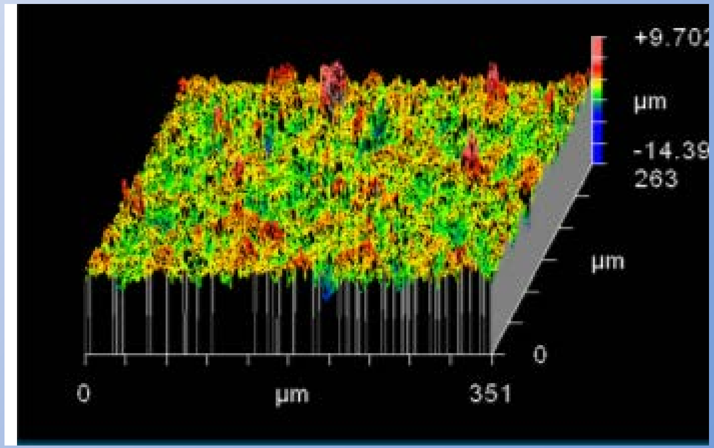
Grit blast and mechanical abrasion creates non-uniform surfaces, leaves loose debris, generates waste



Sanded Surface (220 grit SiC)



Grit Blasted Surface(220 grit SiC)

Laser Ablation Surface Preparation

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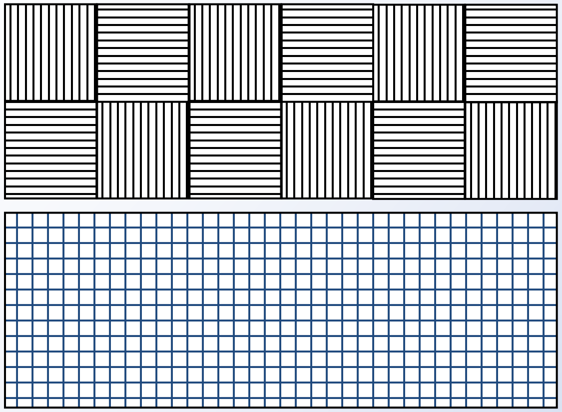
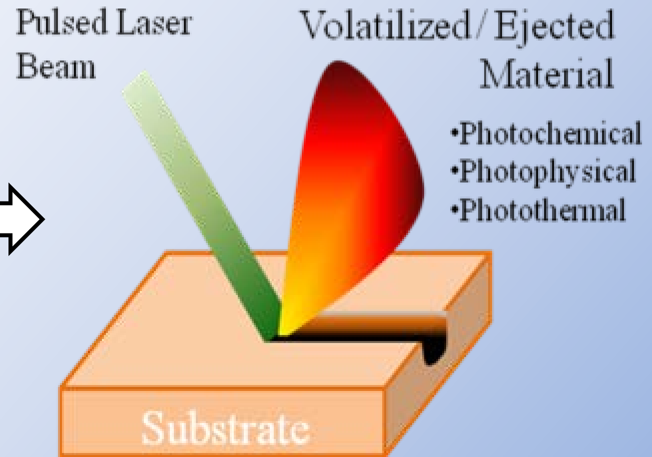


Pattern concepts developed using CAD software



Laser Ablation Processing

<u>Example:</u> Checker board pattern.

- Creates surface patterns on plastics, metals, ceramics and composites on the micron scale with a high degree of precision
- Controls roughness and surface chemistry
- Rapid, reproducible, scalable and practical for production environment

