



Engineered Materials Workshop

Part B: Adhesion Promotion Technologies

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Technologies

Laser Ablation Patterning

Simultaneous Surface Preparation and Shock Peening by Laser

High-Pressure Soft Lithography for Patterning Composites

Tech Transfer Workshop

May 22, 2014



Discussion Outline

- Bonding background
- Laser Ablation Patterning
 - Two case studies: Carbon Fiber Reinforced Plastics (CFRP) and titanium alloy
- Laser Peening/Ablation
- High-pressure soft lithography

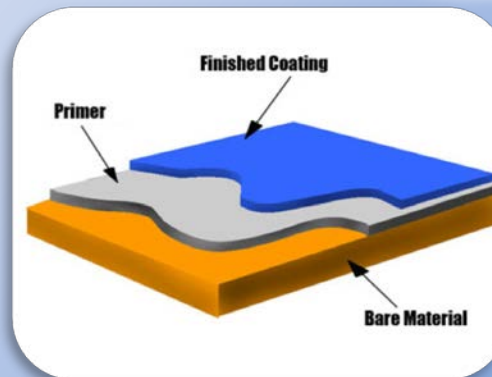


Adhesion Applications

- Structural Assembly
 - Transportation vehicles
 - Dental fixtures/Medical devices
 - Sporting goods
 - Storage vessels



- Coatings
 - Paints
 - Sol-gel





Bonds vs. Bolts

- Less weight
- Small structures
- Corrosion resistant
- Load distribution/fatigue resistant
- Aerodynamics design
- Fewer parts/No hole drilling required

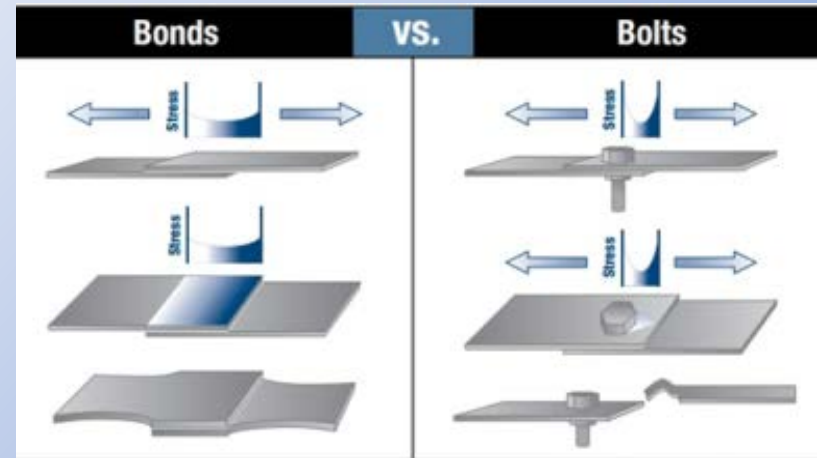


Image publicly available.



Challenges for Bonding

- Application Dependent
 - Vehicles require certification for safety
- No non-destructive assessment techniques
- Surface preparation is critical
- Sensitive to environment
- Not applicable for joints in tension (susceptible to peel failure)
- Bonds are usually permanent

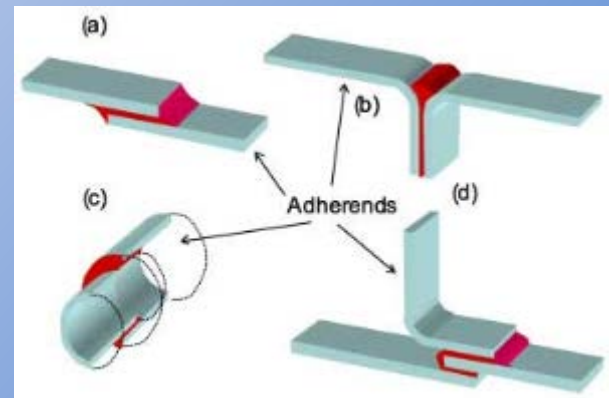
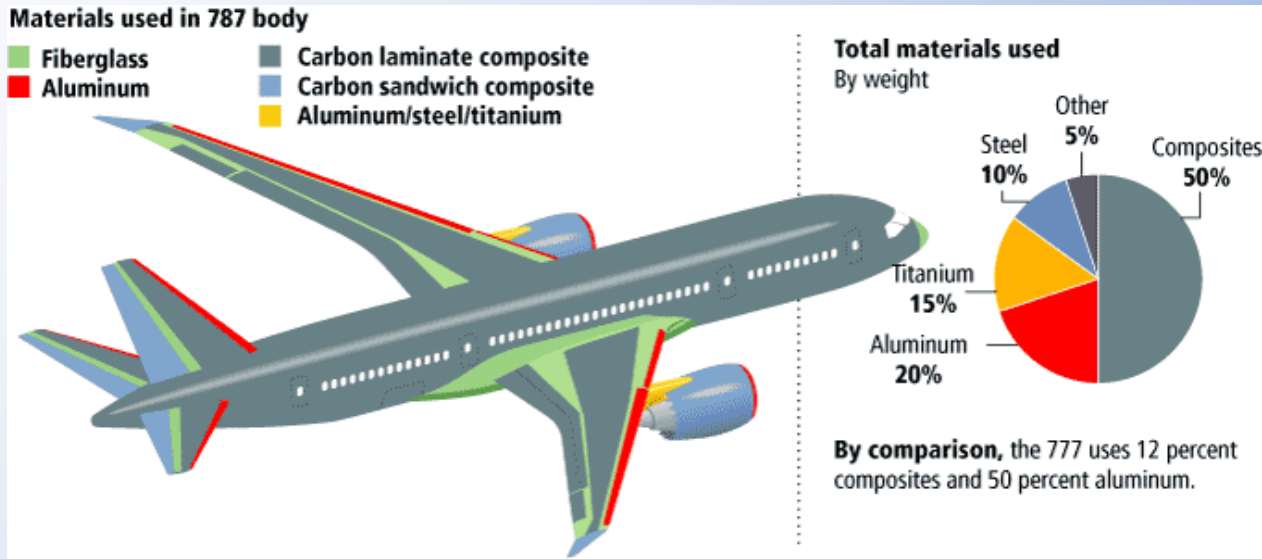


Image publicly available



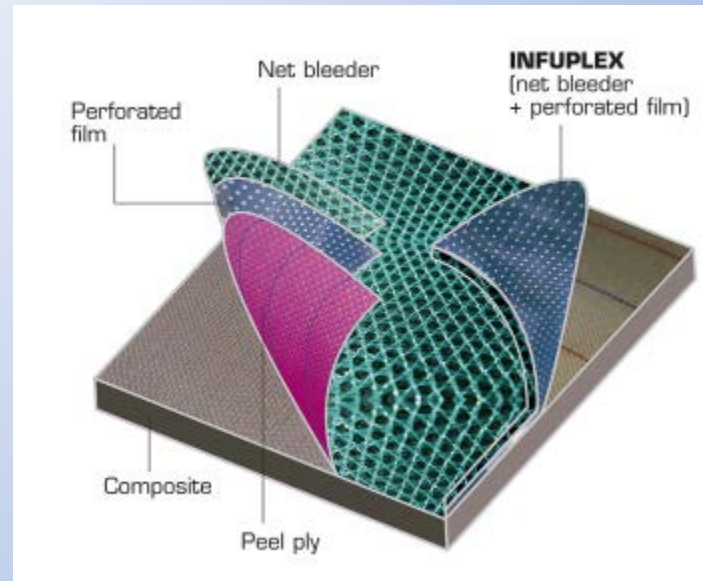
Case Study:

SURFACE PREPARATION OF CFRP



SoA CFRP Bonding

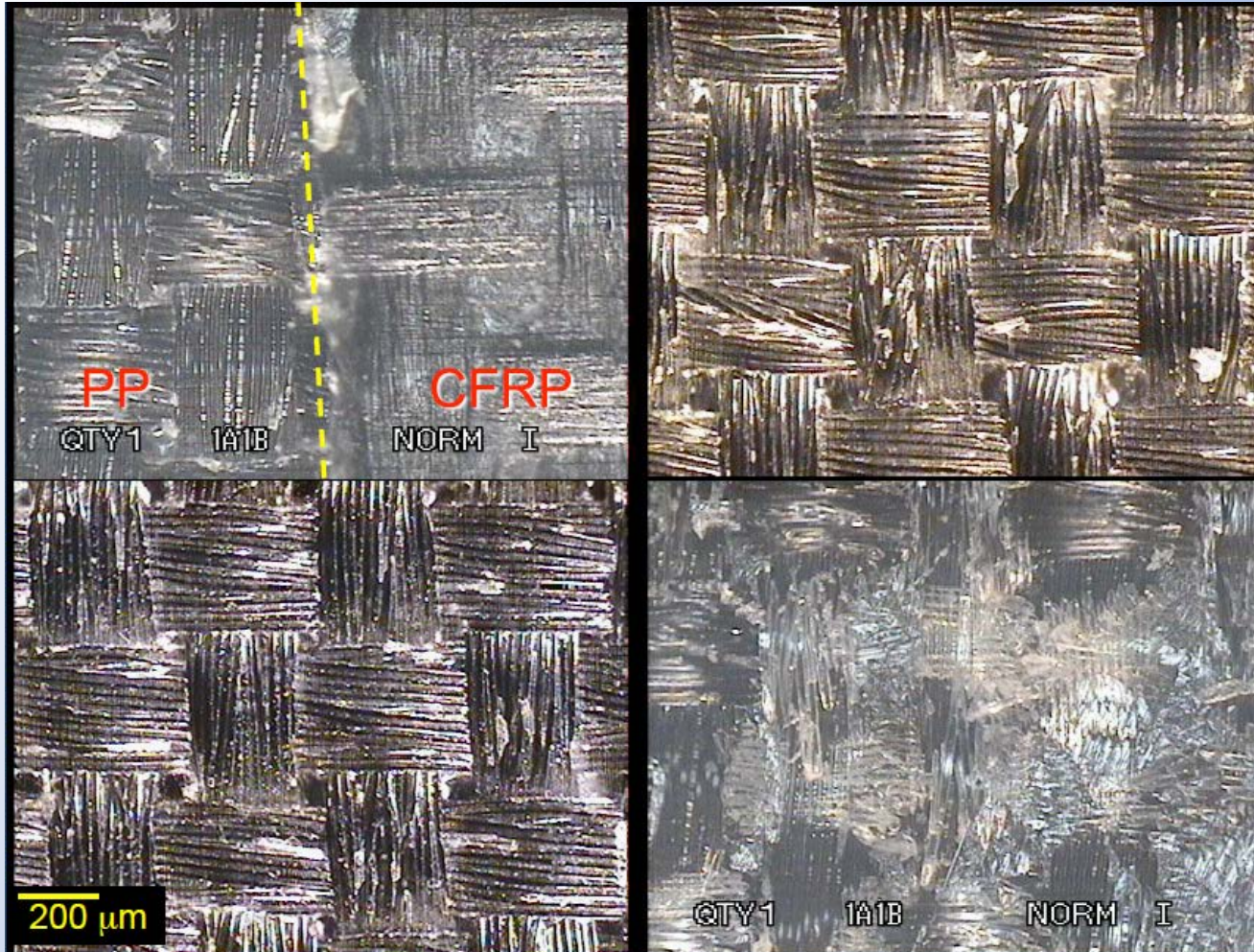
- Uses low-fidelity surface preparation
 - Peel-ply
 - Grit blast
 - Sanding



- Can leave contamination on the surface.

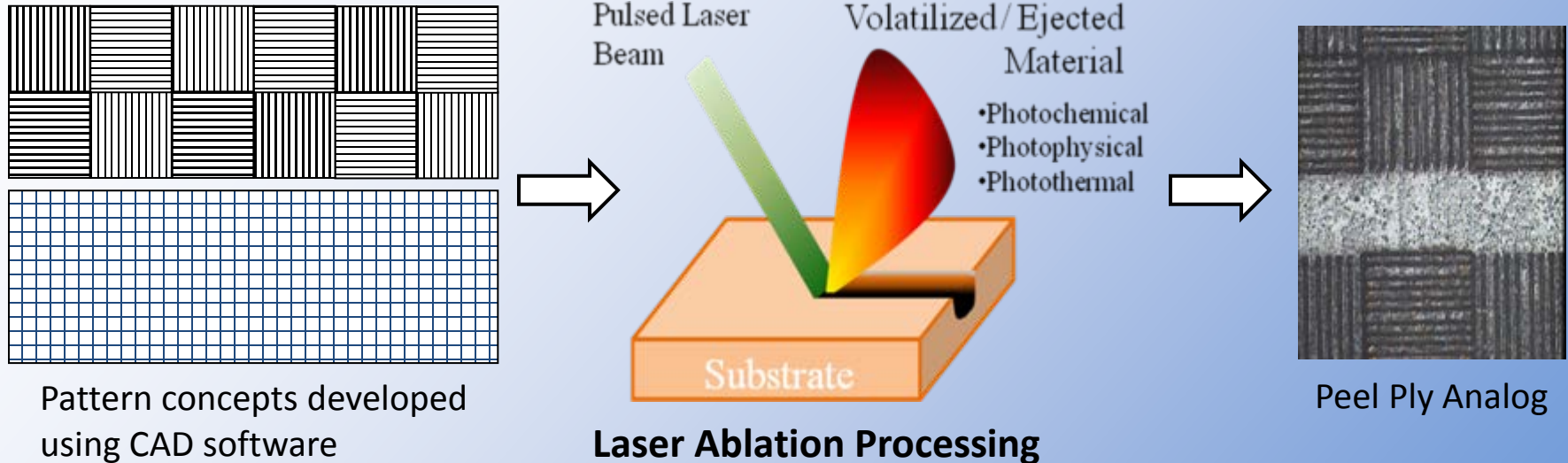


Wet Peel-ply on CFRP





Our Approach: Laser Ablation Surface Preparation

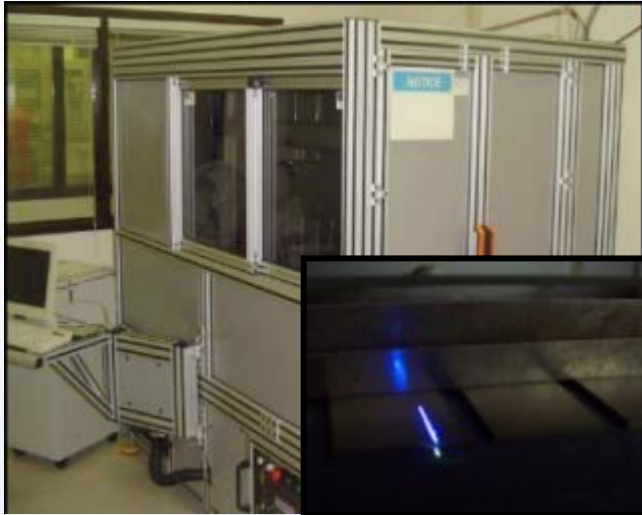


- A direct-write patterning process
- Creates surface patterns on plastics, metals, ceramics and composites on the micron scale with a high degree of precision
- Can control roughness and surface chemistry
- Rapid, reproducible, scalable and practical for production environment



