



Novel Bonding Methodologies Toward the Attainment of Primary Bonded Aircraft Structure

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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.**
- **Using 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 leading to the certification of primary bonded structure on commercial aircraft.**



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!



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, 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 tested
 - Multiple wedge crack specimens were prepared and tested
 - Fatigue behavior tested
 - Surface stability investigated



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

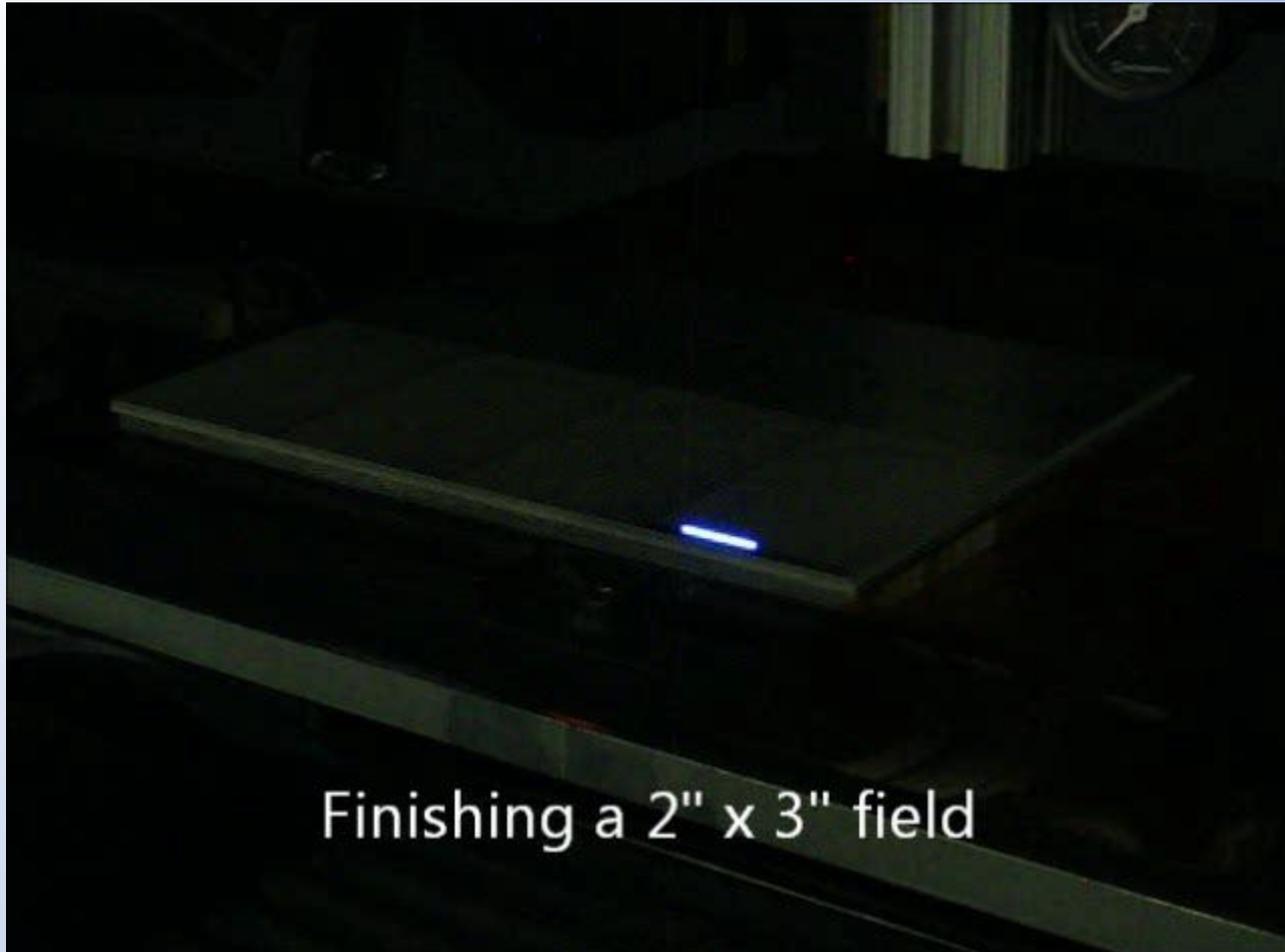
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- U.S. Patent Application 20110086204 “Modification of Surface Energy Via Direct Laser Ablative Surface Patterning” April 14, 2011.
- Palmieri, Frank P.; Wohl, Christopher J.; Morales, Guillermo; Williams, Thomas; Hicks, Robert; Connell, John W., “Laser 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, ACS Applied Materials and Interfaces, 5(4), 1254-1261 (2013).
- First Place NASA Langley Engineering Directorate Innovation Award, Sept. 2011.
- Joint SAMPE paper with Boeing accepted for Spring Meeting (June 2014).



Accomplishments

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Finishing a 2" x 3" field

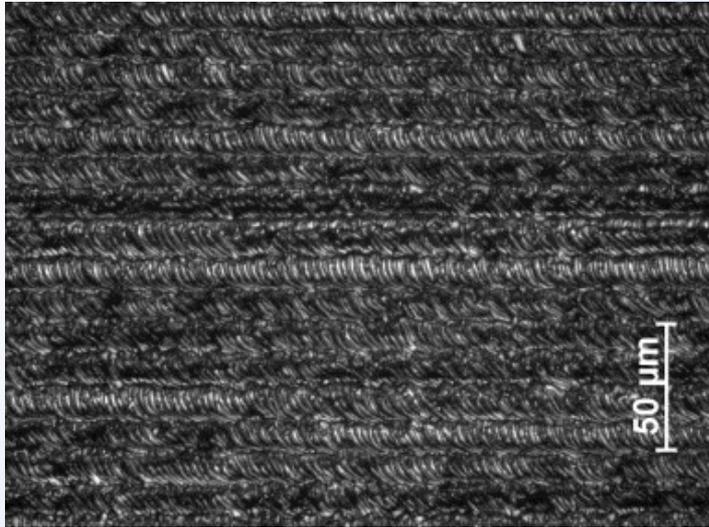


Accomplishments

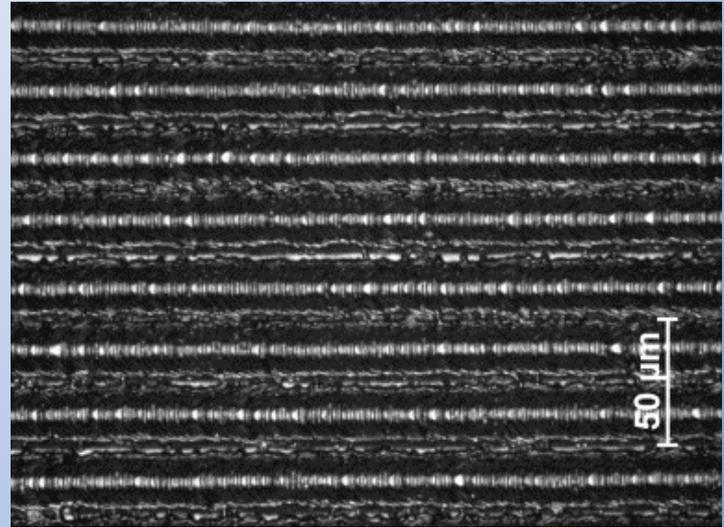
Laser Treated Ti panels

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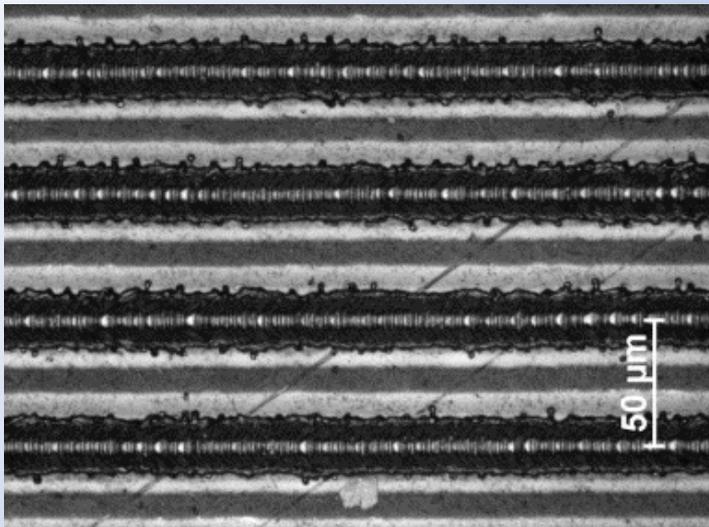
D = 200%



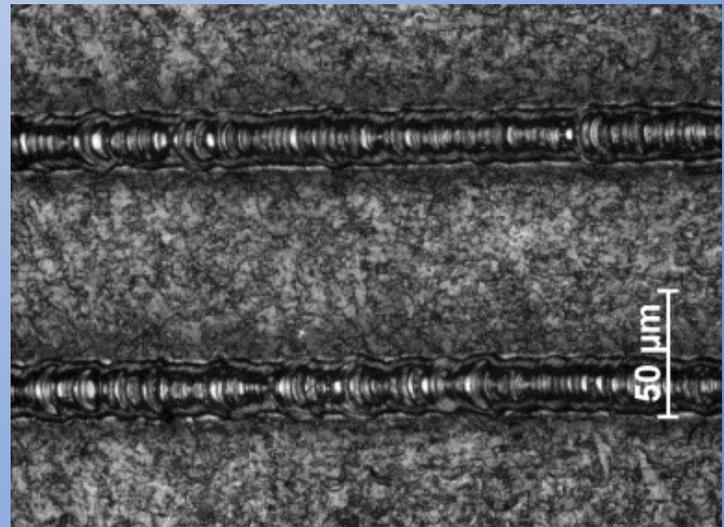
D = 100%



D = 50%



D = 25%



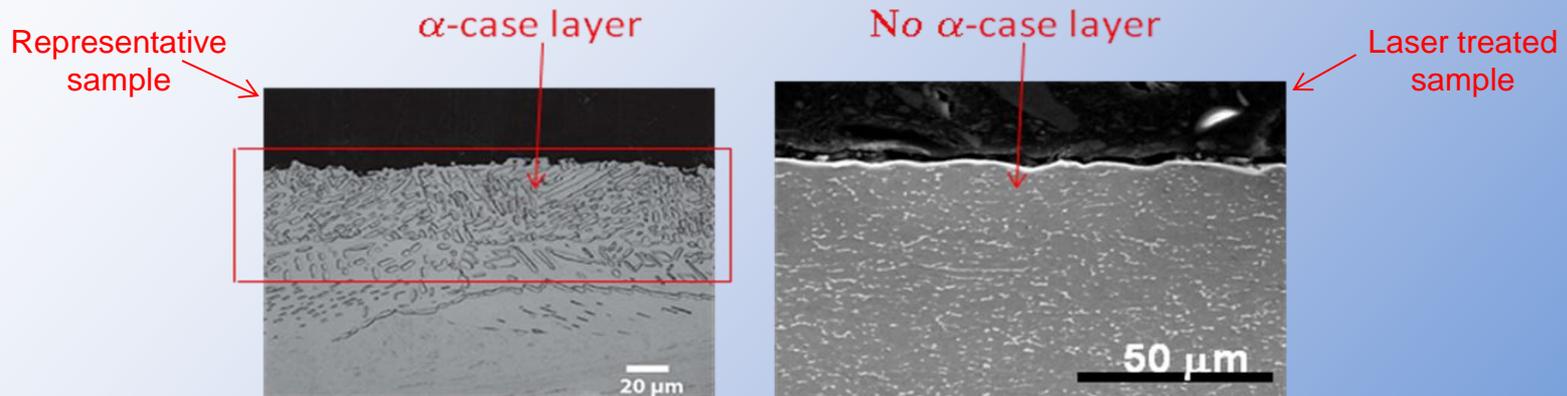
Duty Cycle (D) = $0.001''/\text{pitch} \times 100\%$