Laser Ablation Tooling and Production

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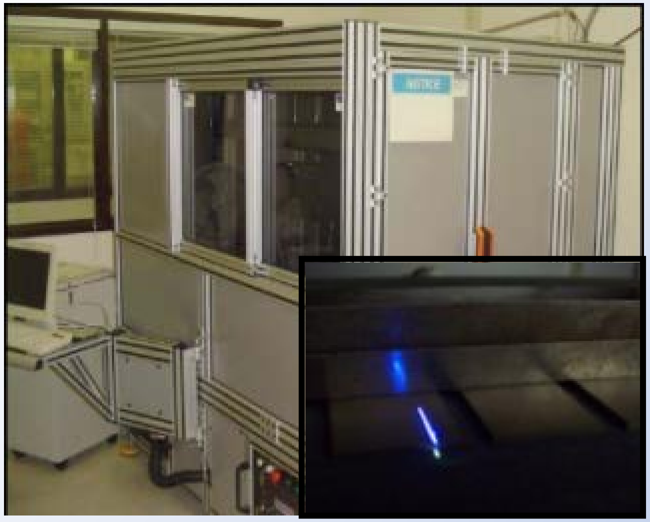
Lab-scale, laser pattern generator



Inset: Ablation of Ti-6Al-4V specimen

System Specifications:

Laser Type – Frequency tripled Nd:YAG

λ = 355 nm

Nominal Power = 7 W

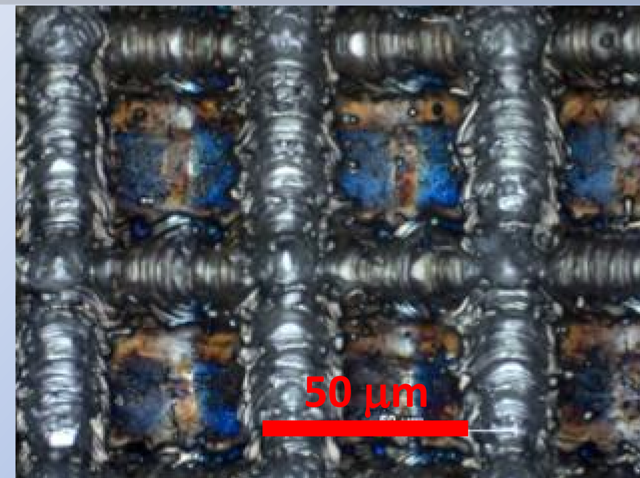
Frequency – 10 – 100 kHz

Beam Width ~ 25 µm

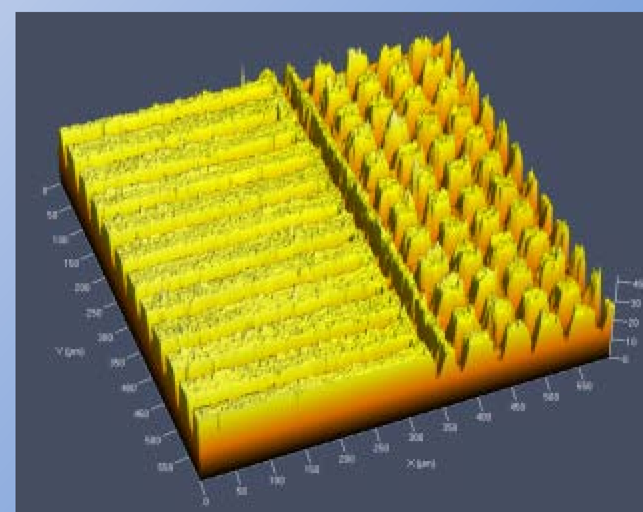
Speed – Up to 50 in/s

Waste:

Aerosols and dust are minimal and are collected in an air filter.



Cross-hatch in Ti-6Al-4V alloy (Optical)



Lines and cross-hatch (Confocal)

Test Plan

- Surface preparation by *laser ablation* and *polishing*
  - Roughness by interferometer microscope
  - Chemistry by X-ray Photoelectron Spectroscopy (XPS)
- Single-lap shear (SLS) tests
  - Apparent shear strength and failure mode
  - Ageing by immersion in boiling water
    - 3 days
- Wedge tests
  - Failure mode
  - Crack length