Laser Ablation Tooling and Production

Lab-scale, laser pattern generator



Inset: Ablation of composite panel

System Specifications:

Laser Type – Frequency tripled Nd:YAG

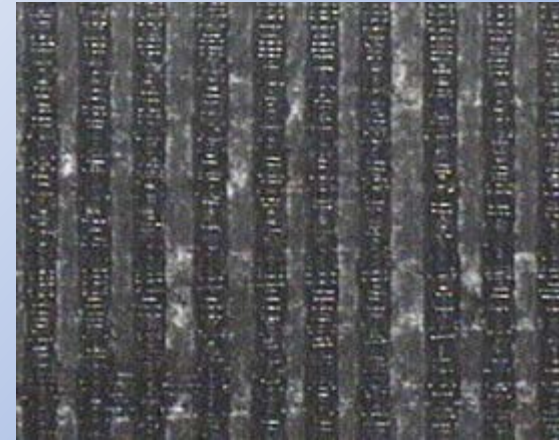
$\lambda = 355 \text{ nm}$

Nominal Power – 7 W

Frequency – 10-100 kHz

Beam Width – $\sim 25 \mu\text{m}$

Speed – Up to 127 cm/s (50 in/s)



Lines in composite panel (Optical)

Waste:

Minimal aerosols, dust collected in an air filter

Advantage
Green Manufacturing



Laser Ablation Process





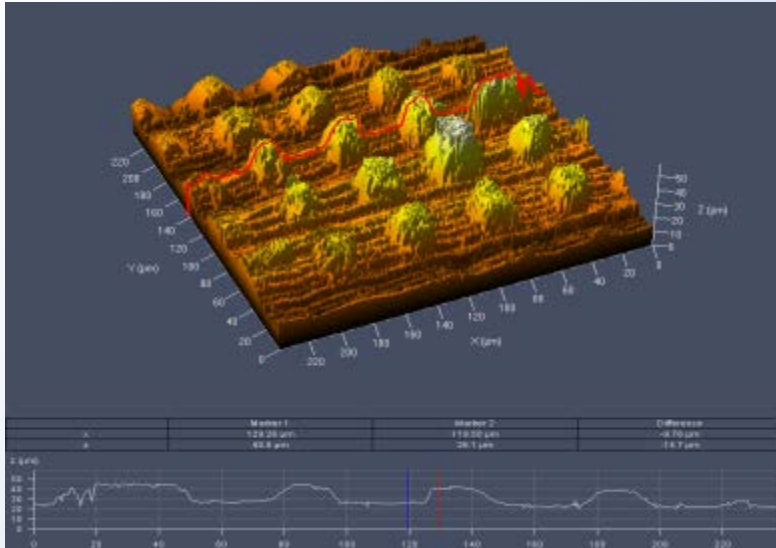
Advantage- Process Control

- Tunable/Traceable parameters
 - Power, pattern, pulse frequency, spot size, scan rate

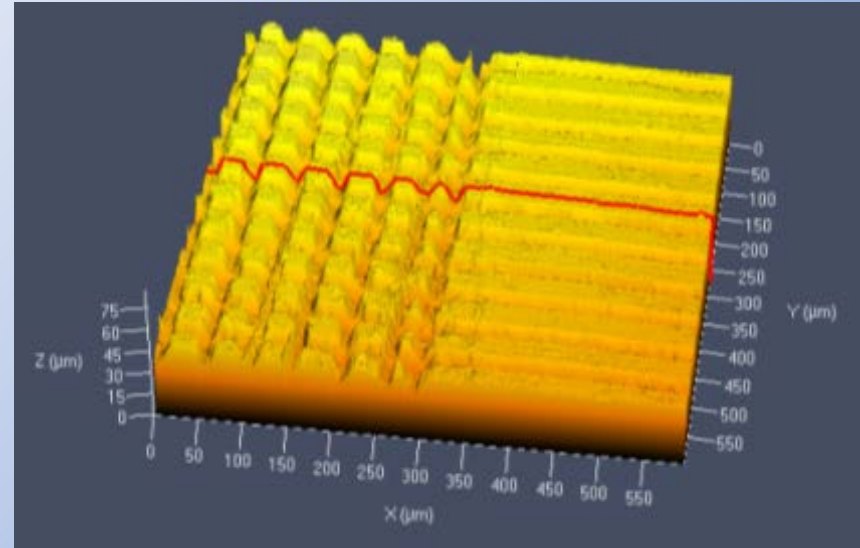




Surface Characterization



Resin Starved



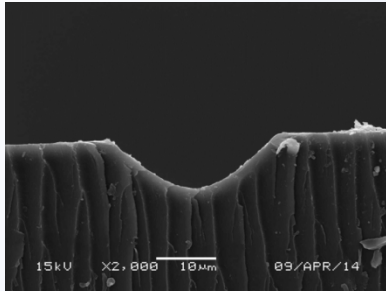
Resin Rich

- **Confocal microscope images of laser ablated composite surfaces**
- **“Pillars” are 10-12 μm in height, $\sim 25 \mu\text{m}$ wide, and $\sim 50 \mu\text{m}$ apart**
- **Resin rich and resin starved areas of the surface can effect the pattern**

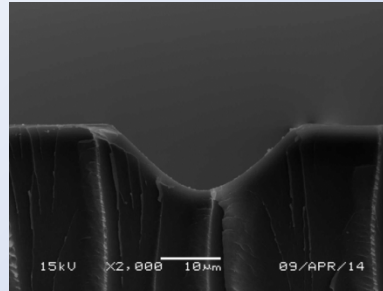


SEM Ablation Analysis

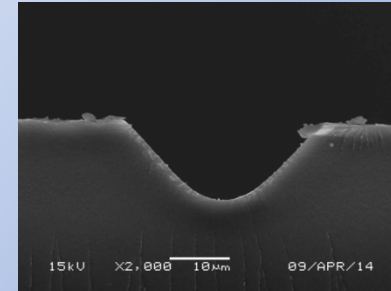
400 mW



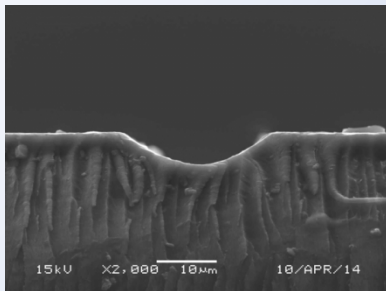
600 mW



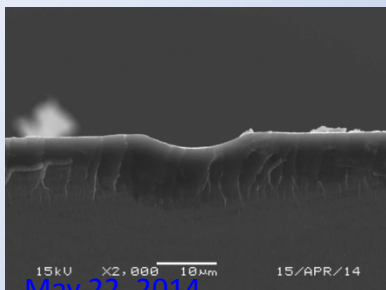
800 mW



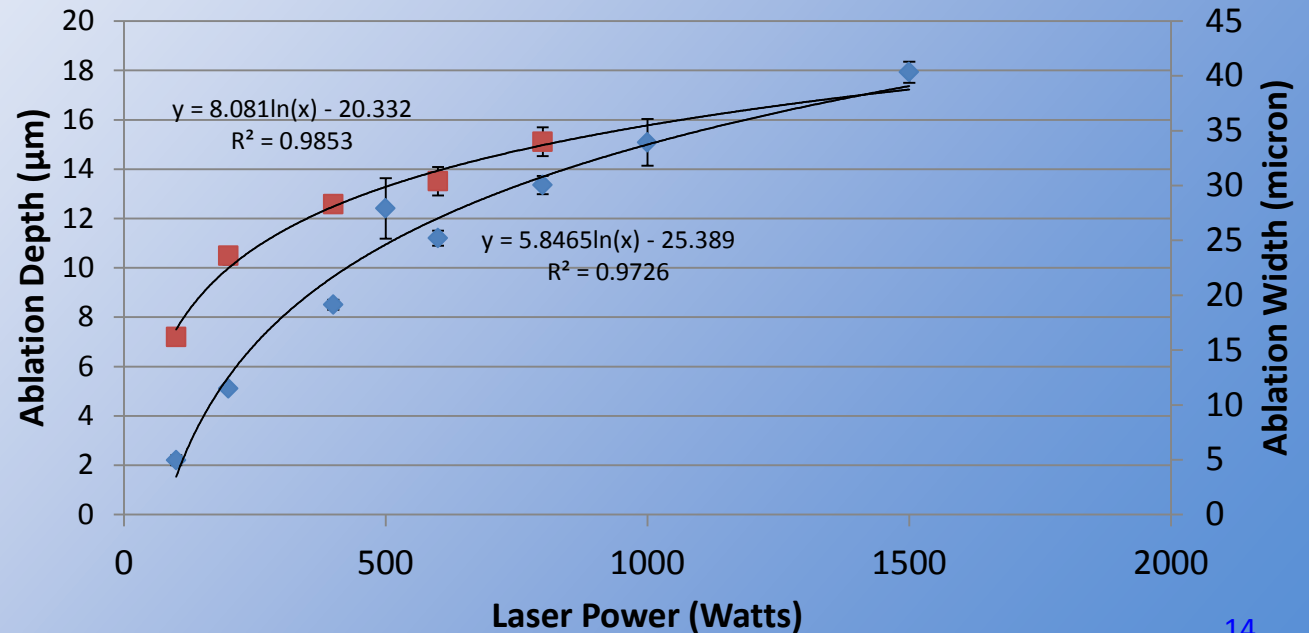
200 mW



100 mW



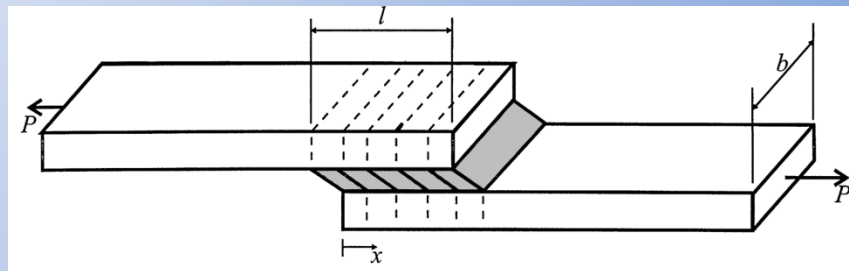
◆ Depth (micron) ■ Width (micron) — Log. (Depth (micron)) — Log. (Width (micron))





Aged Single-Lap Shear Tests

- **Mechanical testing**
 - 138 single-lap shear specimens (SLS)
 - Testing conducted at RT and 71°C (160°F)
 - Specimens aged at 71°C (160°F) and 85% relative humidity
- **Periodic testing over 3 years**
 - Controls specimens (RT and 20% RH) tested in parallel
- **Measured properties**
 - Water uptake
 - Apparent shear strength
 - Failure mode by visual inspection