Accomplishments

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

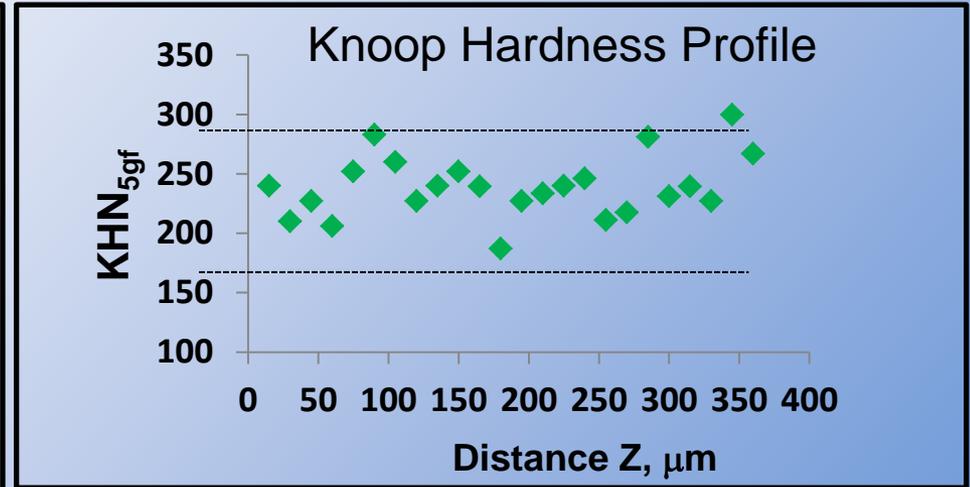
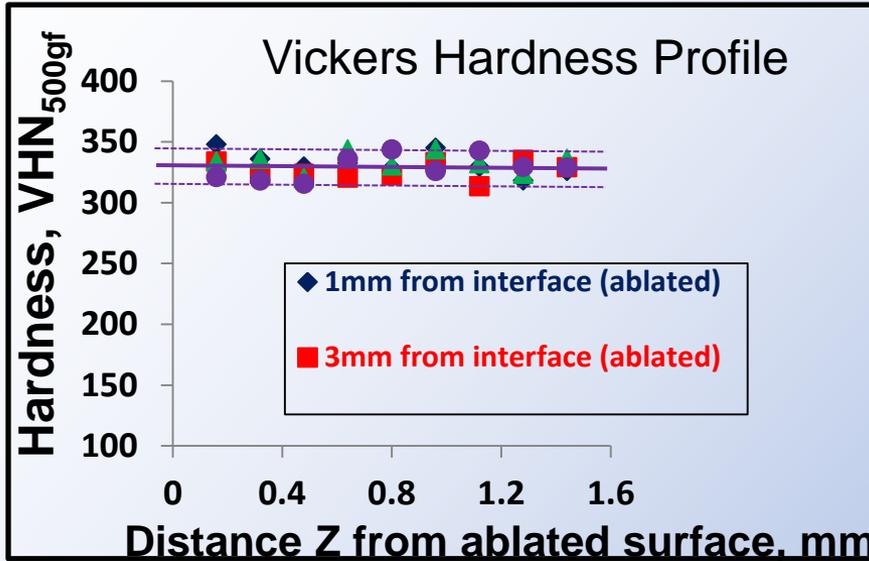


- The α -case layer is a hard and brittle layer caused by oxygen diffusion into the Ti-6Al-4V.
- Microscopic analysis and nanoindentation experiments were conducted on laser etched coupons to determine if any α -case was observed.
- No indication of α -case formation due to the laser ablation surface 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.



Microhardness Profile

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- Microhardness characterization results correlate with SEM data.



Accomplishments

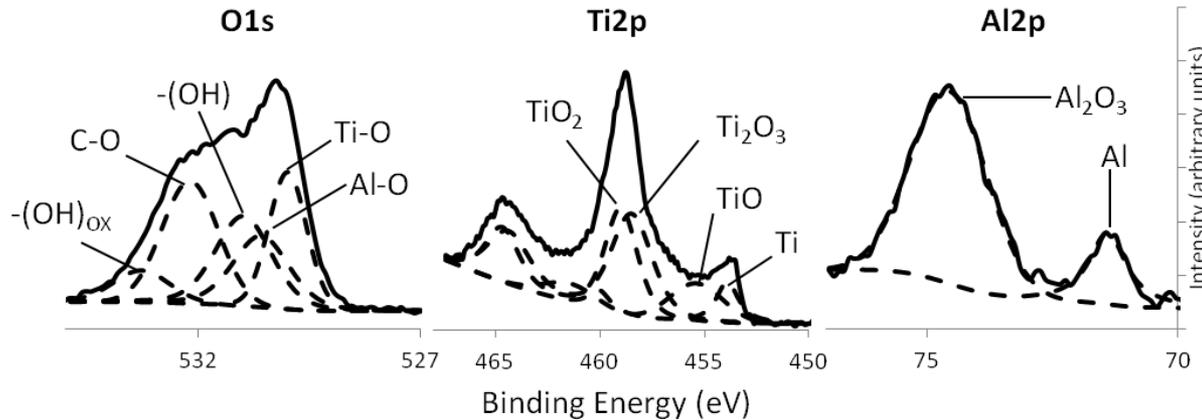
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- **Milestone -determine the surface chemistry that results from the laser ablation process.**
 - Certain chemical species (highly oxidized hydroxyl structures) on the Ti alloy surface are detrimental to the formation of robust and durable adhesive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



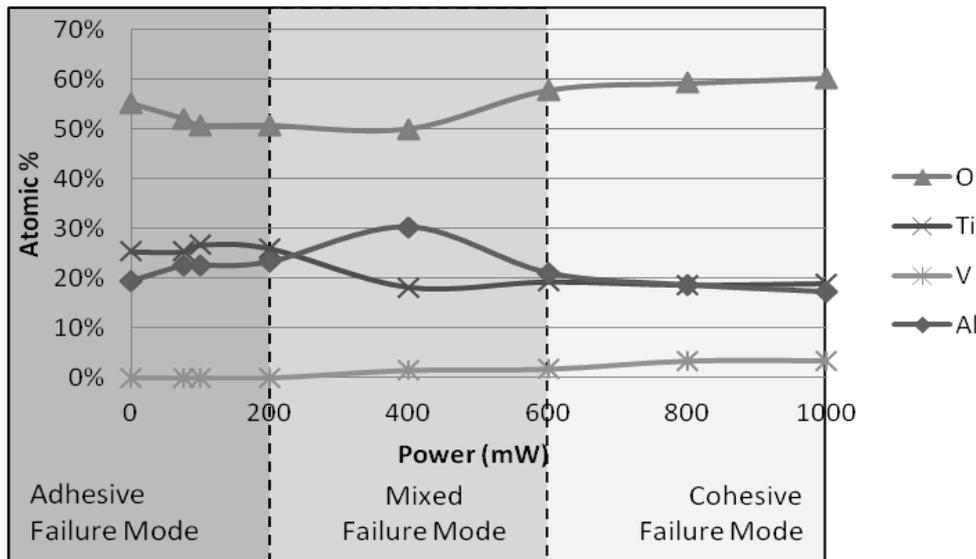
XPS Results

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Peak Identification

XPS Elemental Survey



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

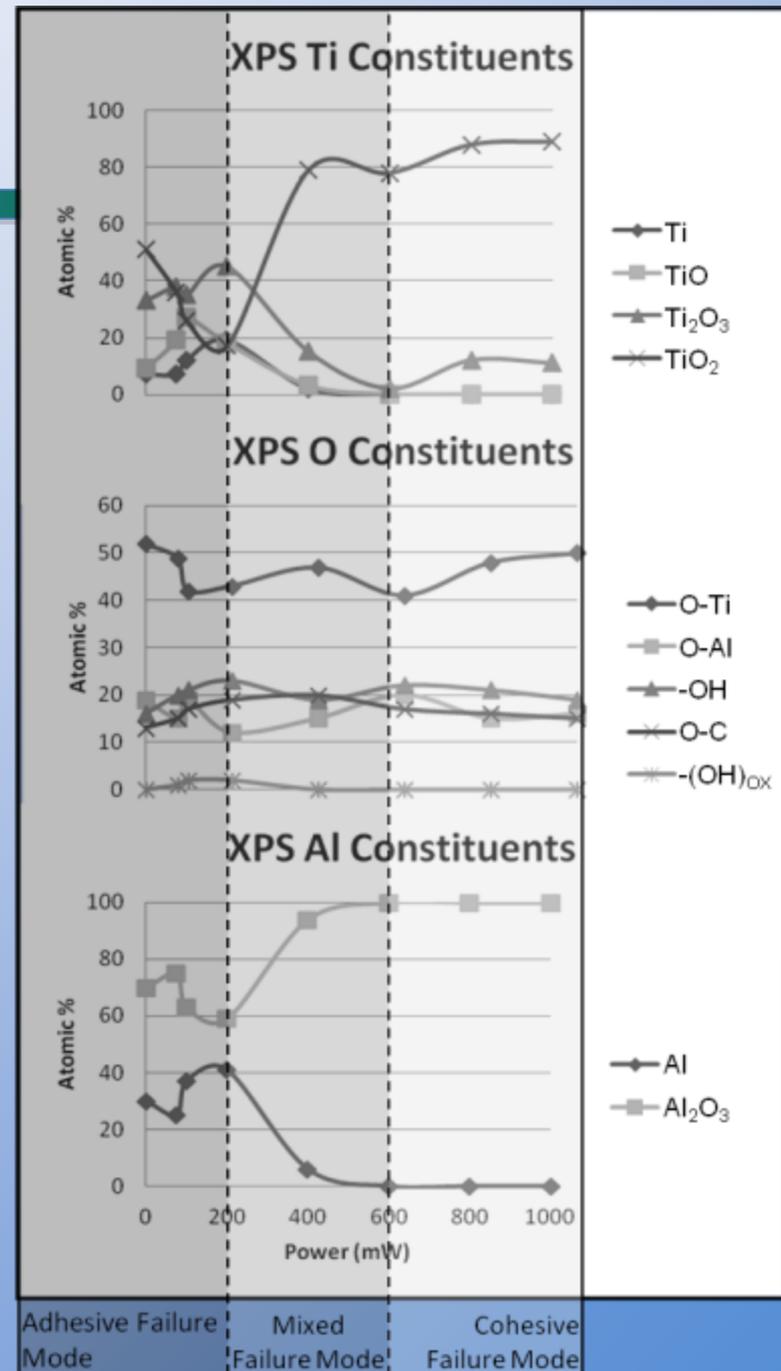


Accomplishments

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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