Specimen to Test for α–case Formation

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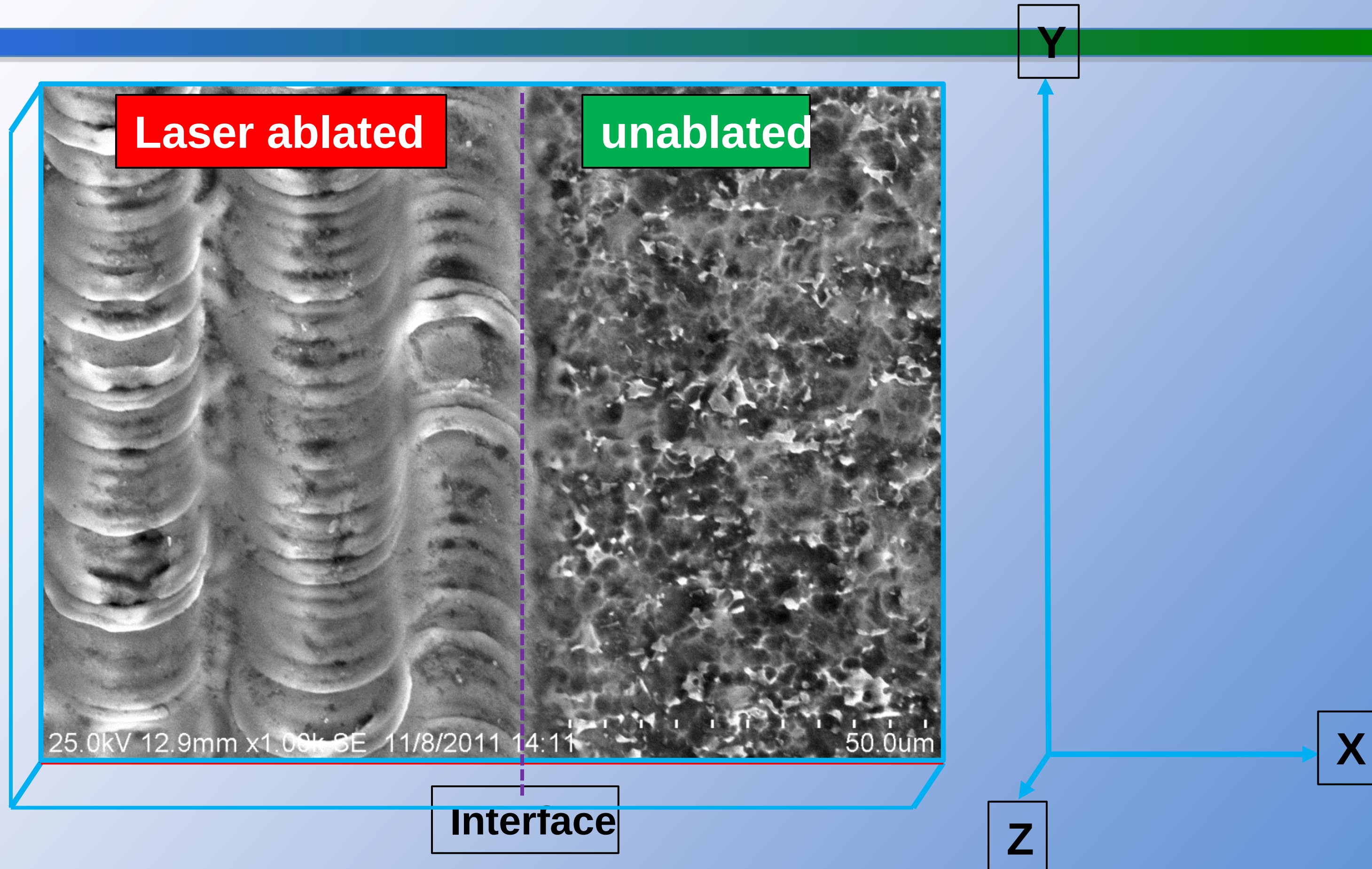
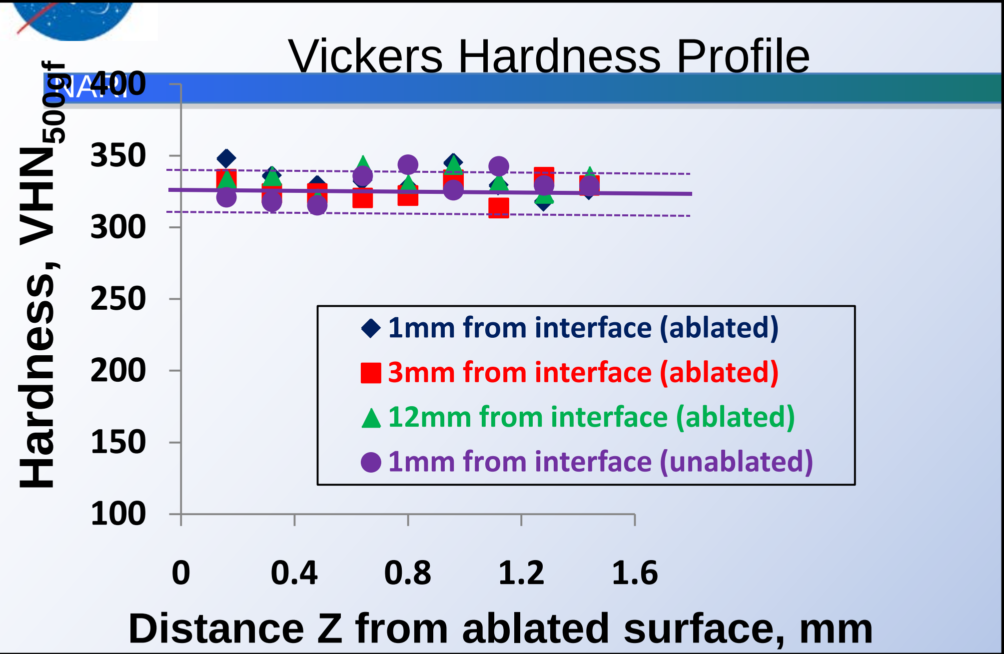
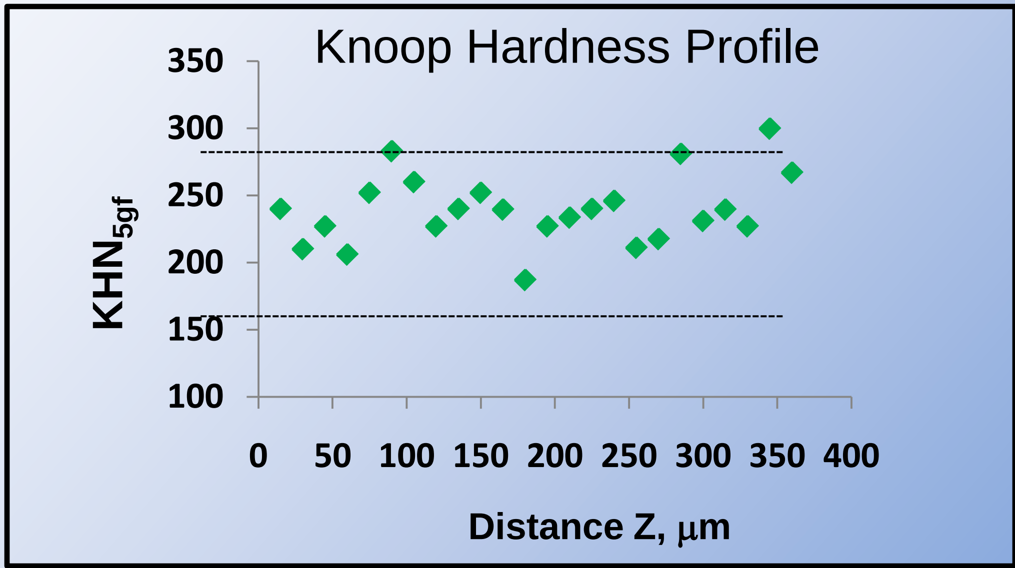