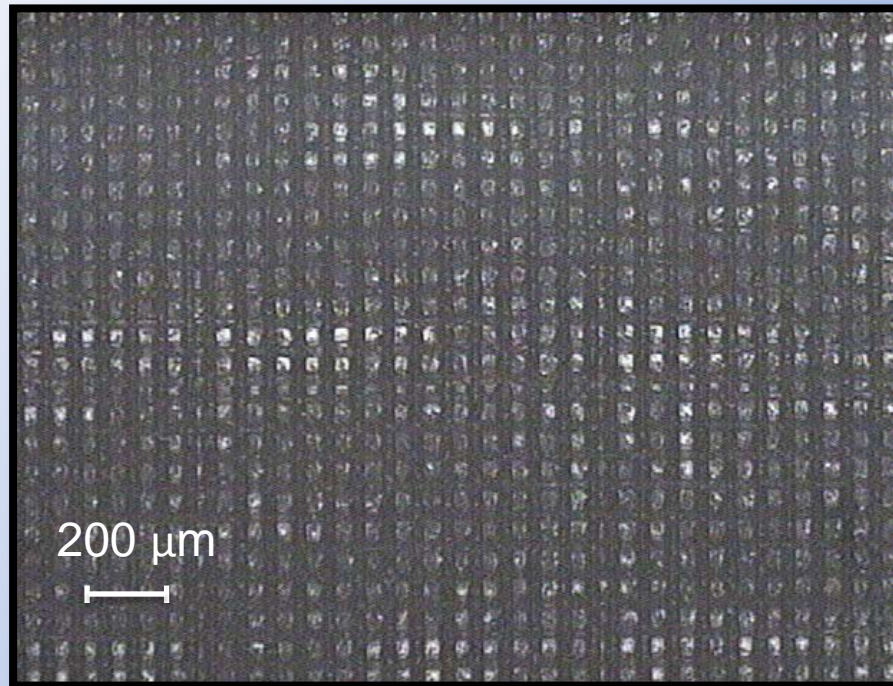




Ablation Details

- **Laser parameters**

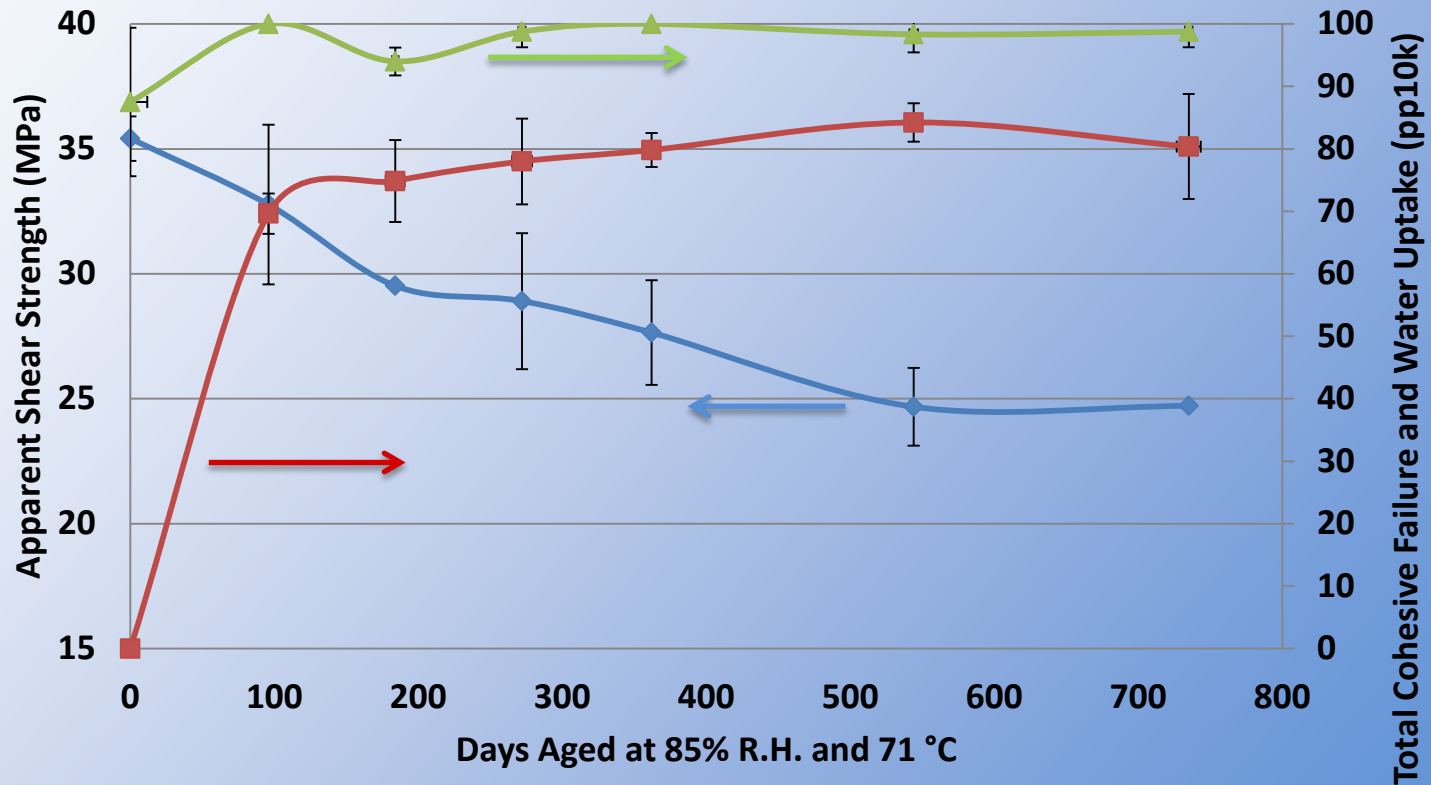
- Nd:YAG Laser (7-watt output at 355 nm)
- 1 W, 80 kHz pulse rate, 25.4 cm/sec scan rate, 25 μm beam width, 1 pass
- Crosshatch pattern with 51 μm line spacing





Aging Results for Tests at RT

- ◆ Apparent Shear Strength (MPa)
- ▲ % Total Cohesive Type Failure
- Water Uptake (pp10k)





Aging Results for Tests at RT

- Baseline data: apparent shear strength 35 Mpa, failure mode ~100% cohesion
- 730 days aged:

| | <u>Hot Humid</u> | <u>RT Dry</u> |
|------------------------------------|------------------|---------------|
| – Water uptake | 0.8% | ~0 |
| – Apparent shear strength | 25 ±0.1 MPa | 36.6 ±2MPa |
| – Loss in apparent shear strength: | 29% | None |
- Mostly cohesion type failure modes
- Comparison with SoA specimens (peel-ply): at 82°C (180°F) and 85% RH, after 720 days aging
 - Apparent shear strength 27.0 ± 6.3 MPa (29% reduction)
 - Predominantly cohesion failure

G. Knight, T.H. Hou, M.A. Belcher, F.L. Palmieri, C.J. Wohl and J.W. Connell, "Hygrothermal Aging of Composite Single Lap Shear Specimens Comprised of AF-555M Adhesive and T800H/3900-2", International Journal of Adhesion and Adhesives, (39), 1-7, Dec 2012.



CFRP Conclusions

- Laser ablation surface preparation
 - Reduces risk of contamination and debris (no peel-ply)
- Similar durability and failure modes for SoA and laser processed surfaces
 - Retention of apparent shear strength ~30%
 - Retention of cohesion type failure modes ~100%
- It was found that measuring laser pulse energy at the substrate provided an effective means of quality control for the preparation of highly uniform faying surfaces
- Laser surface preparation is a high-precision, reproducible surface treatment process that is amenable to scale-up and automation

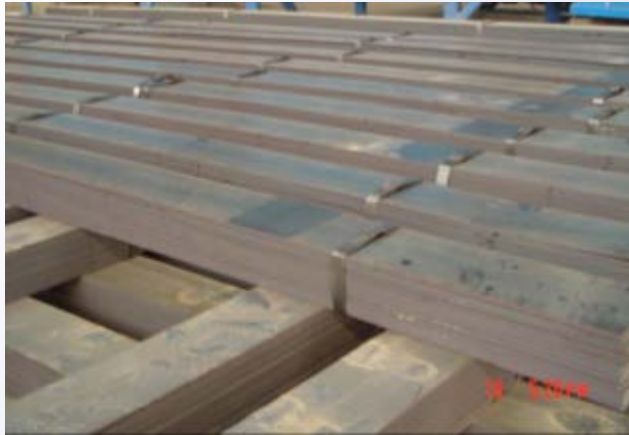


Case Study:

SURFACE PREPARATION OF TITANIUM



SoA Surface Preparation



Chemical Immersion

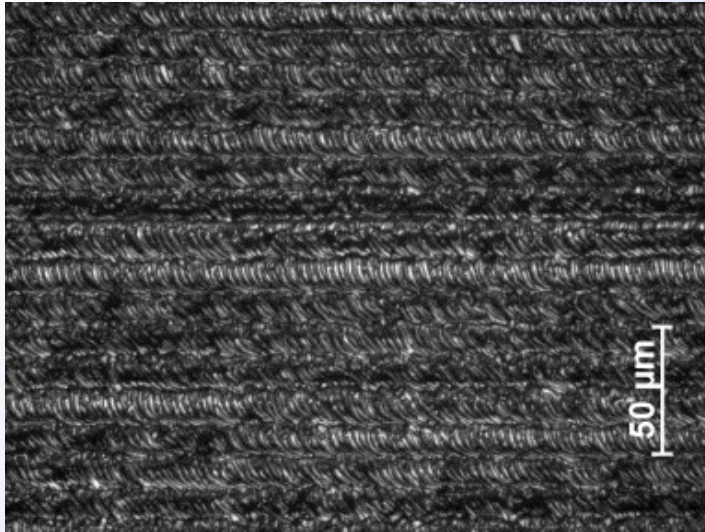


- Processes are polluting, dangerous, and difficult to automate & monitor
 - Acid etching: mill scale/oxide removal (HF)
 - Hot alkaline conditioning (caustics)
 - Grit blast

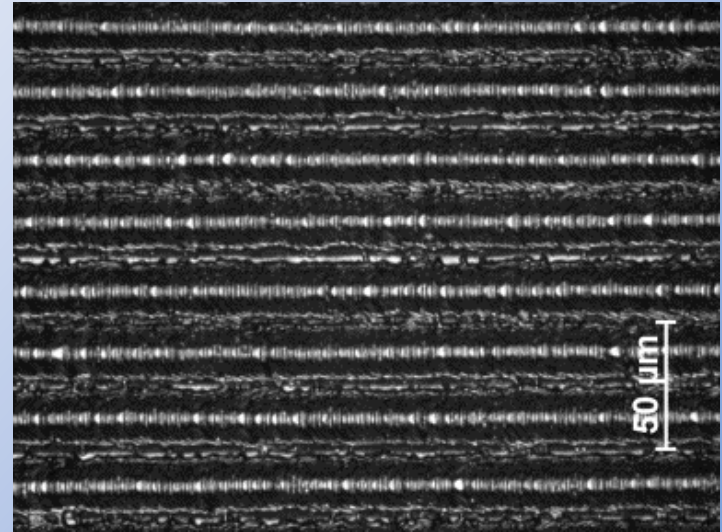


Laser Ablation Patterns

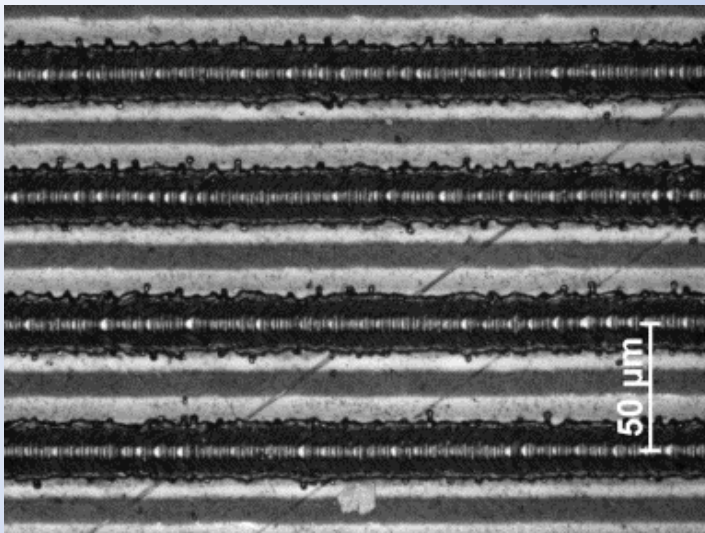
D = 200%



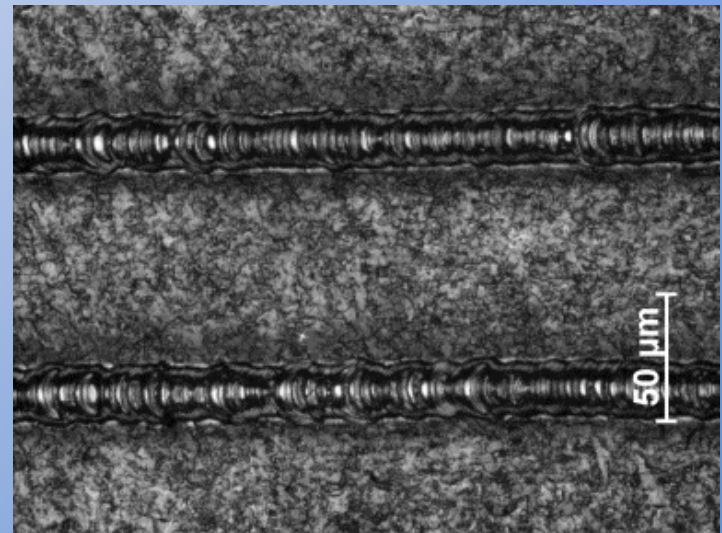
D = 100%



D = 50%



D = 25%





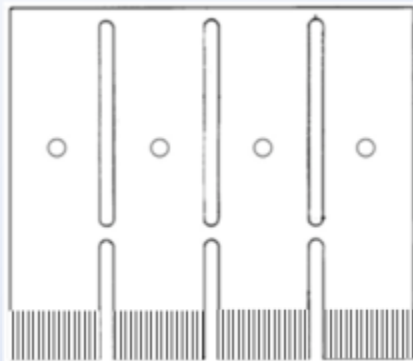
Titanium SLS Testing

Single-lap Shear (SLS) Specimens

Modification of ASTM D1002-10

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

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



Bonding Method

Heated Press

Open air

1hr @ 700°F (371°C)