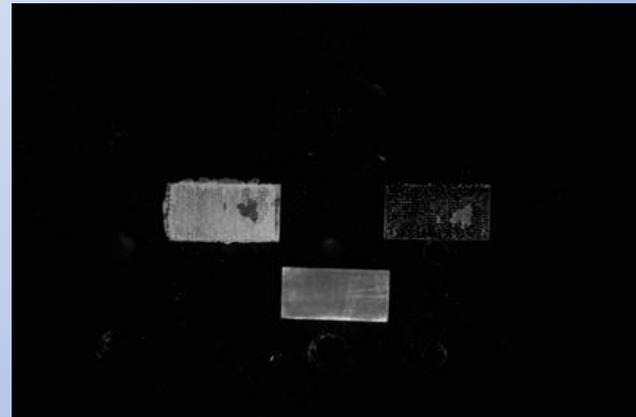
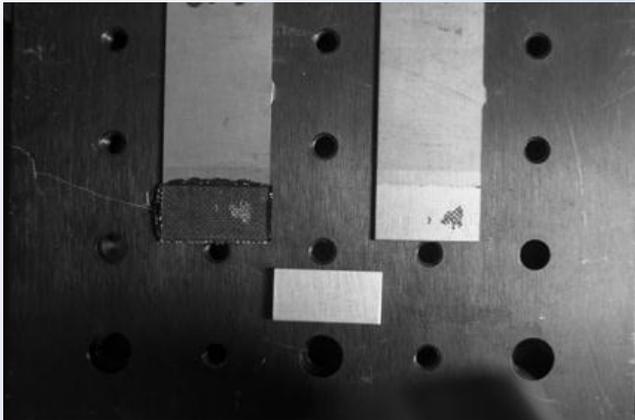




Accomplishments

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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 was executed in Phase II.

Test Number	@Boeing		@NASA	@Boeing			@NASA	
	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
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.

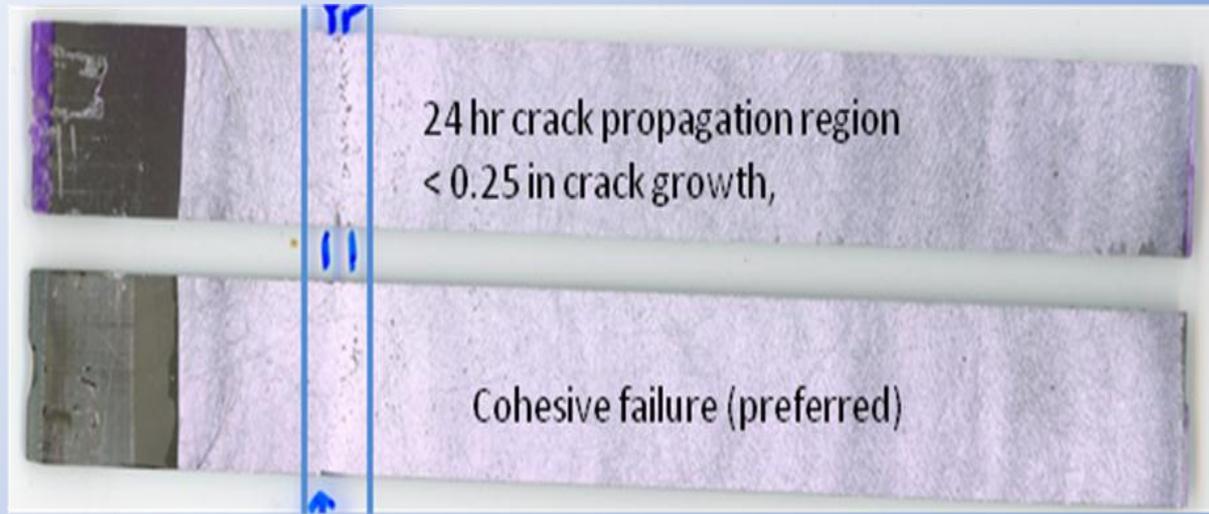
Sol-Gel and Primer steps can be performed at NASA as capabilities are verified (0.15-0.40 is acceptable; 0.20-0.25 mil thick primer is most preferred).



Accomplishments

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- A significant milestone was the results from wedge testing of laser ablated Ti adherends.
 - The as-received adherends were treated with the laser ablation process 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.



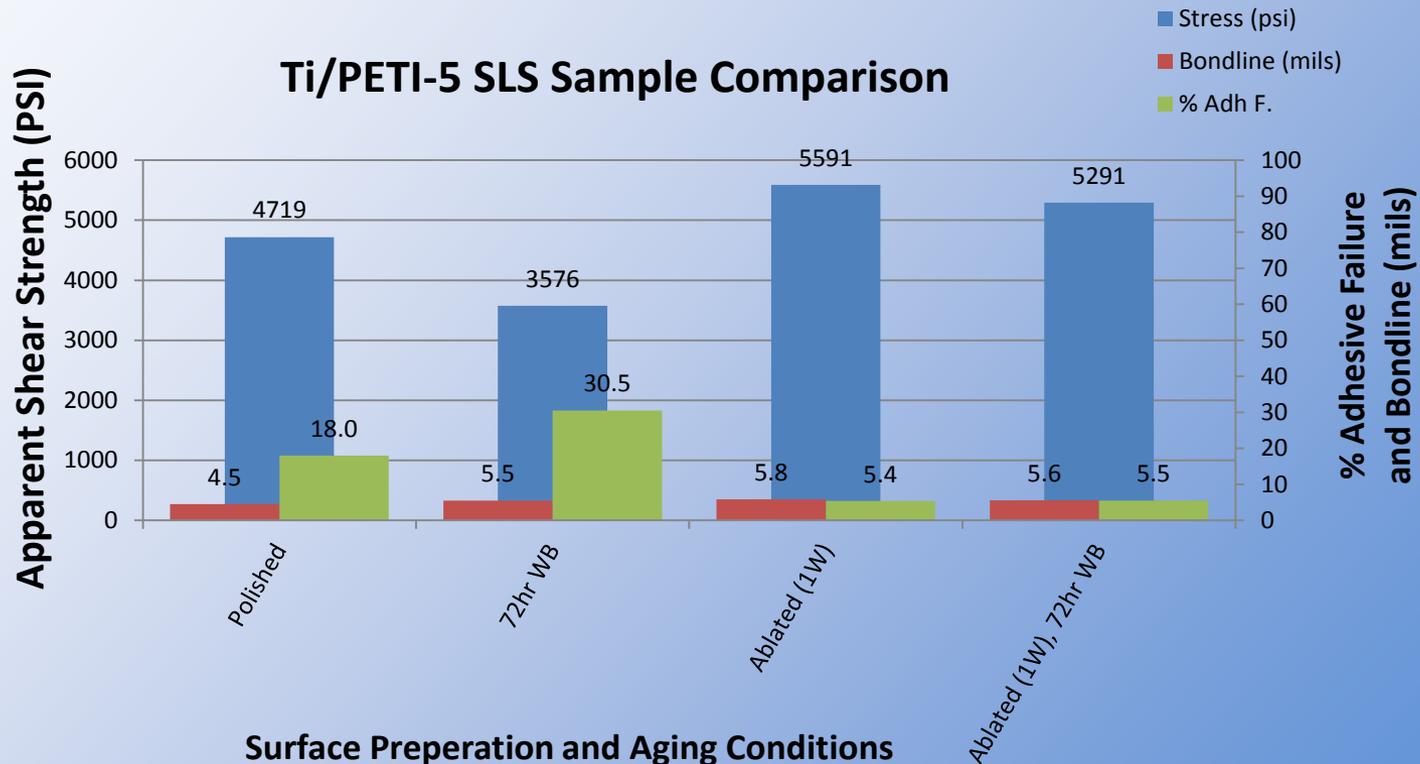
Fractured laser treated Ti-6Al-4V wedge crack specimens



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.





Summary of Phase I Results

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- **No indication of α -case was detected by microstructural characterization or hardness measurements. 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).**



Phase II Effort

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- **Initiate fatigue testing on laser treated Ti fatigue specimens, continue characterization and analysis associated with wedge crack specimen test matrix.**
- **Characterize Ti fatigue specimens and analyze fatigue test results.**
- **Complete characterization and analysis of wedge crack test results.**
- **Assess the out-time behavior of the laser treated specimens by monitoring changes in contact angle over time.**
- **Boeing committed \$100K in-kind funding to the Phase II work.**