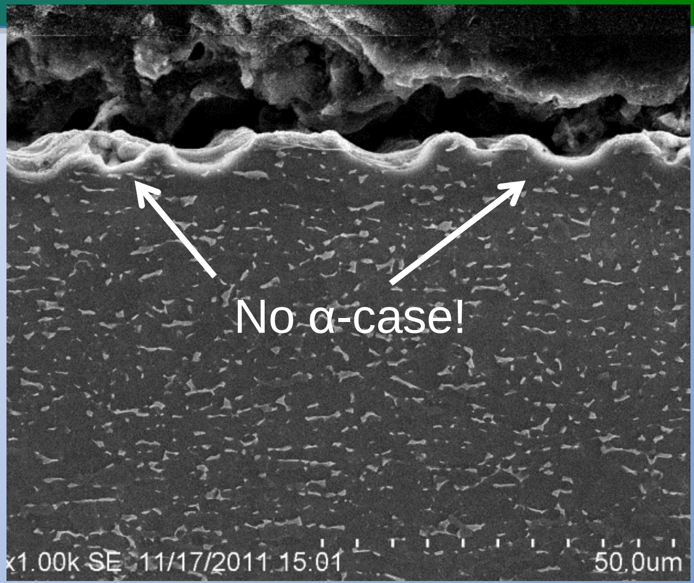
Metallographic cross-section and hardness depth profiles by indentation were examined for signs of an α-case