Active cooling

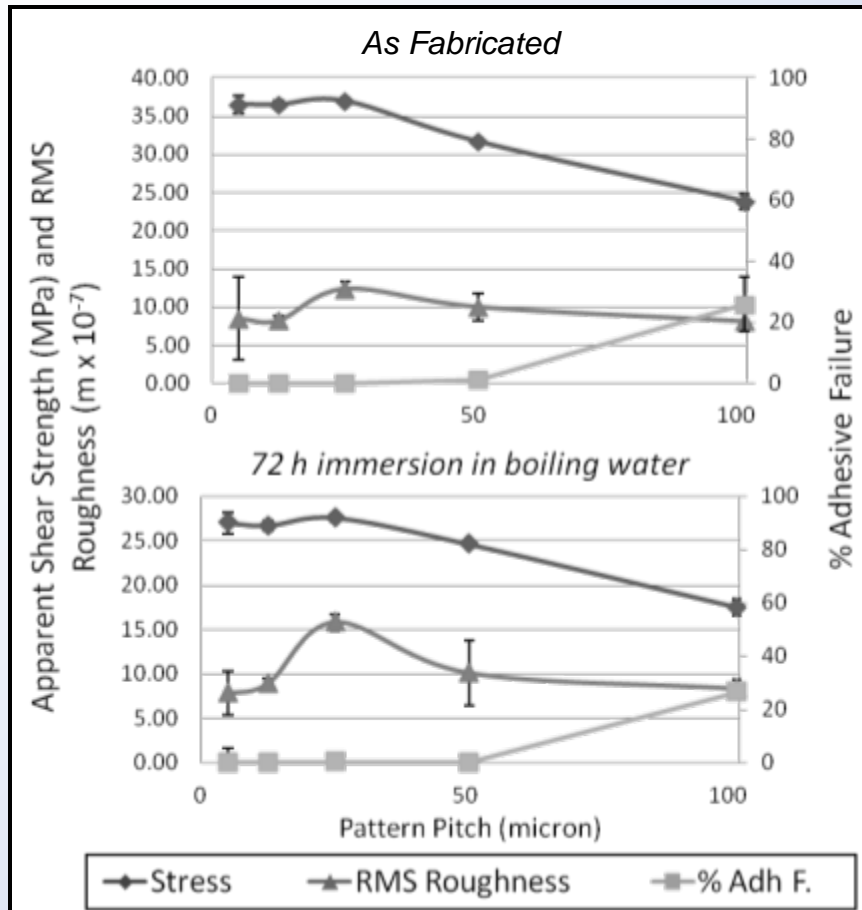


Measured

Apparent shear strength, bondline thickness, and failure mode (digital image analysis)



Effect of Pitch on Lap Shear



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= Increase Apparent Shear Strength
Decrease Adhesive Failure



Effect of Power on Lap Shear

Pitch = 50 μm

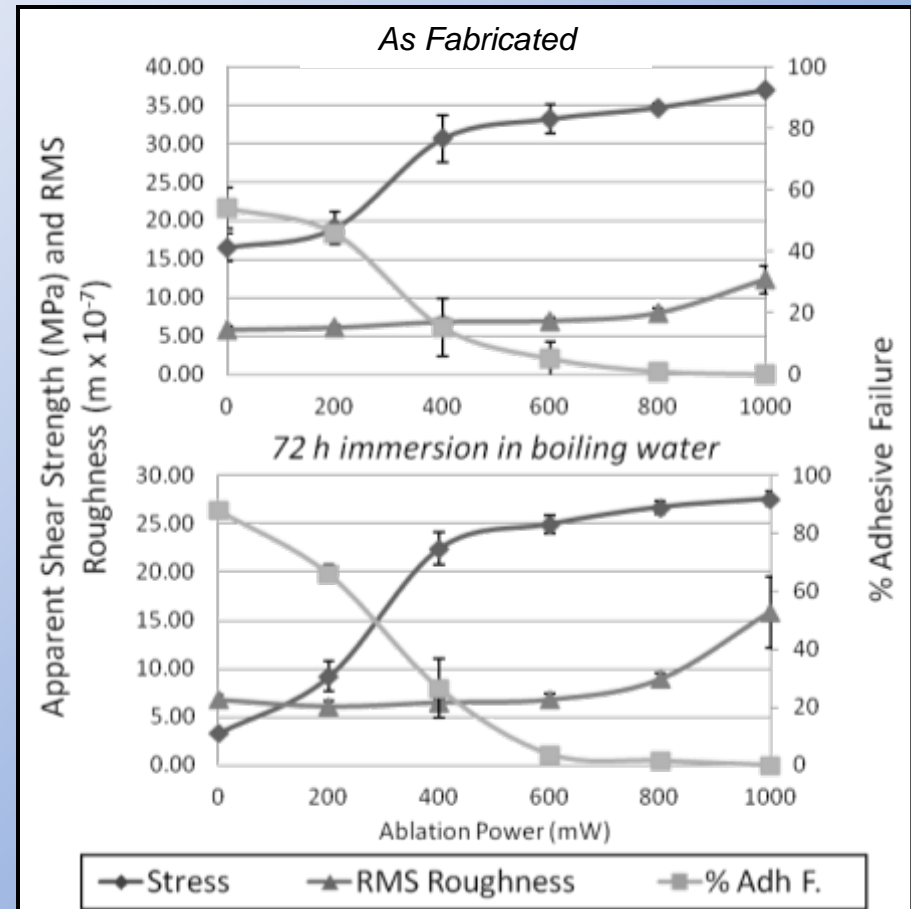
At an ablation power ≥ 600 mW

- 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 $\sim 25\%$ loss in properties
- Does not affect failure mode significantly

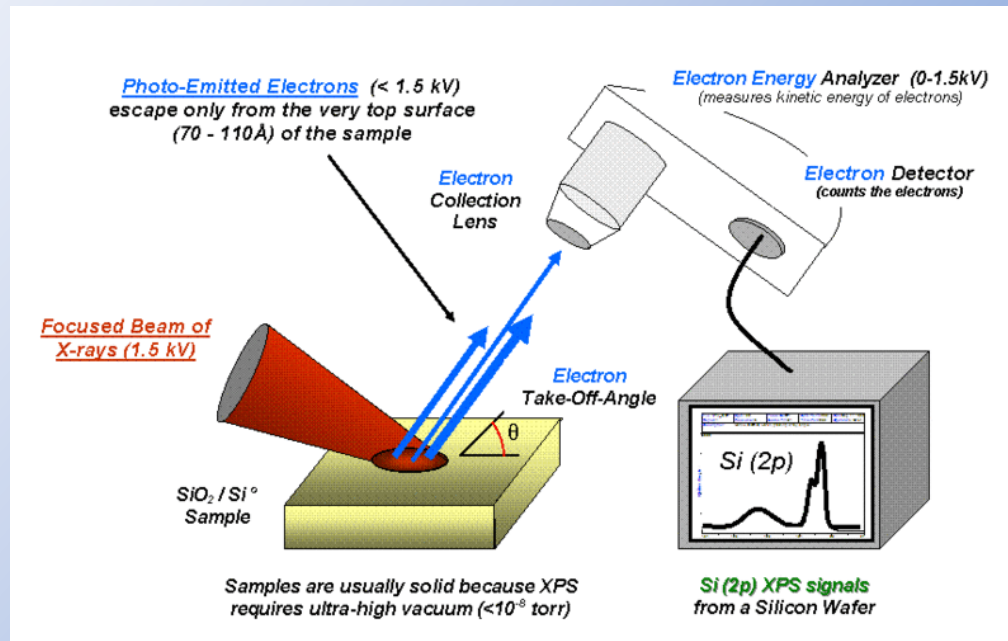


Higher Power = Apparent Shear Strength Increases
Adhesive Failure Decreases



X-Ray Photoelectron Spectroscopy (XPS)

- Surface chemical species
- Ablation power varied (0 – 1 W)
- X-rays eject electrons from sample
 - Electron energy indicates chemical bonds
- Depth of interrogation < 2 nm

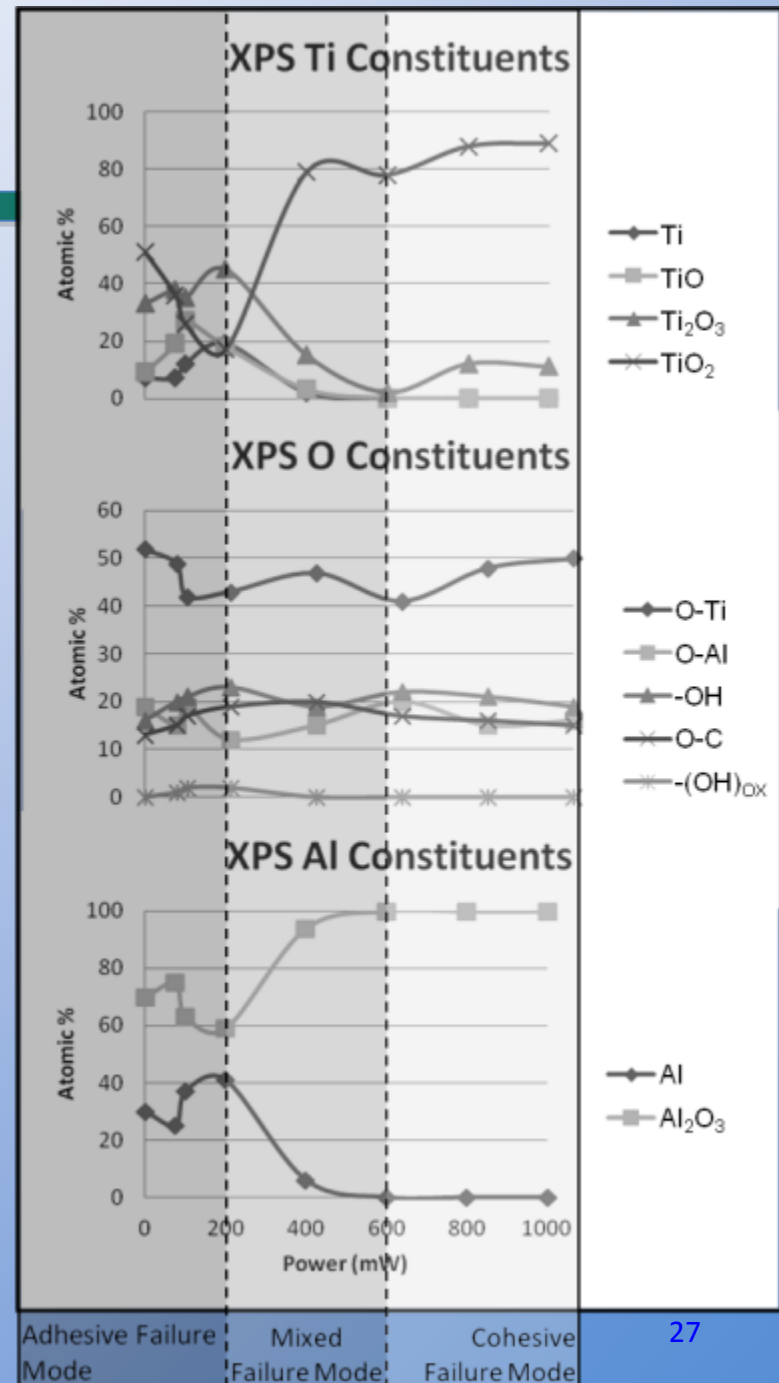




XPS Results

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





Wedge Test Experiments

- **Systematic replacement of SoA processes with laser ablation surface preparation**
 - SoA processes
 - Nitric acid/hydrofluoric acid “*deoxidation*”
 - Hot alkaline conditioning “*HAC*”
 - Sol-gel coating “*Boegel*”
 - Bond primer (not removed)
 - Control specimens
 - No laser treatment, full SoA process
- Initiate Crack
- Age in hot/humid environment
- 250° F cure adhesive





Ti Wedge Test Matrix

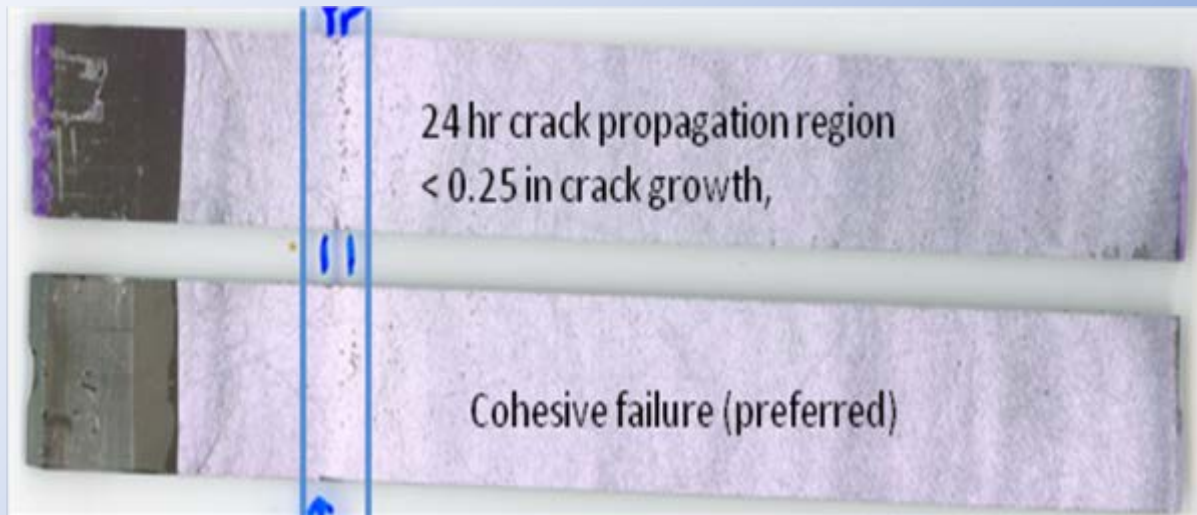
| Test Number | Nitric/HF preclean | Laser Prep | SoA Processes | | | Bond Primer |
|-------------|--------------------|------------|---------------|-----|--------|-------------|
| | | | Deoxidation | HAC | Boegel | |
| 1 | | A | | | | |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | | | | | | |
| 5 | | B | | | | |
| 6 | | | | | | |
| 7 | | | | | | |
| 8 | | | | | | |
| 9 | | C | | | | |
| 10 | | | | | | |
| 11 | | D | | | | |
| 12 | | | | | | |
| 13 | | E | | | | |
| 14 | | | | | | |
| Control | | none | | | | |

- Systematic removal of SoA processes
 - Deoxidation, Hot Alkaline Conditioning (HAC) and BoeGel EP-II
- Replace tankline process with laser ablation dry process