Fatigue Test Details

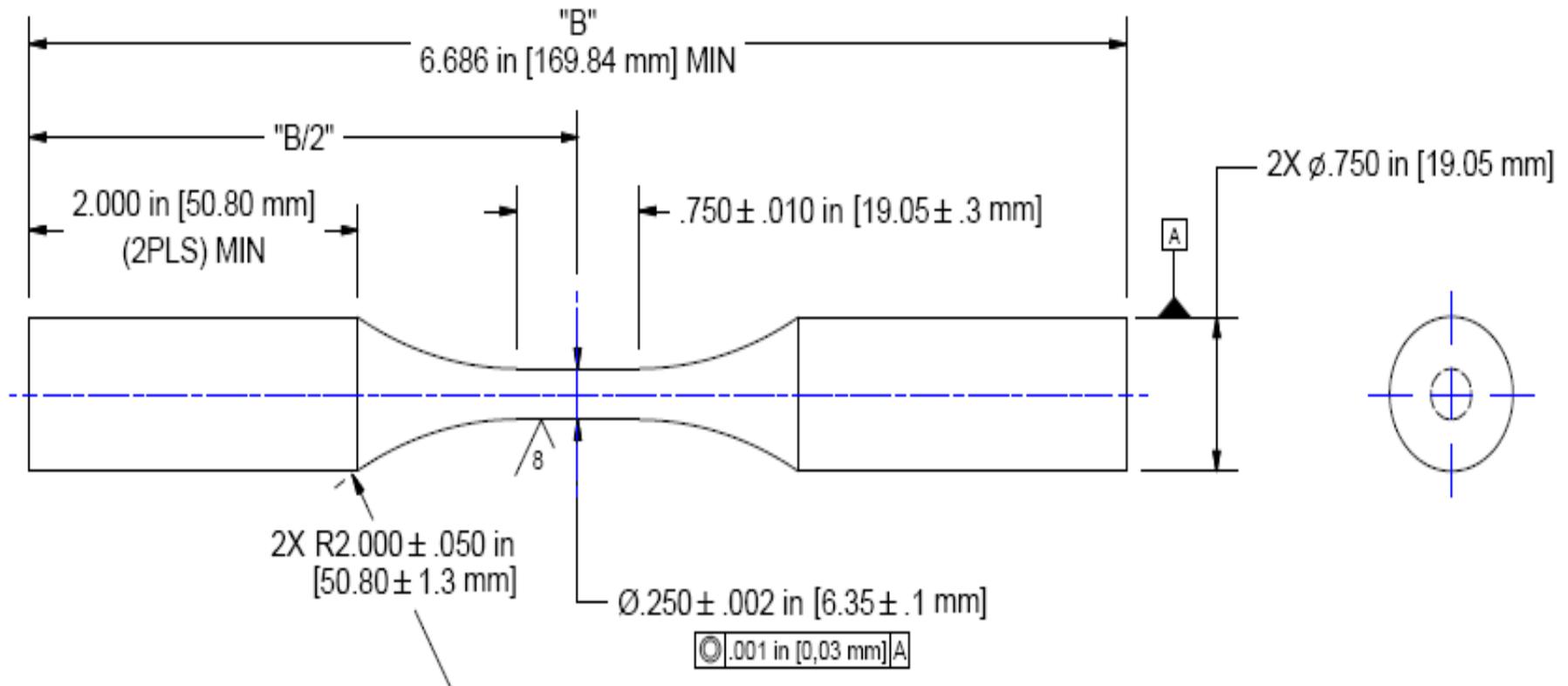
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- **ASTM E466-07: Conducting Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials**
- **Fatigue test matrix @ 30 Hz cyclic loading**
 - **Test: parent material (no surface treatment), SOA process, and laser ablation surface treatment**
 - **Load range: 450 – 900 MPa**
 - **Cycle range: 2×10^4 to 2×10^7**
 - **Test duration: 5 months**



Cylindrical Fatigue Test Specimen

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Wedge Test Details

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Test Number	Nitric/HF preclean	Thermal Age	Laser Process	State-of-the-Art Processes			Bond Primer
				Nitric/HF	TiBoe	Sol-Gel	
1a	X		A	X	X	X	X
2a	X		A		X	X	X
3a	X		A			X	X
4a	X		A				X
1b	X		B	X	X	X	X
2b	X		B		X	X	X
3b	X		B			X	X
4b	X		B				X
3c	X		C			X	X
4c	X		C				X
3d	X		D			X	X
4d	X		D				X
3e	X		E			X	X
4e	X		E				X
5	X	X	A	X	X	X	X
6	X	X	A		X	X	X
7	X	X	A			X	X
8	X	X	A				X
Control 1	X			X	X	X	X
Control 2	X	X		X	X	X	X



Laser Ablation Patterns Used in Wedge Test Matrix

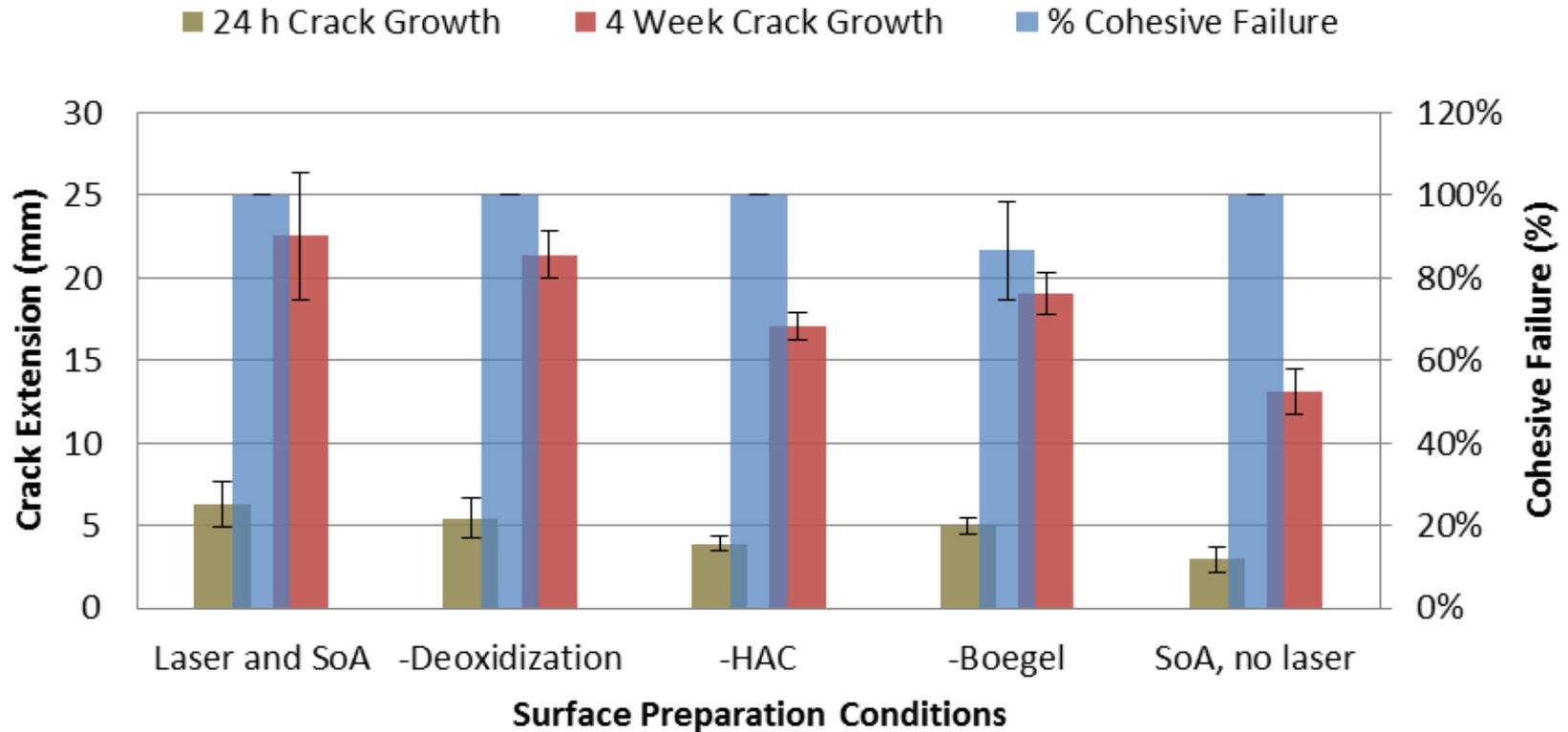
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Experiment Designation	Pitch, in microns (mil)	Line Pattern	Duty Cycle (%)
A	102 (4)	Crosshatch	44
B	406 (16)	Crosshatch	12
C	51 (2)	Parallel	50
D	25 (1)	Parallel	100
E	25 (1)	Crosshatch	200
F	12.5 (0.5)	Parallel	200



Wedge Test Results (44% Duty Cycle)

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Out Time Study Details

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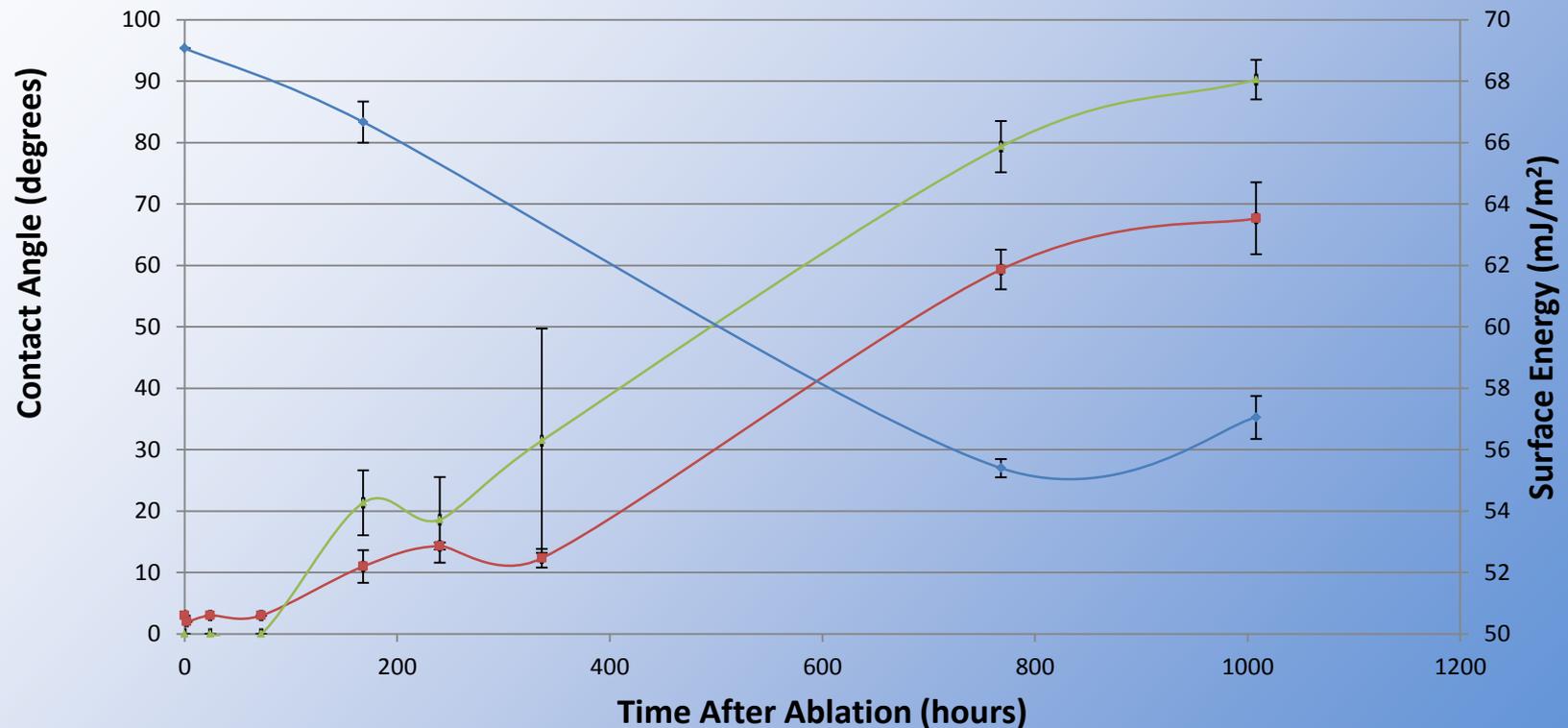
- **Titanium panels (100 mm x 150 mm) were ablated with 12.5 mm (0.5 in) squares.**
- **Each measurement was made on an isolated square to prevent interference from previous measurements.**
- **Two laser ablation patterns, A and F were tested for out-time stability.**
- **Specimens were wrapped in paper and placed in a dessicator with a relative humidity between 20% and 40%.**
- **Contact angles (room temperature) were measured at 0 h, 2 h, 24 h, 72 h, 1 week, 10 days, 2 weeks, 3 weeks, 4 weeks, 6 weeks, 8 weeks, and 10 weeks.**