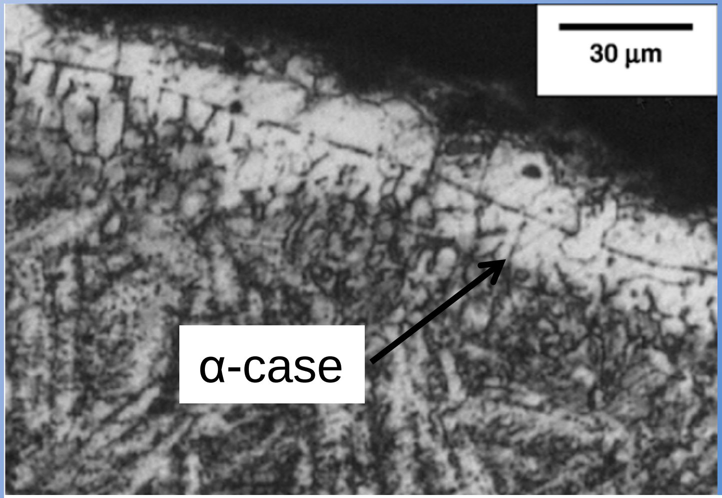
Microhardness Profile and X-Section Images





Metallographic x-sections





F. Smeacetto et al. / Surface & Coatings Technology 201 (2007) 9541–9548

Preparation of Adhesive Bonds

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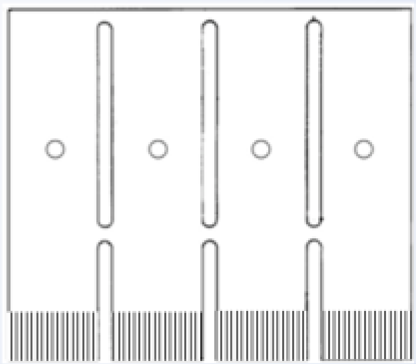
Single-lap Shear Testing

Modification of ASTM D1002-10
Titanium adherends (Ti-6Al-4V alloy)
Specimens: 1” wide, 0.063” thick, ½” overlap

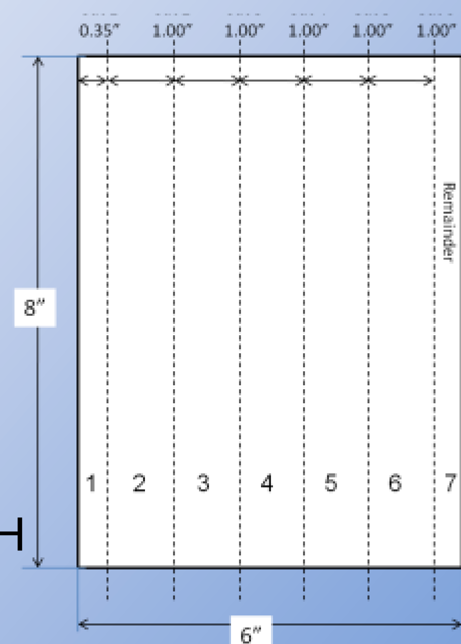


Bonding Method

Heated Press
Open air
1hr @ 700 ° F (371 ° C)
Active cooling

Wedge Testing

ASTM D3762-03
Ti alloy
6” x 8” x 0.125” adherends
1” x 8” x ¼” specimens
Ageing: 60 ° C and >95% RH