Wedge Test Inspection

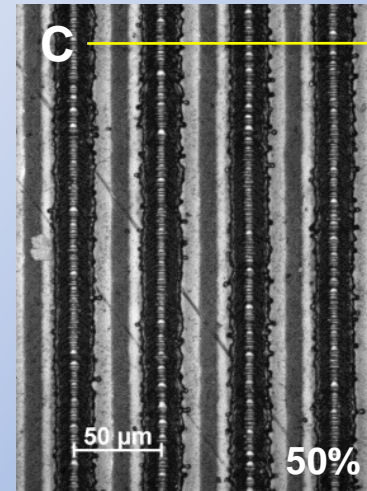
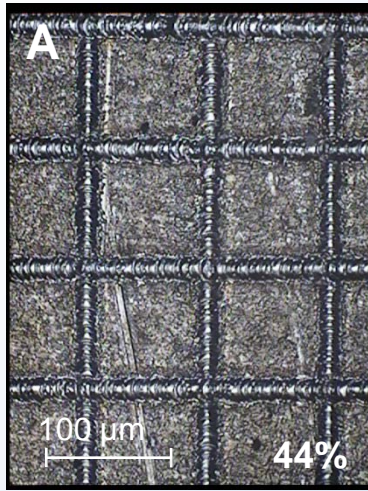
- Crack propagation during hygrothermal aging
 - Less than 0.25" crack growth during initial 24 h.
- Failure mode predominantly cohesion failure
 - Technique developed for near quantitative measurement of failure mode



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



Laser Ablation Patterns from Wedge Test Matrix



Laser pattern designation from test matrix

Duty cycle = % surface area processed by laser





Wedge Test Experiments

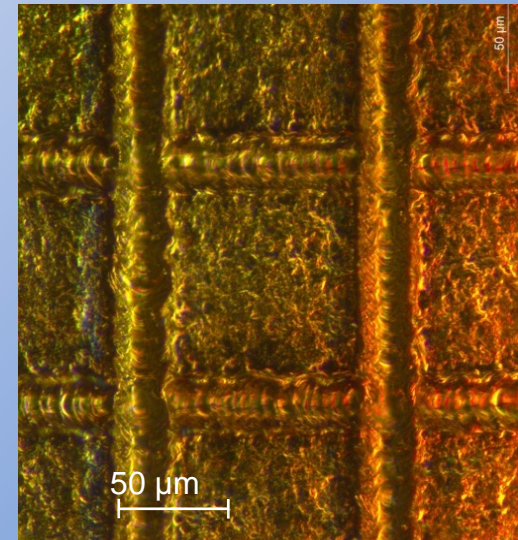
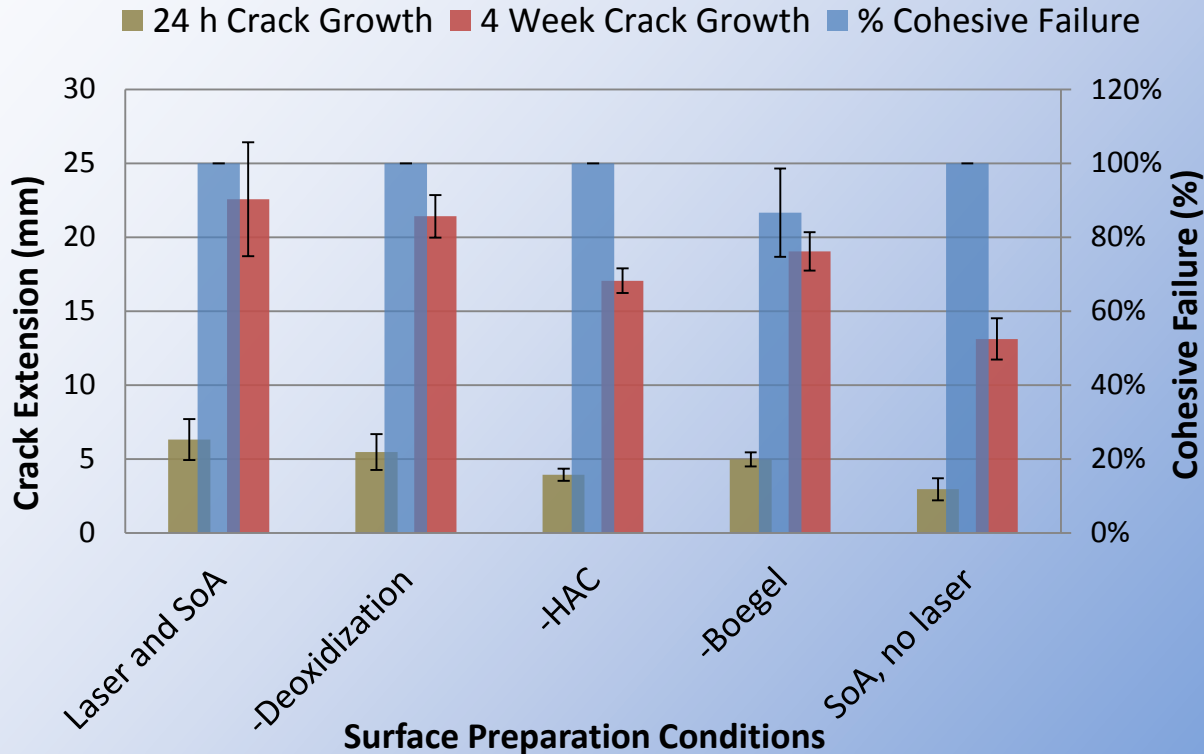
- ASTM D3762
- Surface preparation
- Bonding
- Initiate crack
 - Wait 1 h
- Age in hot/humid environment
 - 60° C (140° F), >98% RH
 - Mark crack tip over 4 weeks
- Open specimens
 - Inspect failure mode
 - Measure crack extension





Wedge Test Results

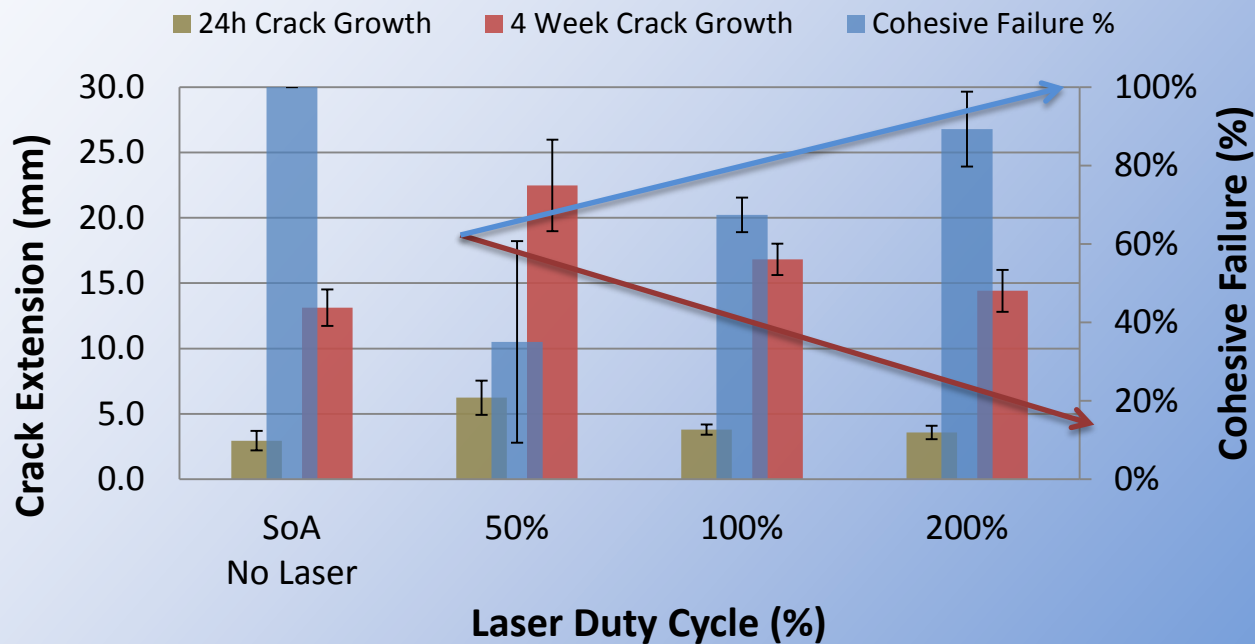
- Crosshatch pattern on 100 μm (4 mil) pitch
 - 44% duty cycle





Duty Cycle Effects

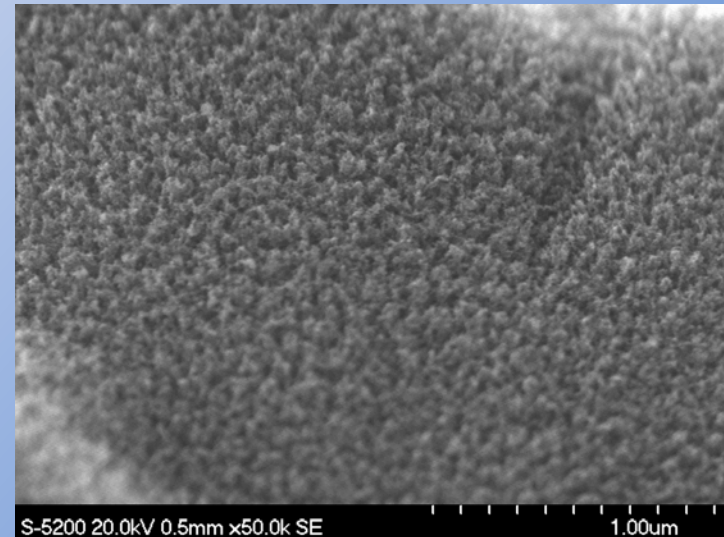
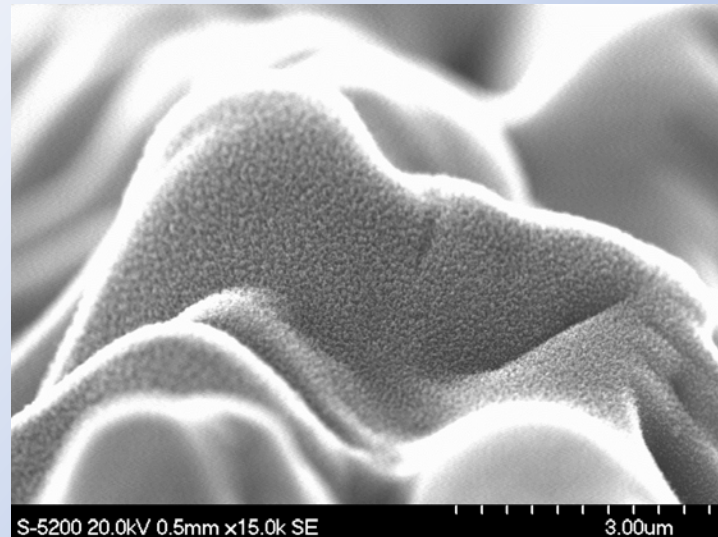
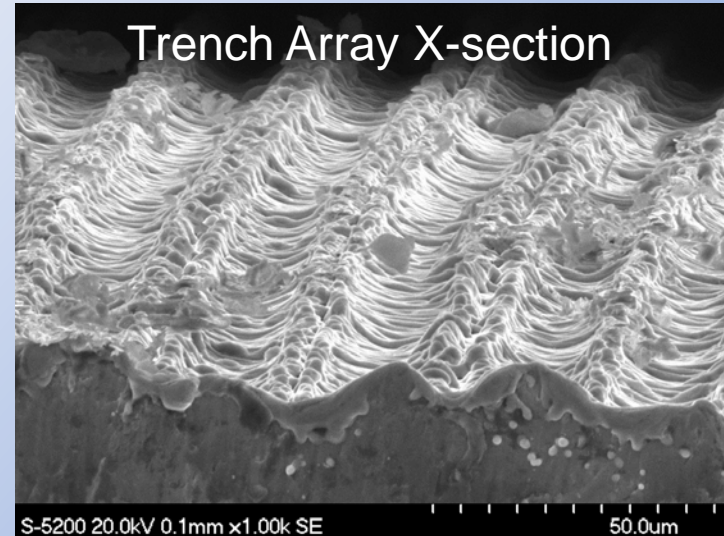
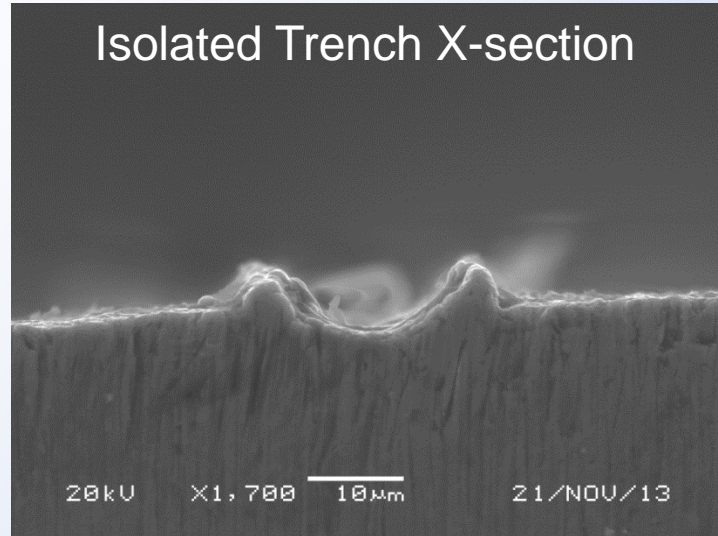
Removed deoxidation, HAC, and BoeGel
Retained primer