Out Time Study Results (44% Duty Cycle)

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Hand-Held Surface Analyst Goniometer Surface Energy

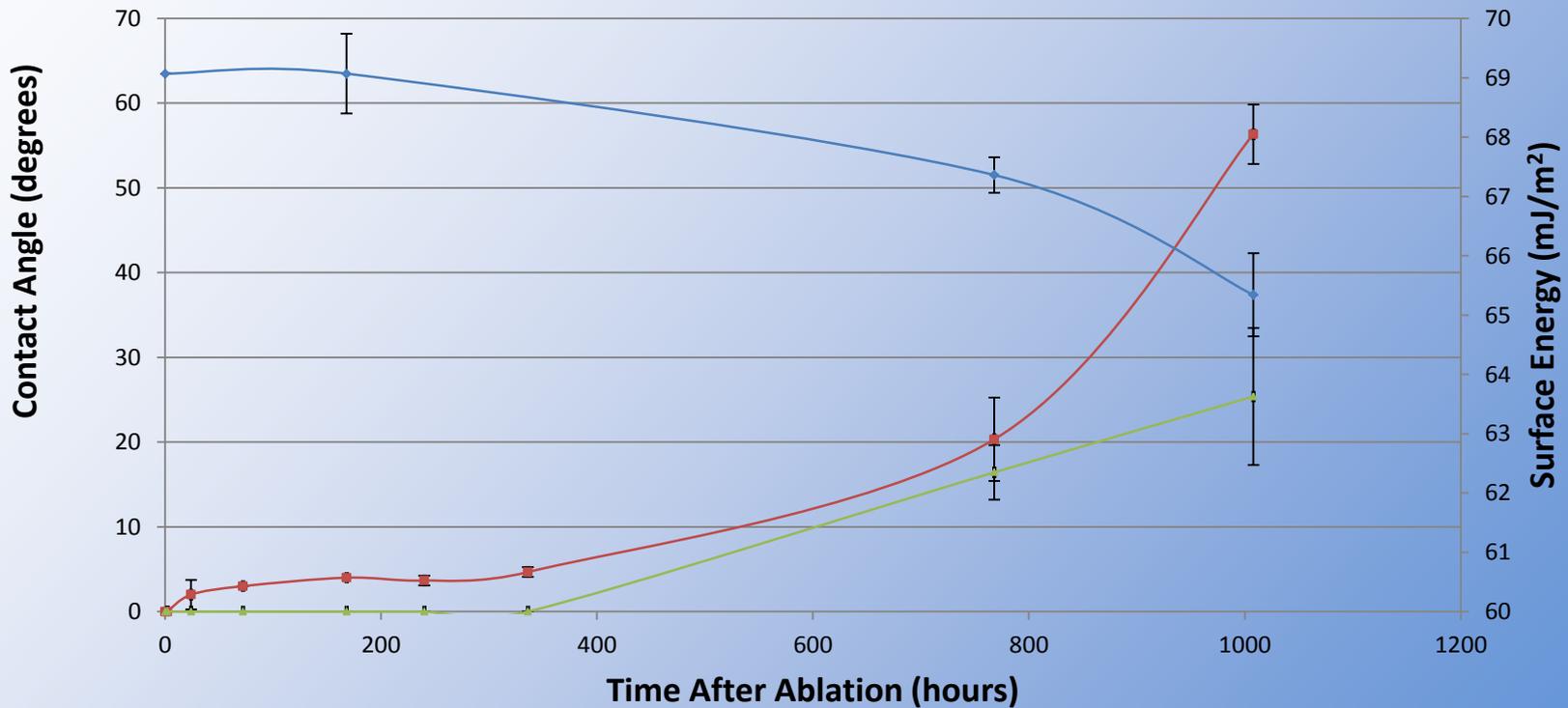




Out Time Study Results (200% Duty Cycle)

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Hand-Held Surface Analyst Goniometer Surface Energy





Summary of Phase II Results

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- **Adhesion testing results indicated that laser ablation could replace both the chemical deoxidation process using nitric and hydrofluoric acids and the hot alkaline conditioner pretreatment steps with no loss in adhesion performance.**
- **Fatigue behavior results indicated that laser ablation did not significantly reduce fatigue lifetime of Ti-6Al-4V substrates compared to SoA surface treatment.**
- **Based on the out time study results, laser ablation patterning can provide sufficiently stable surfaces for use with current manufacturing practices.**



Overall Project Outcome

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- **Boeing is actively pursuing internal opportunities to demonstrate this technology on prototype parts.**
- **This work is transitioning to the NASA Advanced Composites Program with a focus on process control and investigation of metal to composite bonding.**



Acknowledgements

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- **The authors thank Will Johnston, Jim Baughman, and Keith Bird from NASA Langley Research Center for discussions about metal fatigue testing and for metallographic inspection.**
- **Thanks are due also to Hoa Luong for tool fabrication and to Mike Oliver for specimen machining, both from NASA LaRC.**
- **The authors appreciate discussions about fatigue test materials and practices with James Pehoushek-Stangeland of The Boeing Company.**
- **NARI ARMD Seedling Fund for supporting this work.**



Appendix

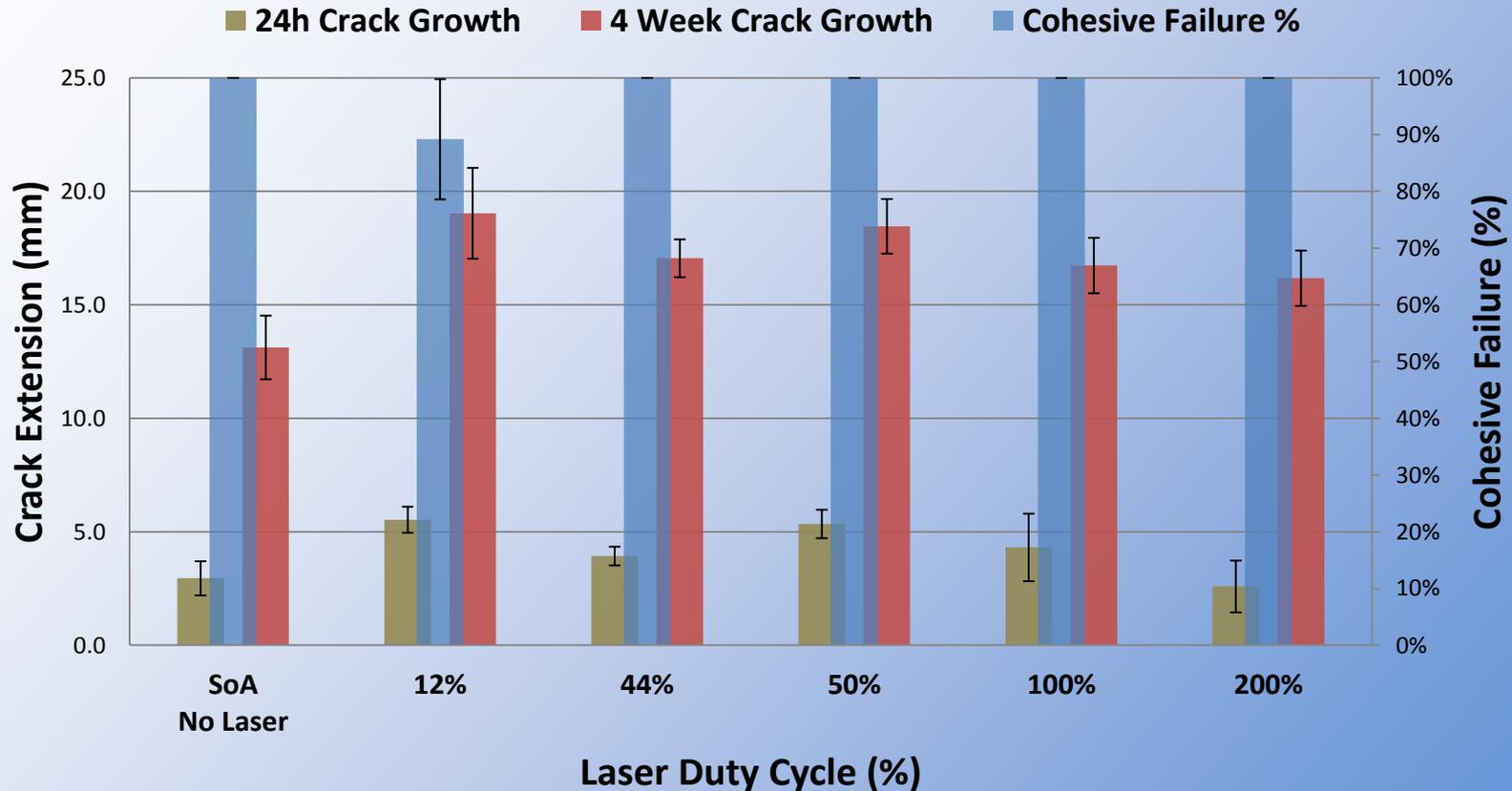
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Backup Charts



Wedge Test Results

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Wedge test results for specimens that received Boegel-EPII coating and bond primer after laser ablation. The deoxidation and HAC process steps were removed.