Effect of Pitch on Lap Shear

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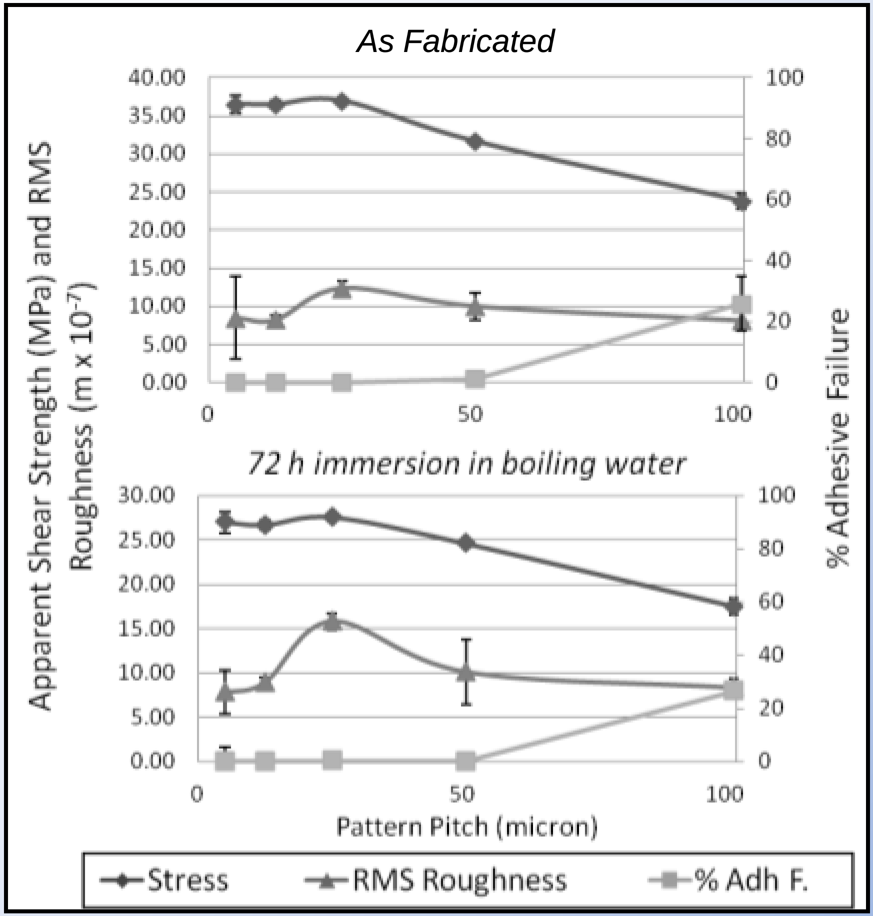
Power = 1 W



For pitch ≤ 50 µm:
•Failure mode is predominantly cohesive
•Apparent shear strength is a maximum

Roughness is a maximum at about 25 µm pitch.

Immersion in boiling water for 72 hrs
•Causes ~35% loss in properties
•Does not affect failure mode significantly.