- Multiple passes improves performance



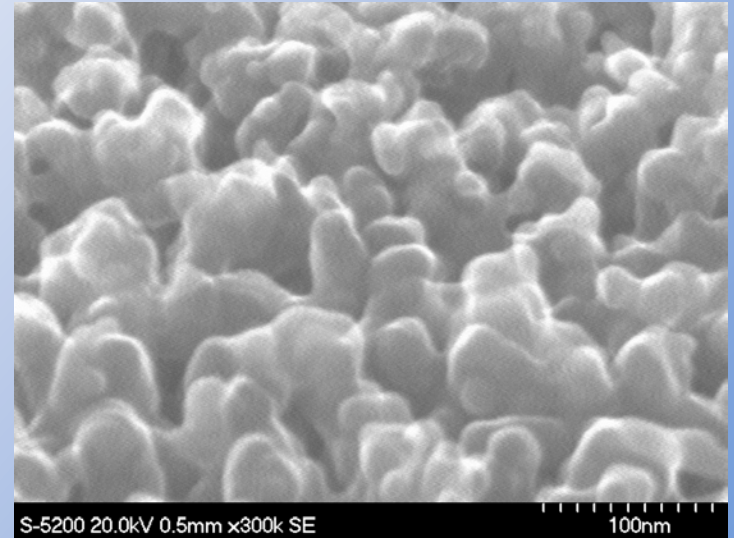
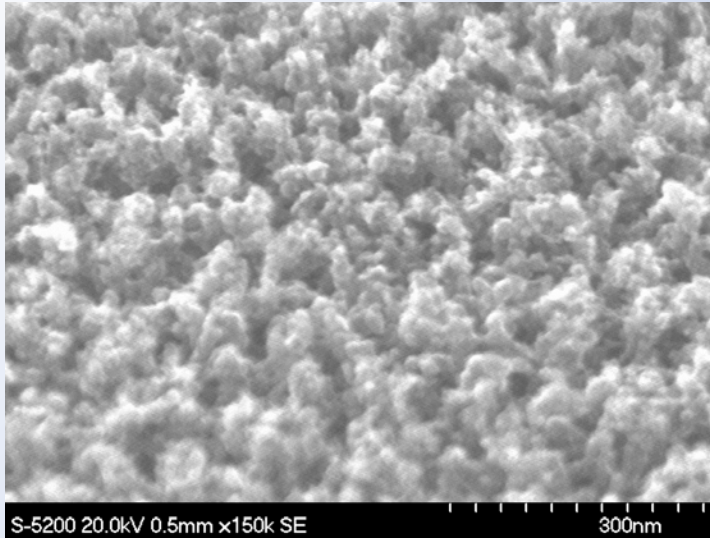
SEM Microscopy



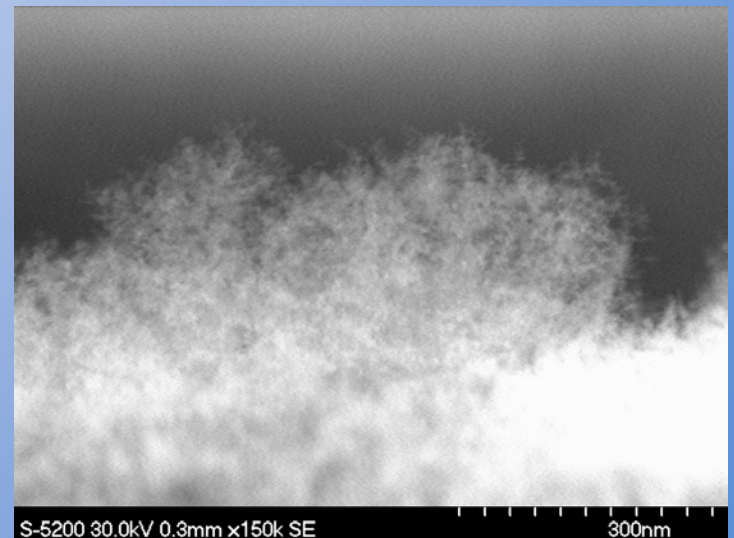
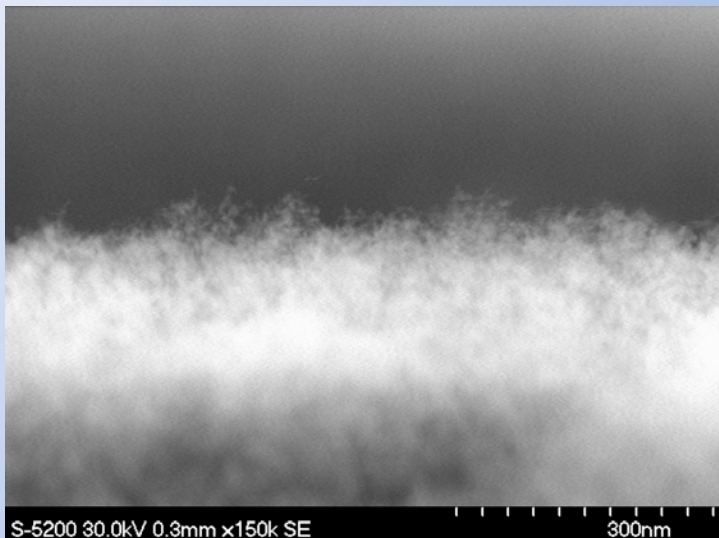


Surface Nanostructures

1x ablation

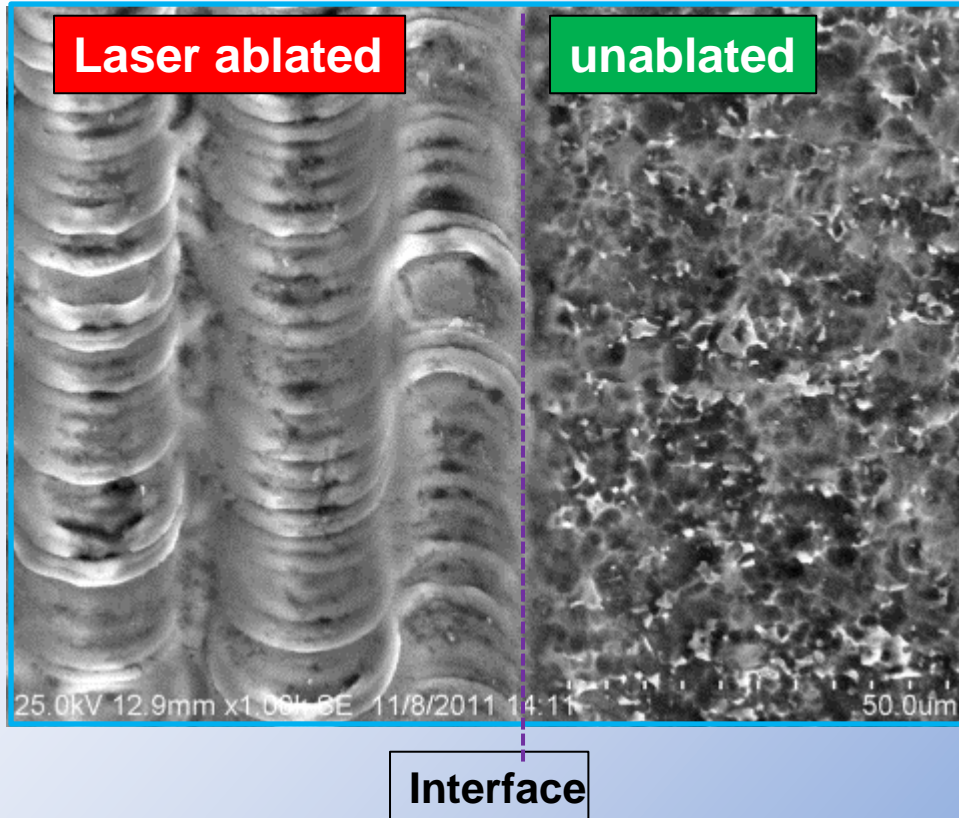


2x ablation





Concern over α -case Formation



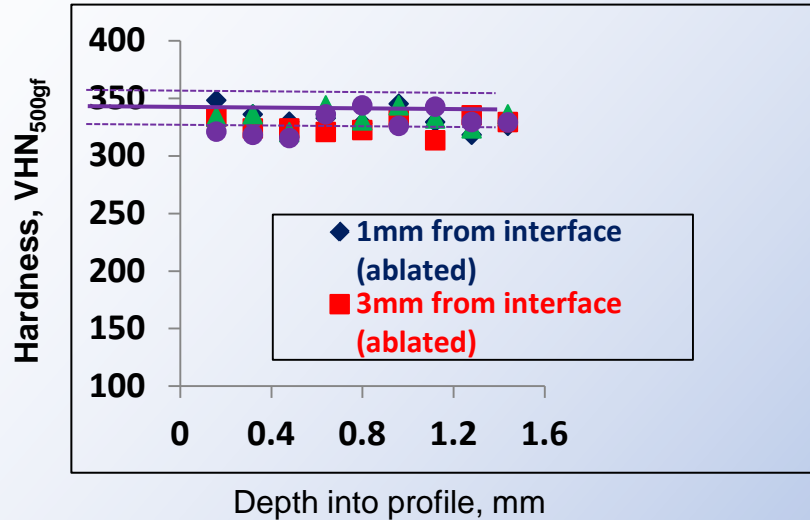
What is alpha-case?

- Alpha-*phase* rich surface layer
- Formed during heat treatment
- Surface embrittlement
- Increased hardness

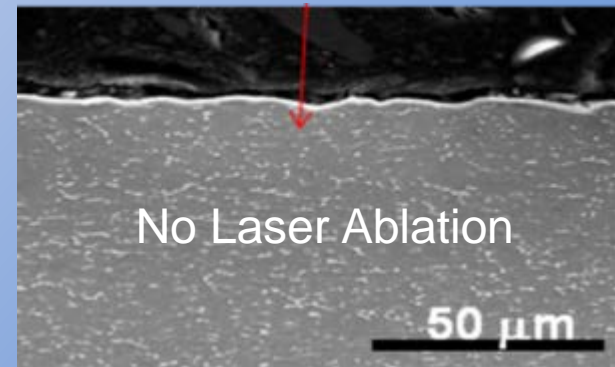
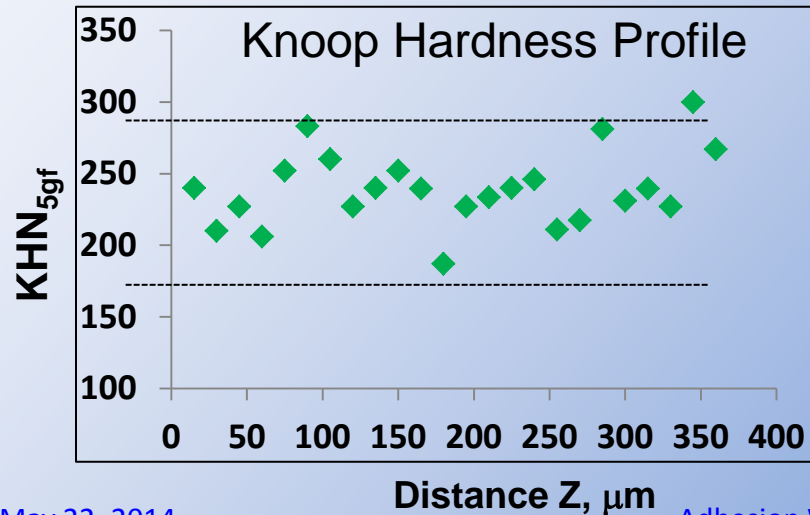
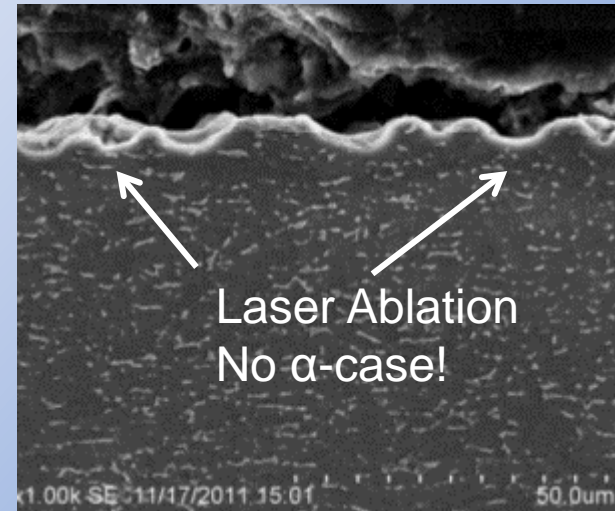


Microhardness Profile and SEM Metallographic X-Section

Vickers Hardness Profile

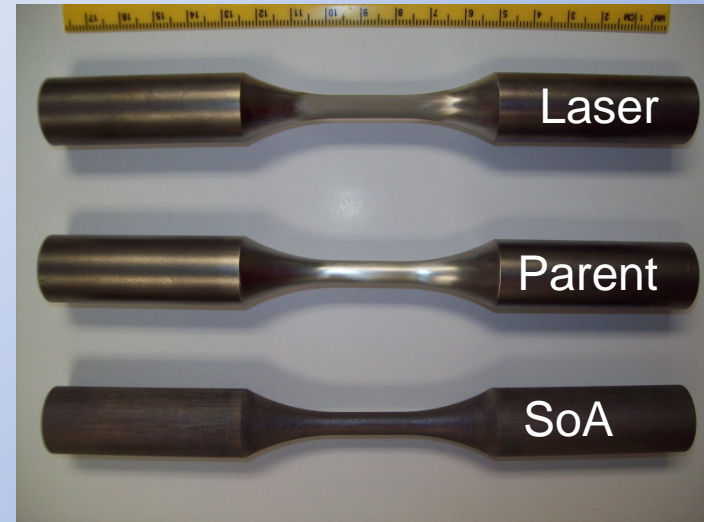
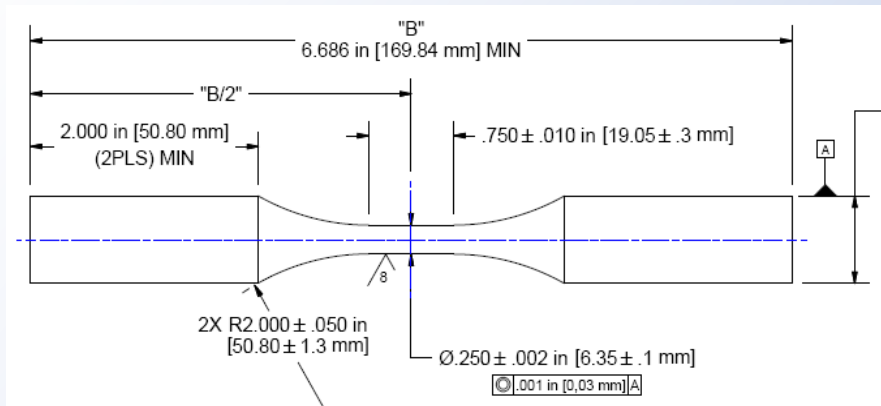