Wedge Test Matrix

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Test Number	Nitric/HF preclean	Thermal Age	Laser Process	State-of-the-Art Processes			Bond Primer
				Nitric/HF	TiBoe	Sol-Gel	
1a	X		A	X	X	X	X
2a	X		A		X	X	X
3a	X		A			X	X
4a	X		A				X
1b	X		B	X	X	X	X
2b	X		B		X	X	X
3b	X		B			X	X
4b	X		B				X
3c	X		C			X	X
4c	X		C				X
3d	X		D			X	X
4d	X		D				X
3e	X		E			X	X
4e	X		E				X
5	X	X	A	X	X	X	X
6	X	X	A		X	X	X
7	X	X	A			X	X
8	X	X	A				X
Control 1	X			X	X	X	X
Control 2	X	X		X	X	X	X



Laser Ablation Patterns

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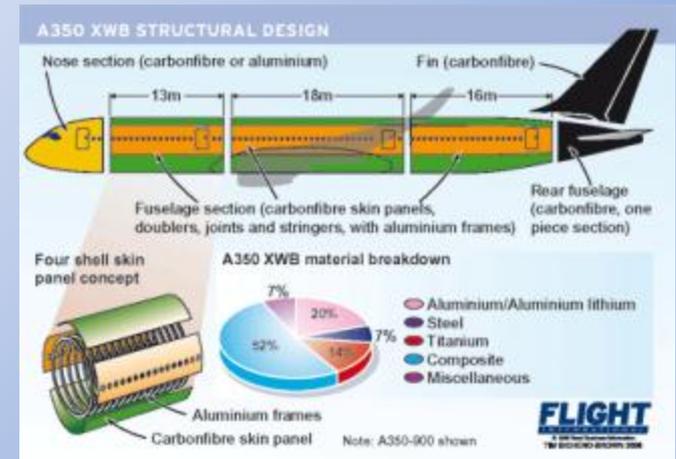
Experiment Designation	Pitch (micron)	Pattern	Duty Cycle (%)
A	102 (4 mil)	Crosshatch	44
B	406 (16 mil)	Crosshatch	12
C	51 (2 mil)	Parallel	50
D	25 (1 mil)	Parallel	100
E	25 (1 mil)	Crosshatch	200
F	12.5 (0.5 mil)	Parallel	200



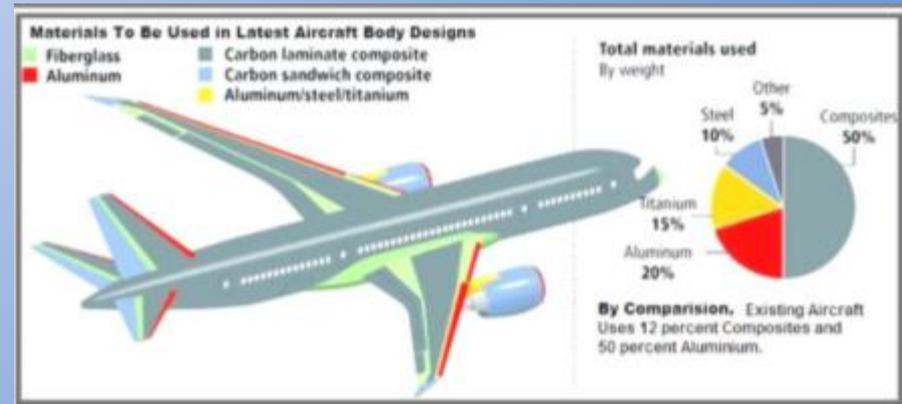
Motivation for Bonding

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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



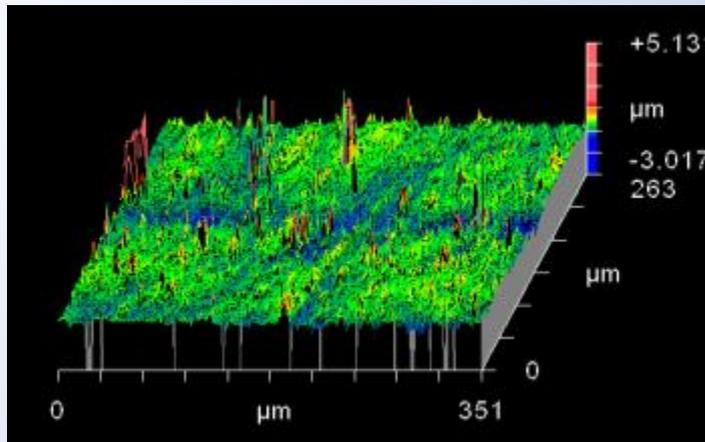
Images publicly available on the web.



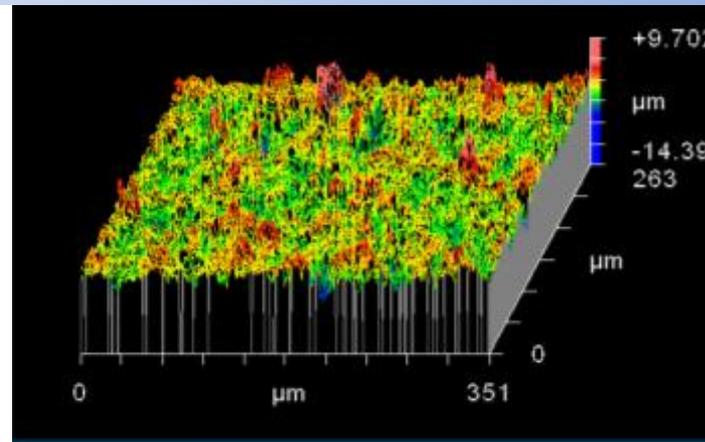
Mechanical Surface Preparation

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



Sanded Surface (220 grit SiC)

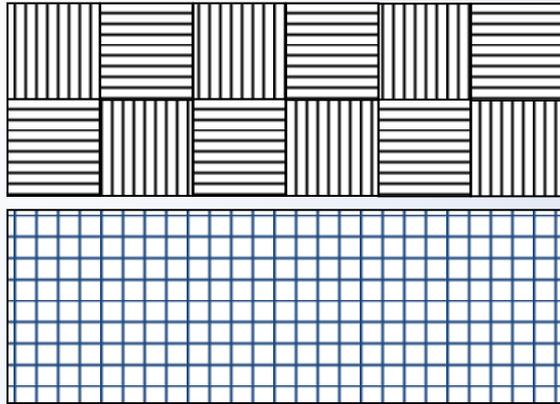


Grit Blasted Surface(220 grit SiC)

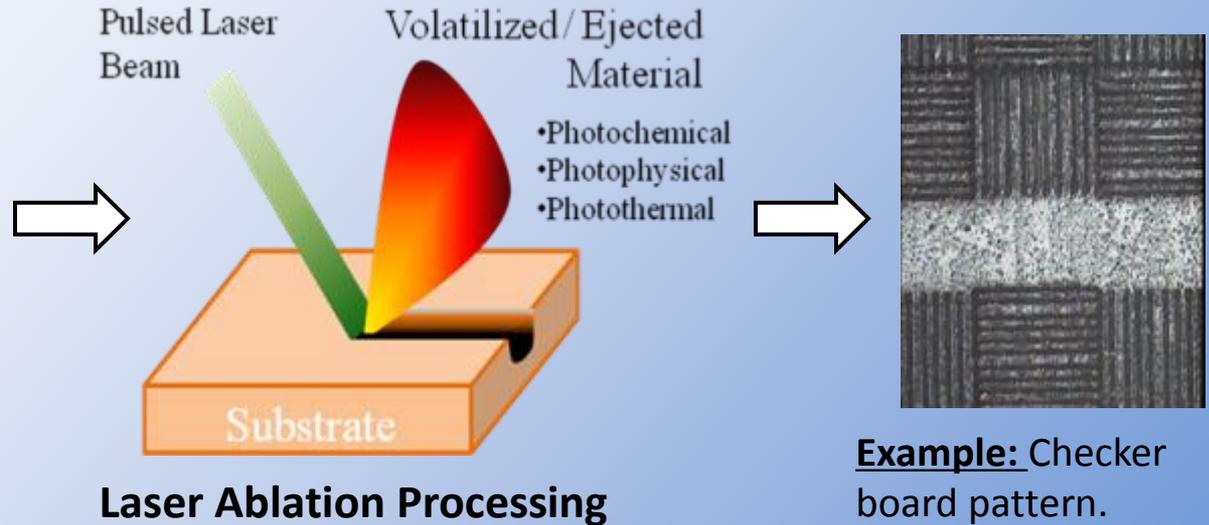


Laser Ablation Surface Preparation

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Pattern concepts developed using CAD software



Example: Checker board pattern.

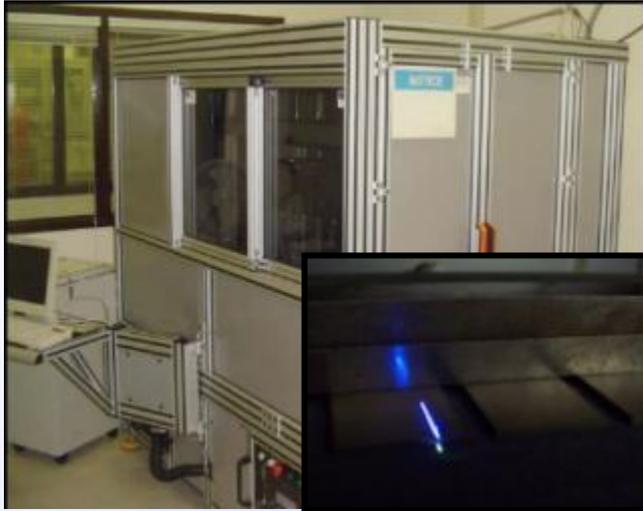
- Creates surface patterns on plastics, metals, ceramics and composites on the micron scale with a high degree of precision
- Controls roughness and surface chemistry
- Rapid, reproducible, scalable and practical for production environment