Smaller Pitch= **Apparent Shear Strength Increases**
Adhesive Failure Decreases

Effect of Power on Lap Shear

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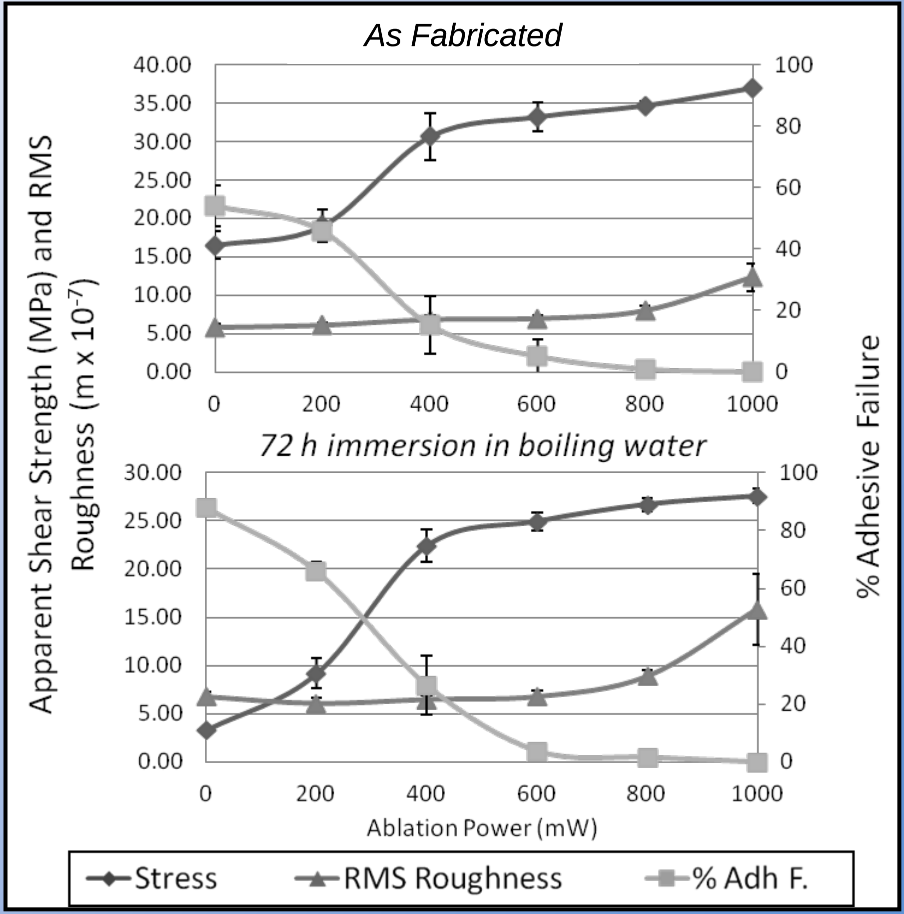
Pitch = 50 µm



At an ablation power ≥ 600 mW
- Failure mode is predominantly cohesive
- Apparent shear strength approaches maximum

Roughness increased only at higher ablation powers.

Immersion in boiling water for 72 hrs
- Causes ~25% loss in properties
- Does not affect failure mode significantly.

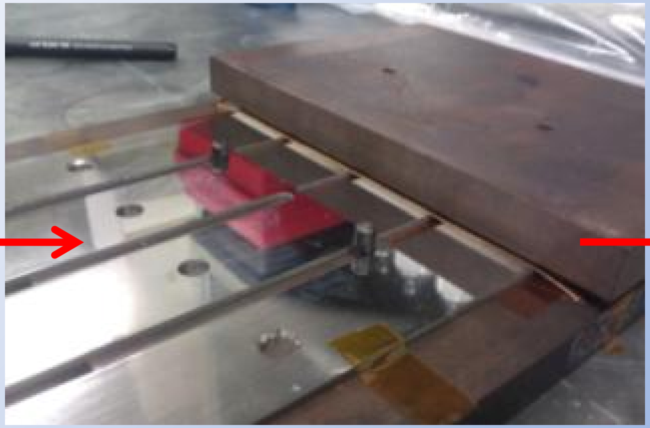
Higher Power = **Apparent Shear Strength Increases**
Adhesive Failure Decreases

Lap Shear Preparation

NARI

PETI-5 adhesive
tape preparation

Lay-up in bonding jig



Bonding in heated press

Separated specimens