Metallographic x-sections





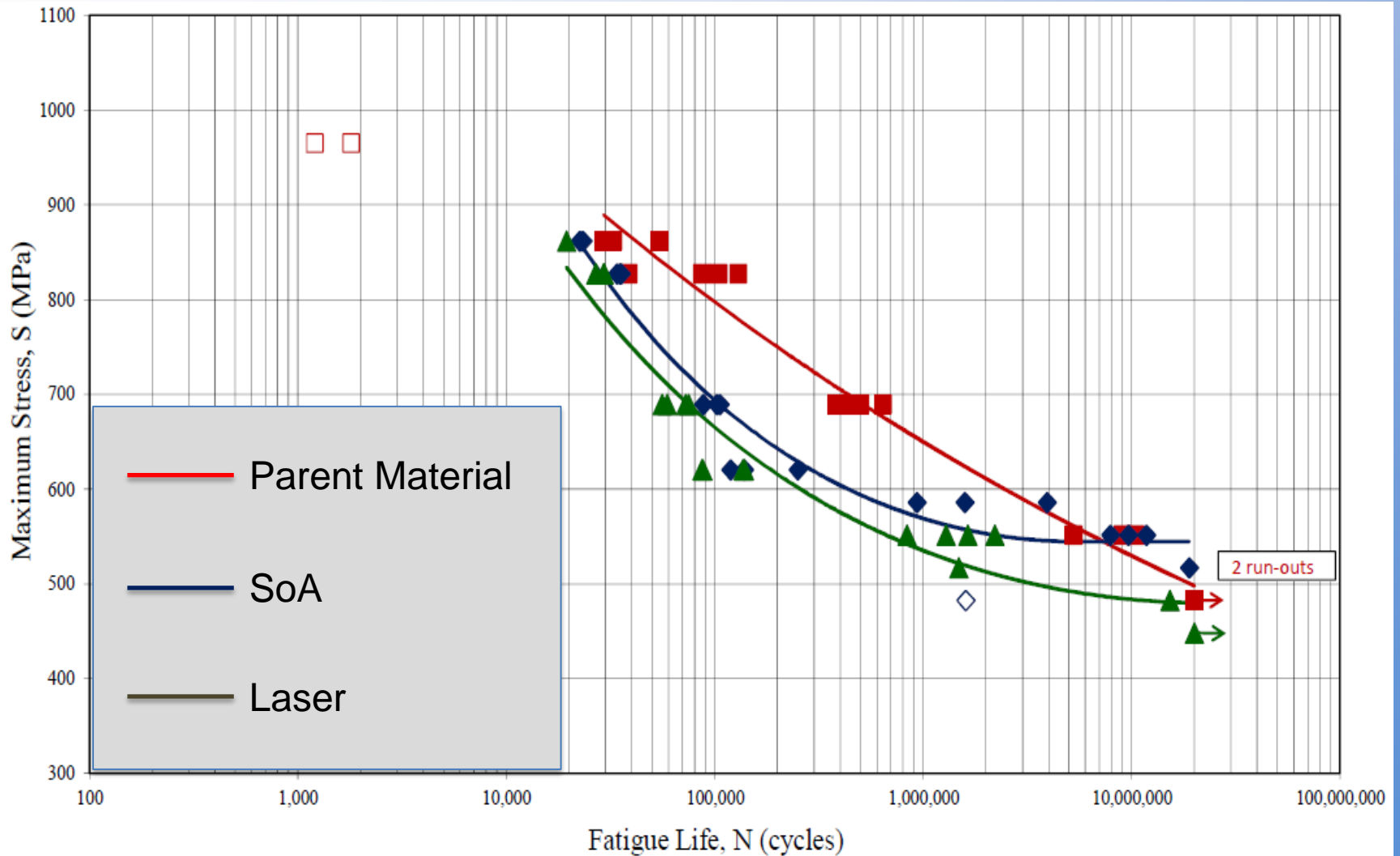
Fatigue Test Details



- ASTM E466-07: Force Controlled Constant Amplitude Axial Fatigue Tests of Metallic Materials
- Fatigue test @ 30 Hz cyclic loading
 - Tests: parent material, SoA process, and laser ablation surface preparation process
 - Load range: 700 – 1000 MPa, R=0.06
 - Run-out: 20 million cycles



Fatigue Life Behavior





Titanium Conclusions

- SLS and wedge tests indicate that laser ablation can replace chemical deoxidation and hot alkaline conditioner processes
- XPS indicates TiO_2 and Al_2O_3 are present on surface for best bond performance
- No alpha-case is formed during ablation and fatigue tests show similar lifetimes for SoA and laser treated surfaces



Laser Shock Peening

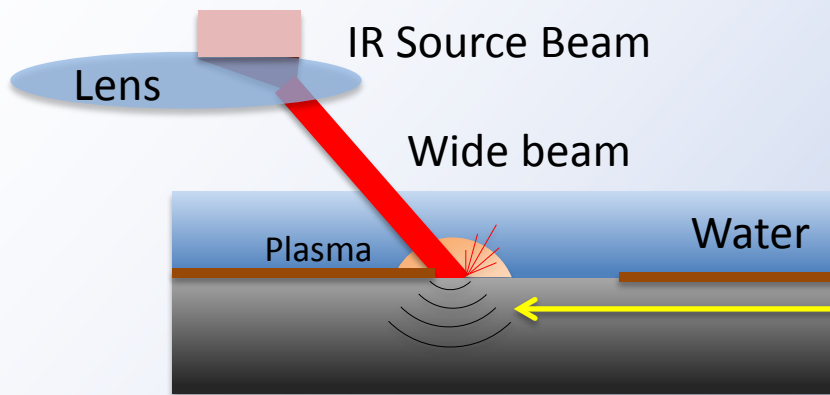
- Increases fatigue life of metals
 - Surface compressive stresses
 - Prevents surface crack initiation & propagation
 - Used commercially on high-fatigue parts
 - Turbine blades
- Ablation is avoided
 - Ablative coating (paint)
 - Couplant (water)



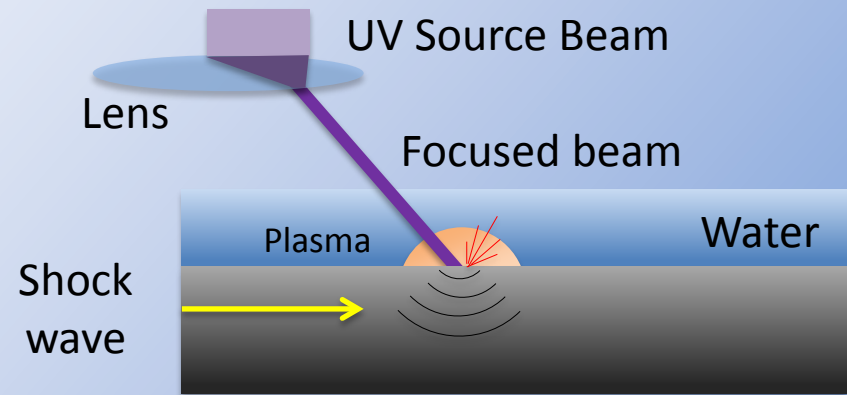
Image publicly available on web



Laser Ablation/Peening



Laser peening process

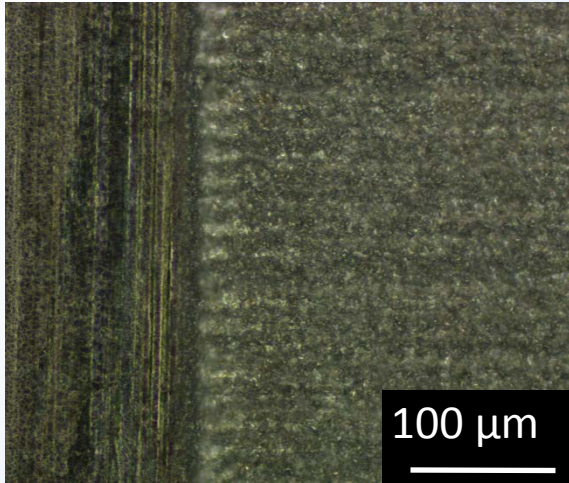


Laser ablation/peening process

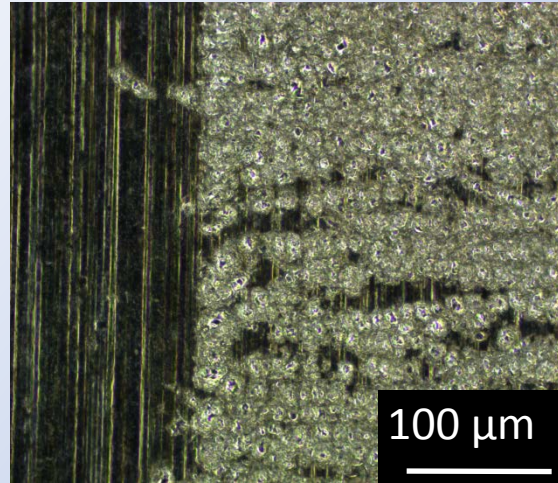
- Ablative layer removed
- Beam energy shared by both processes
- Peening reduces ablation
 - Multiple passes used to create sufficient ablation



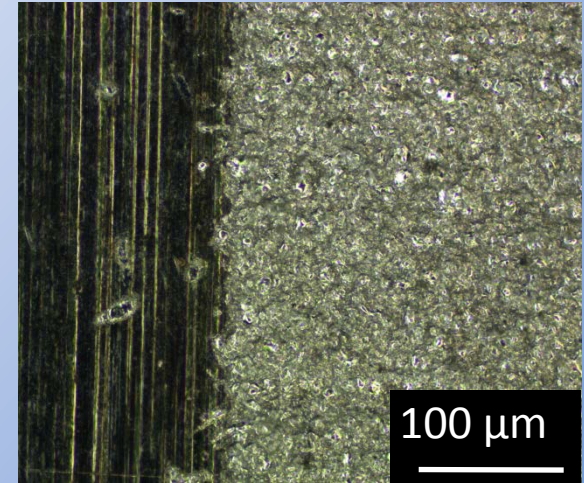
Preliminary Results on Al



Dry ablation surface



Wet ablation & Peening
Single application

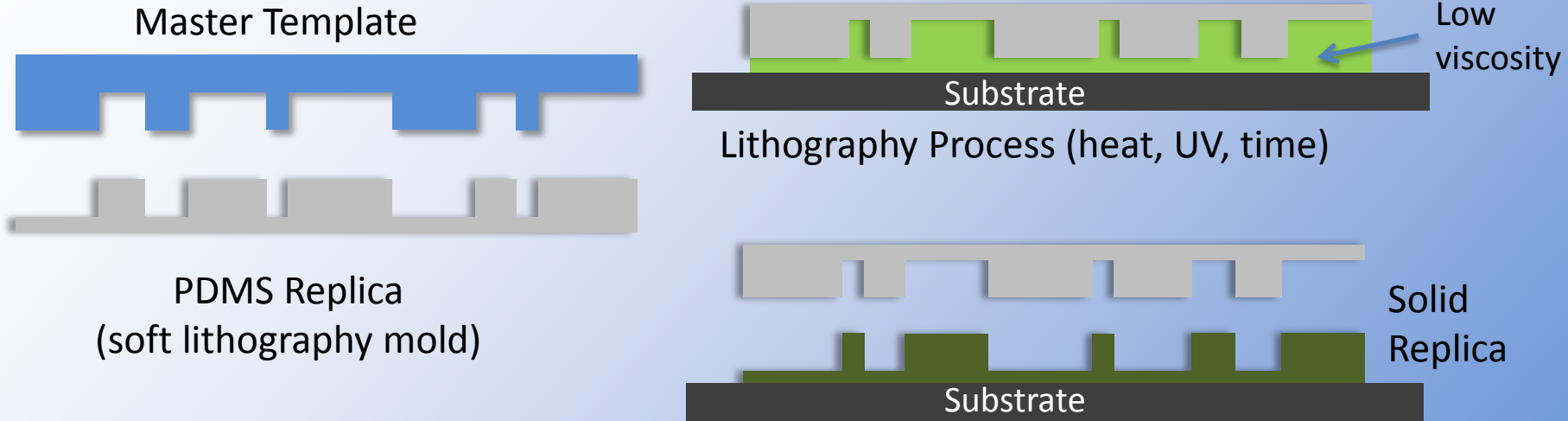


Wet ablation & Peening
Double application

- Dry ablation is deeper than wet peened surfaces



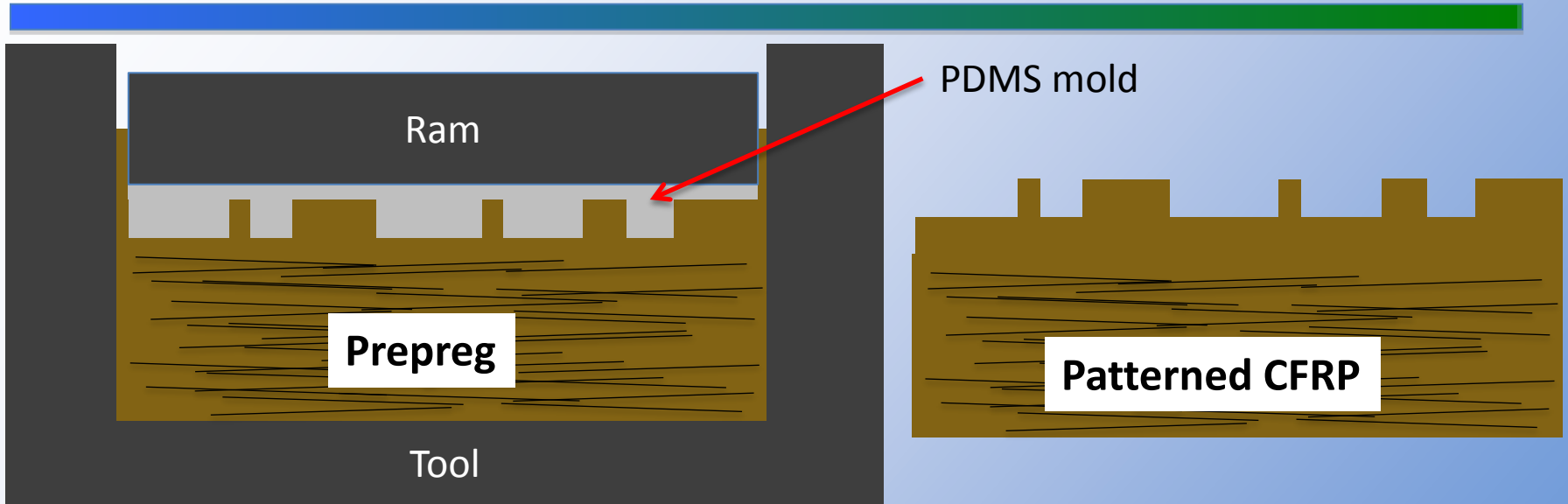
Soft Lithography



- Master copied with PDMS elastomer
- PDMS is used to mold a low-viscosity pre-polymer
 - Pre-polymer vitrified before mold is removed
- Resolution limit $\sim 1 \mu\text{m}$
- Used for low-cost manufacturing