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

$\lambda = 355 \text{ nm}$

Nominal Power = 7 W

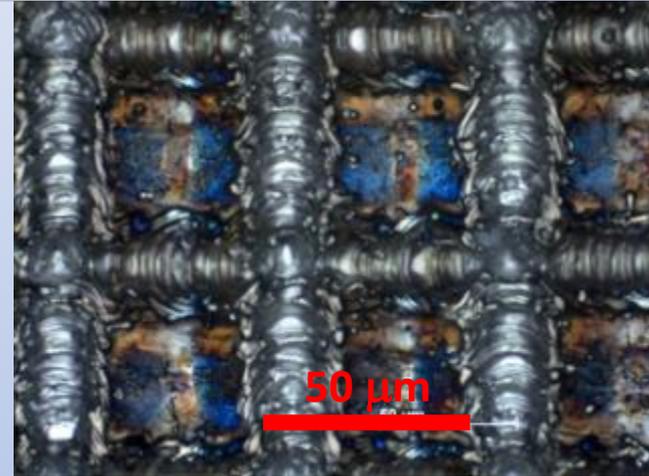
Frequency – 10 – 100 kHz

Beam Width $\sim 25 \mu\text{m}$

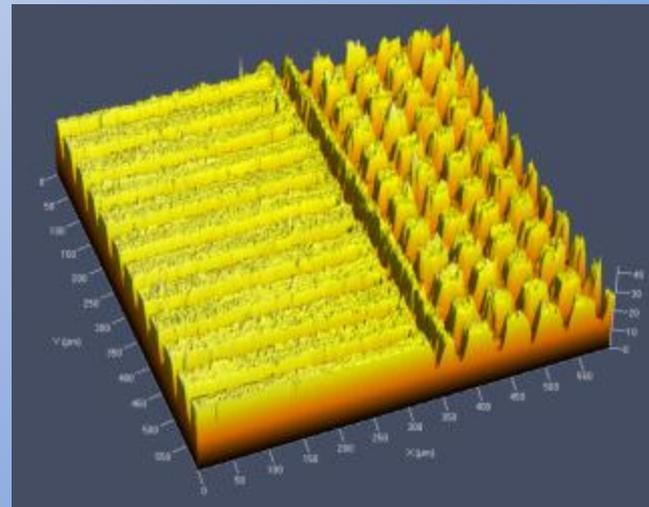
Speed – Up to 50 in/s

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

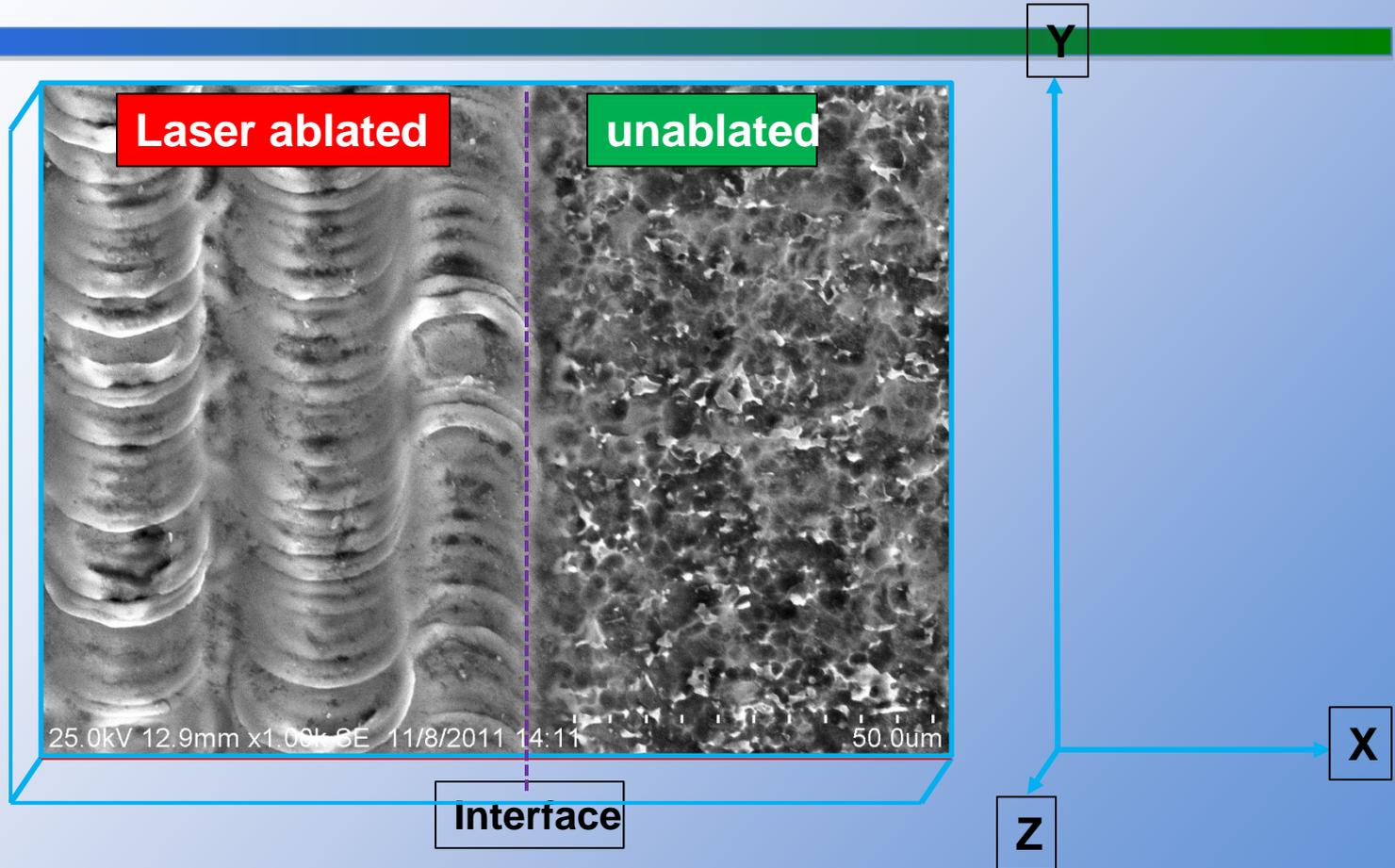
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- Surface preparation by laser ablation and polishing
 - Roughness by interferometer microscope
 - Chemistry by X-ray Photoelectron Spectroscopy (XPS)
- Single-lap shear (SLS) tests
 - Apparent shear strength and failure mode
 - Ageing by immersion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



Specimen to Test for α -case Formation

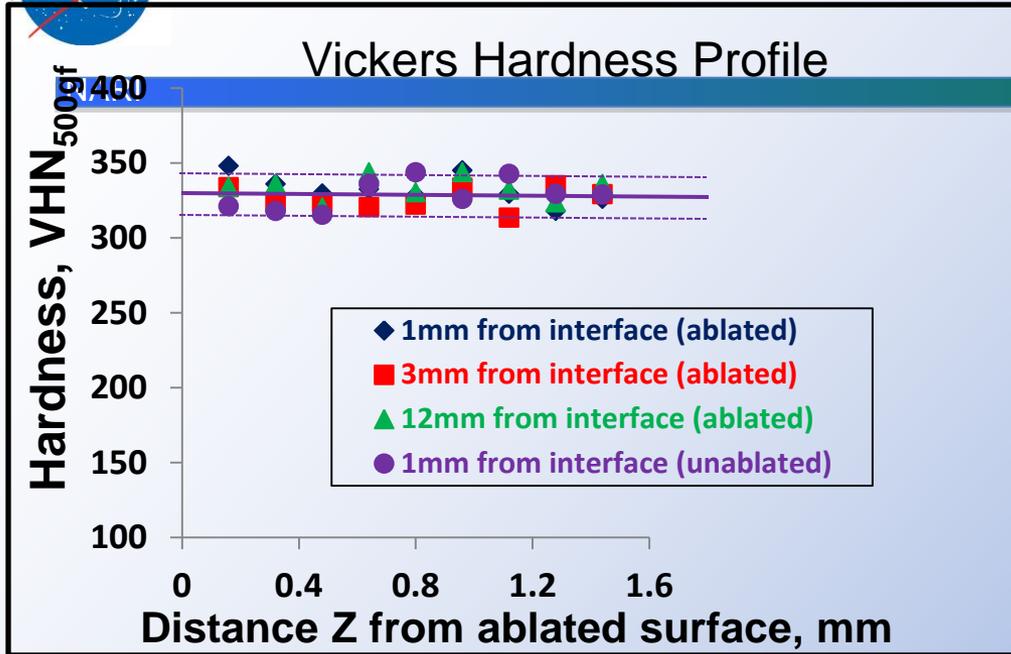
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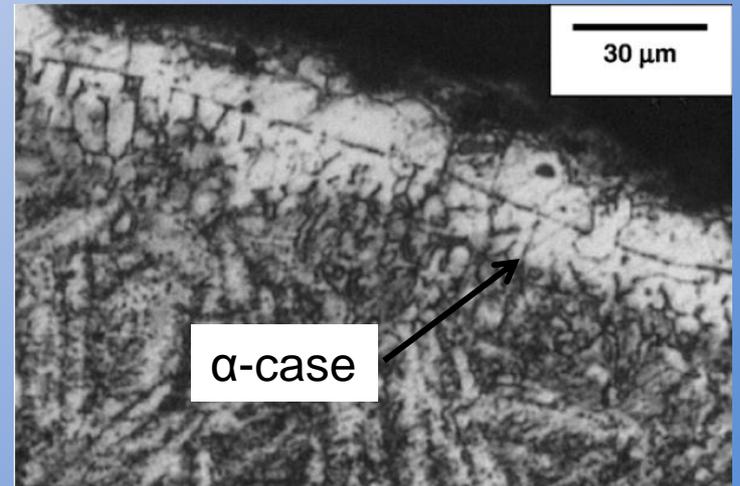
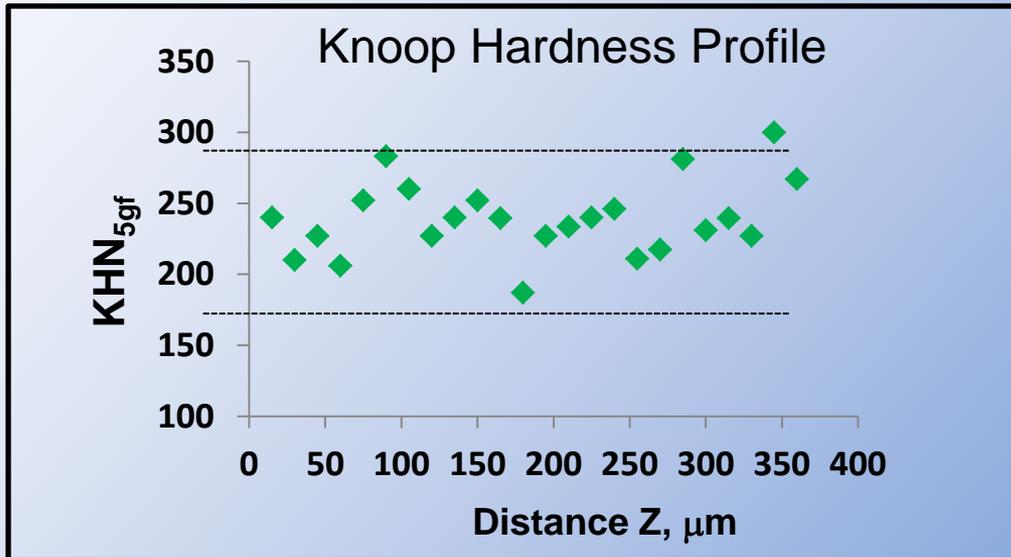
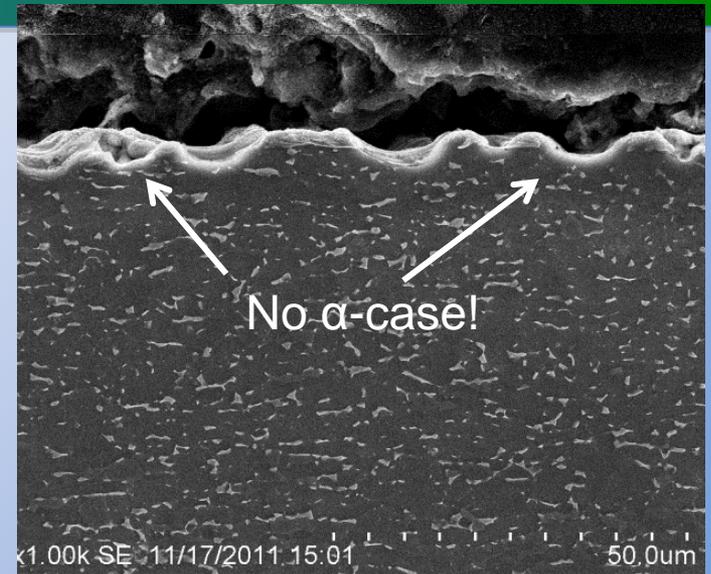
Metallographic cross-section and hardness depth profiles by indentation were examined for signs of an α -case



Microhardness Profile and X-Section Images



Metallographic x-sections





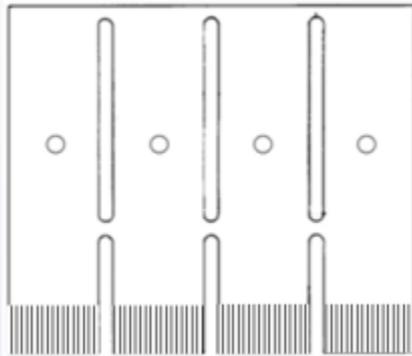
Preparation of Adhesive Bonds

Single-lap Shear Testing

Modification of ASTM D1002-10

Titanium adherends (Ti-6Al-4V alloy)

Specimens: 1" wide, 0.063" thick, 1/2" overlap



Wedge Testing

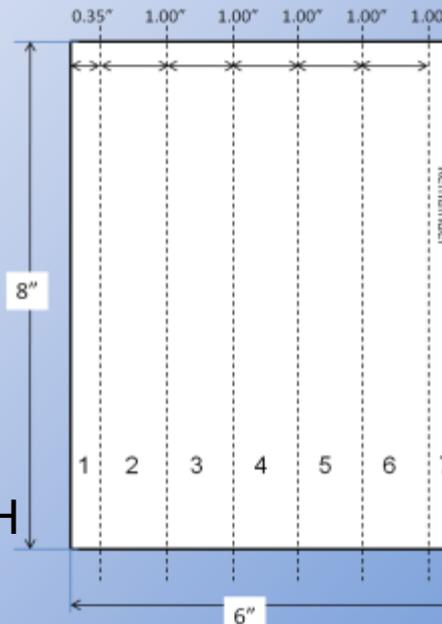
ASTM D3762-03

Ti alloy

6" x 8" x 0.125" adherends

1" x 8" x 1/4" specimens

Ageing: 60 ° C and >95% RH



Bonding Method

Heated Press

Open air

1hr @ 700 ° F (371 ° C)

Active cooling

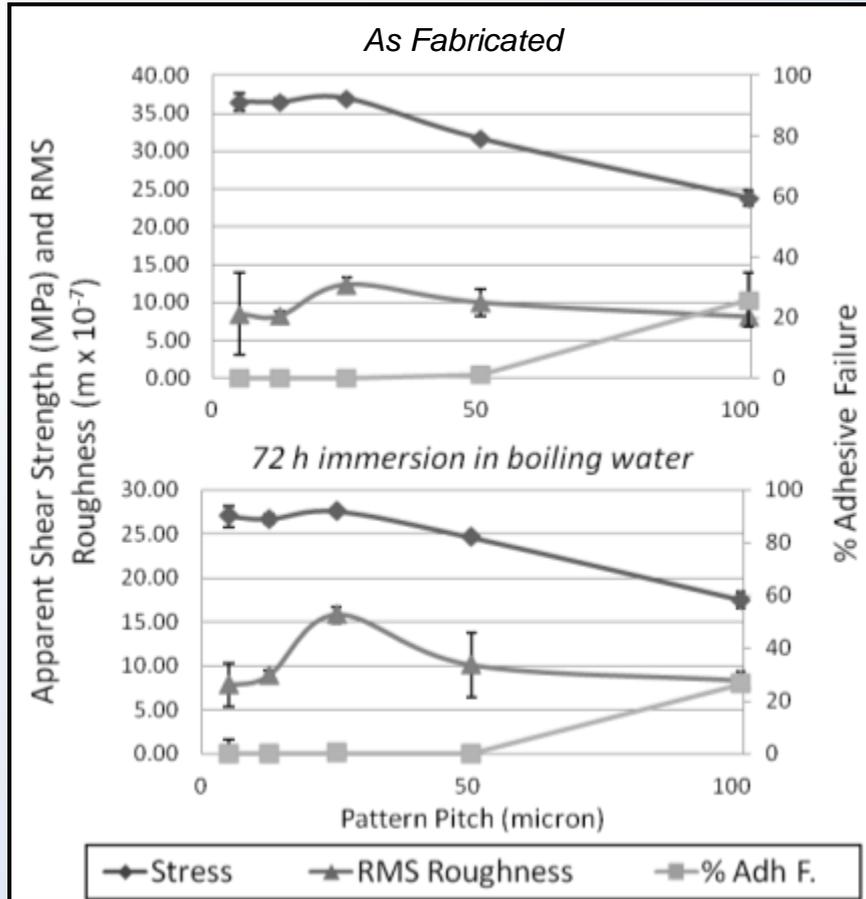




Effect of Pitch on Lap Shear

NARI

Power = 1 W



For pitch $\leq 50 \mu\text{m}$:

- 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

NARI

Pitch = 50 μm

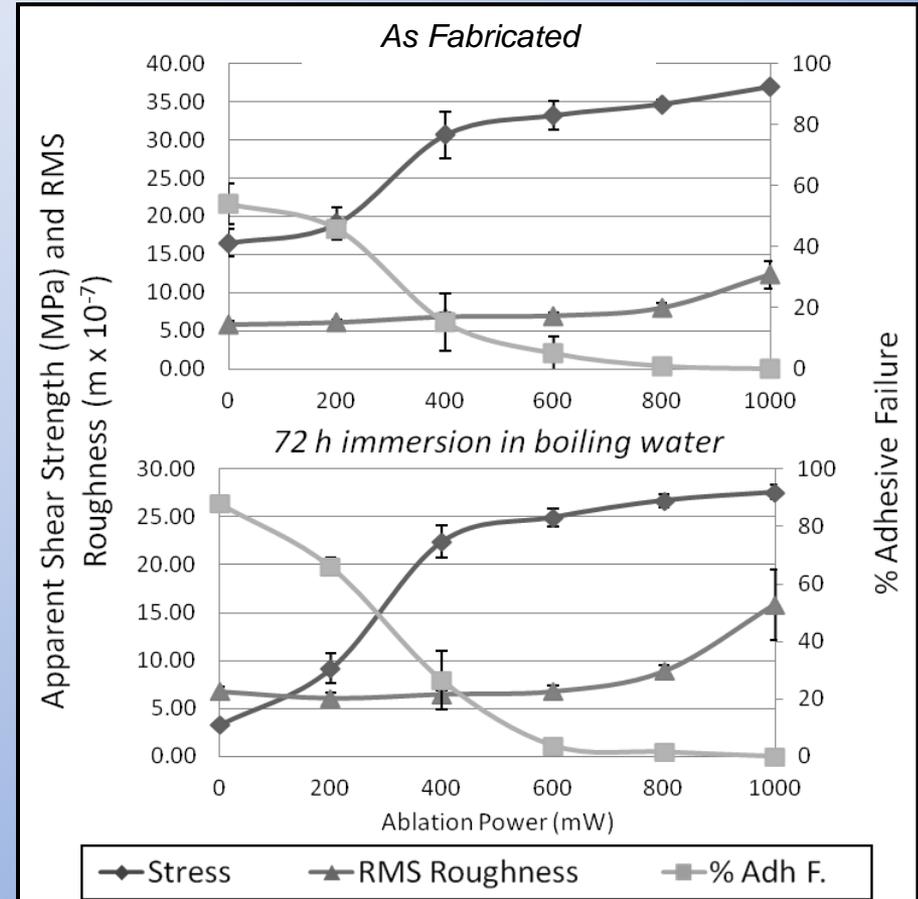
At an ablation power ≥ 600 mW

- 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



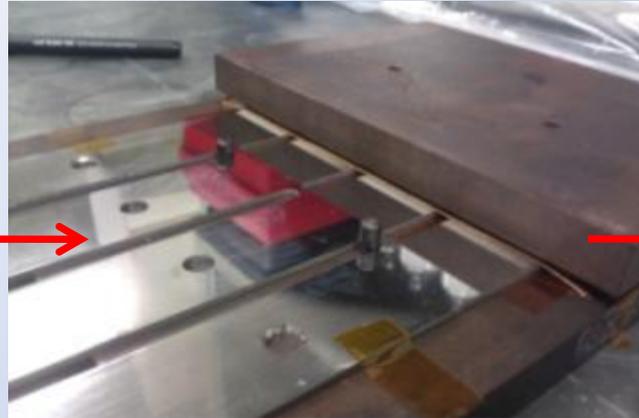
Lap Shear Preparation

Bonding in heated press

NARI
PETI-5 adhesive
tape preparation



Lay-up in bonding jig



Separated specimens



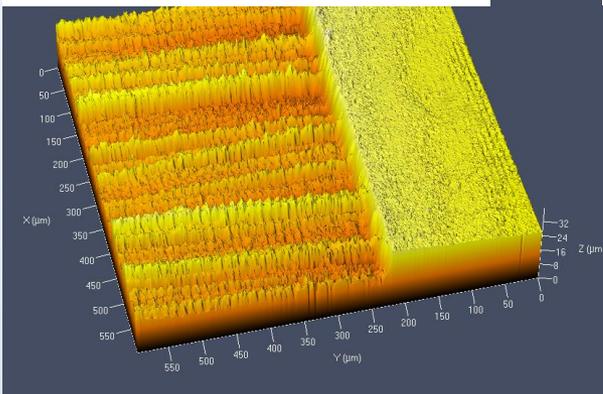


Composite Ablation & Bonding

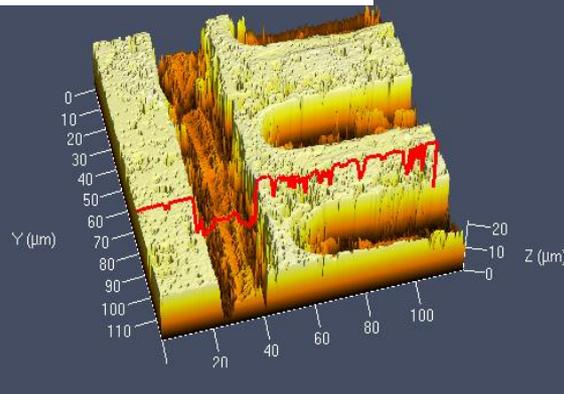
NARI

- 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)