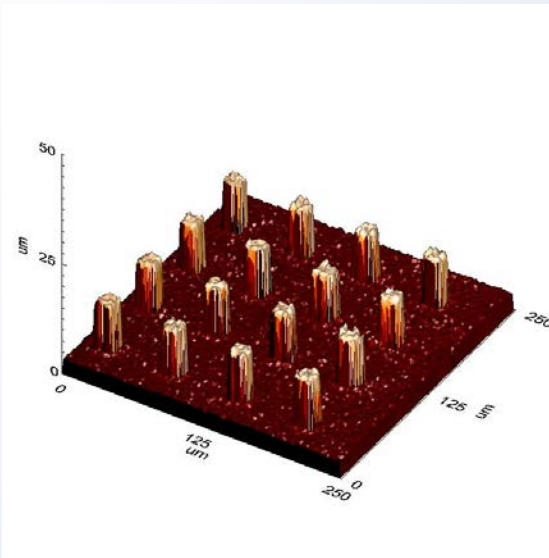
High-pressure Soft Lithography



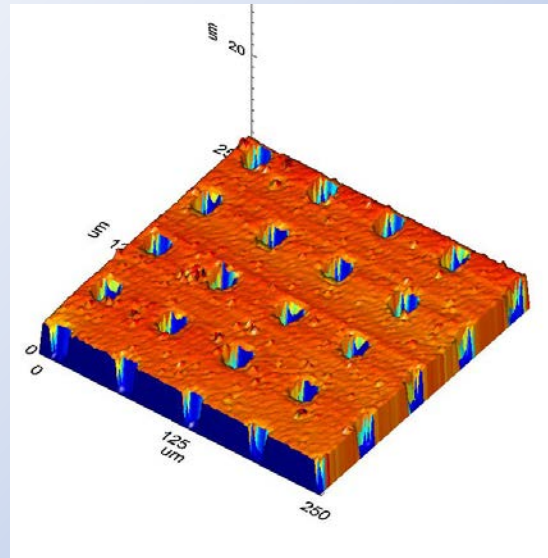
- PDMS applied to prepreg, etc.
- PDMS conforms to tool shape
- Viscous resin flows into mold at elevated temperature



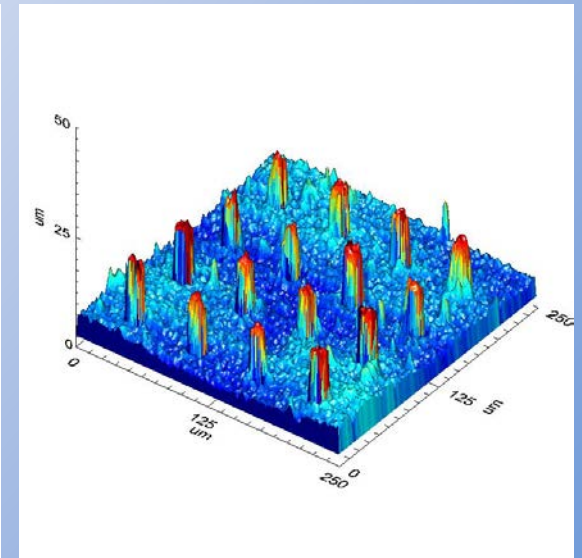
Process Demonstration



Master Template (Kapton)



PDMS mold (Sylgard 184)



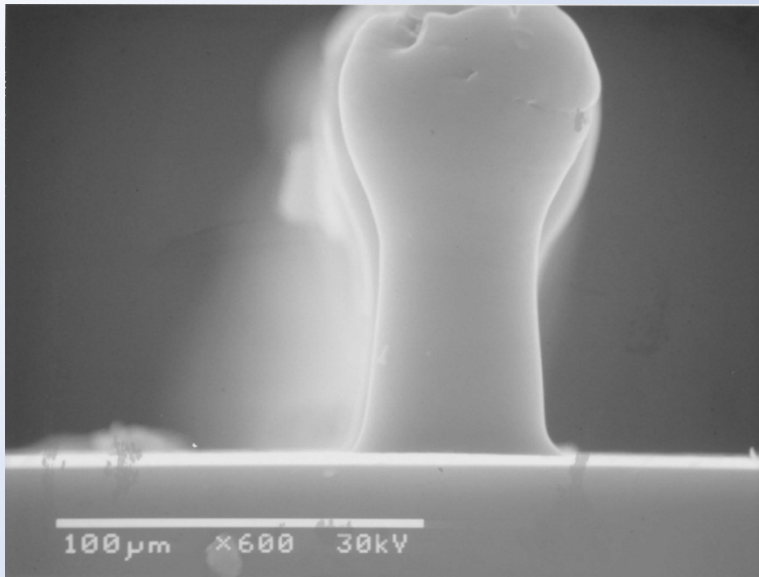
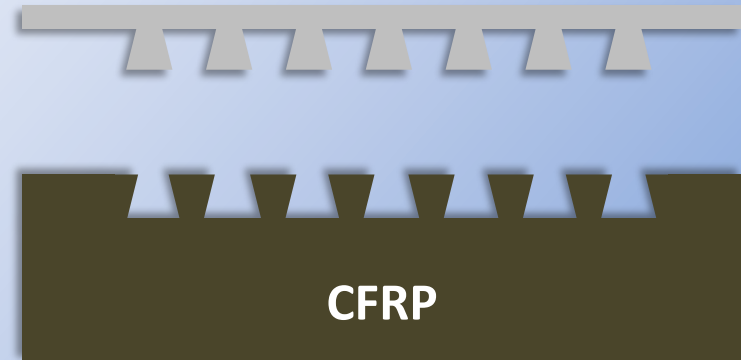
CFRP replica (Epoxy)

- Faithful reproduction of pillar structures in CFRP resin
 - Rough surface from master fabrication replicated as well
 - High-pressure does not reduce feature height



Applications for Adhesion

- Negative angled sidewalls
 - “dovetailed structures”



Example
Micropillar (PDMS elastomer)



Summary

- Adhesion promotion via laser ablation
 - Many materials (titanium and composites)
 - Excellent durability
 - Critical applications (safety)
- Peening/ablation
 - Critical lightweight joints
- High-Pressure Soft Lithography



Acknowledgements

- **NASA Langley Research Center**
 - Project team members: John Connell, Chris Wohl, and John Hopkins
 - Fatigue test/metallurgy support: Will Johnston, Jim Bauman, and Keith Bird
 - Machining and tool fabrication: Hoa Luong and Mike Oliver
- **Boeing Research and Technology**
 - Technical guidance: Kay Blohowiak, Tony Belcher, James Pehoushek-Stangeland
- **University of California Los Angeles**
 - XPS analysis: Robert Hicks and Thomas Williams
- **NASA**
 - Financial support: NARI ARMD Seedling fund



Questions

?



Appendix

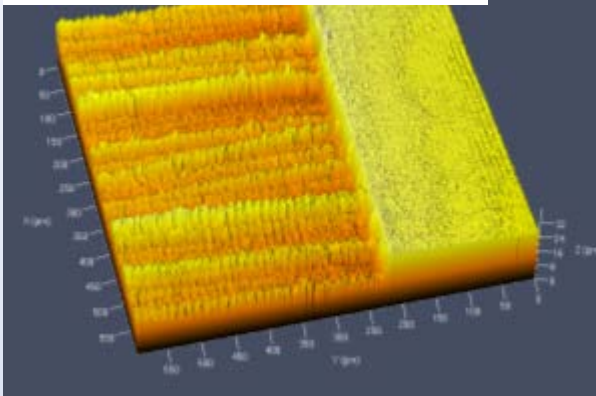
Backup Charts



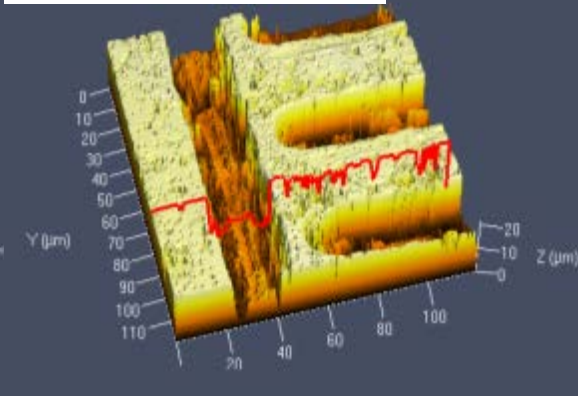
Composite Ablation Depth

- Ablation depth depended on laser process
 - Power, rep. rate, scan speed, passes, pattern
- Fiber exposure/fiber damage is a concern

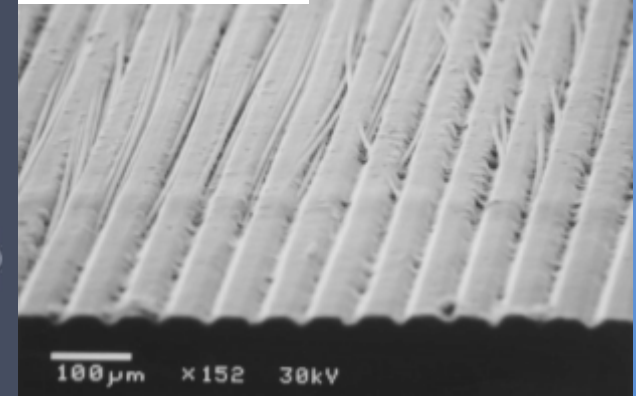
Blanket Ablation (confocal)



Line Ends (confocal)



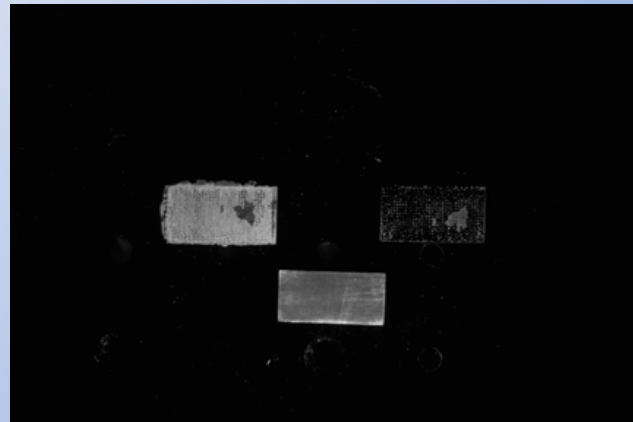
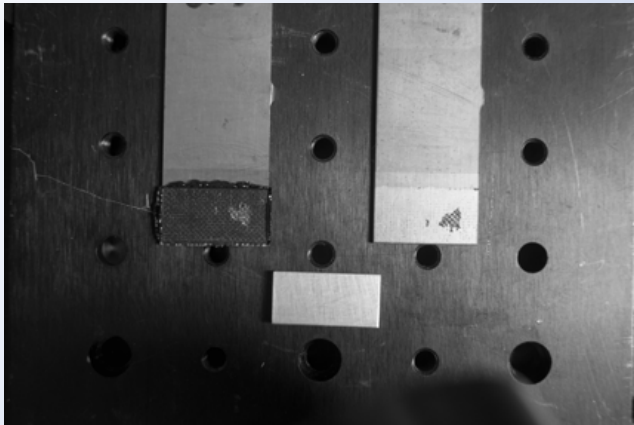
Tilt view (SEM)





Failure Mode Analysis

- 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.



Laser Ablation Patterns used in Wedge Test Matrix

| 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 |

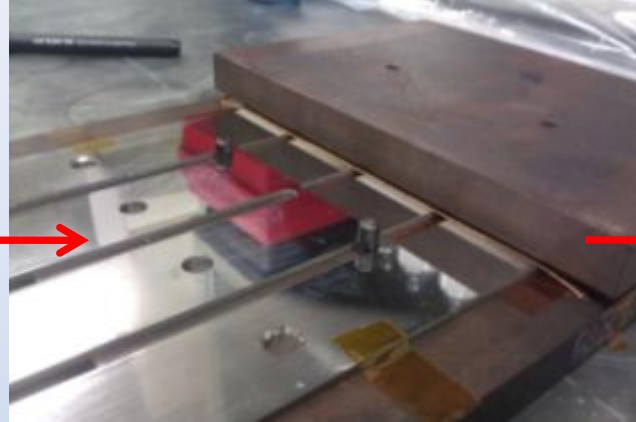


Lap Shear Preparation

PETI-5 adhesive tape preparation



Lay-up in bonding jig



Bonding in heated press



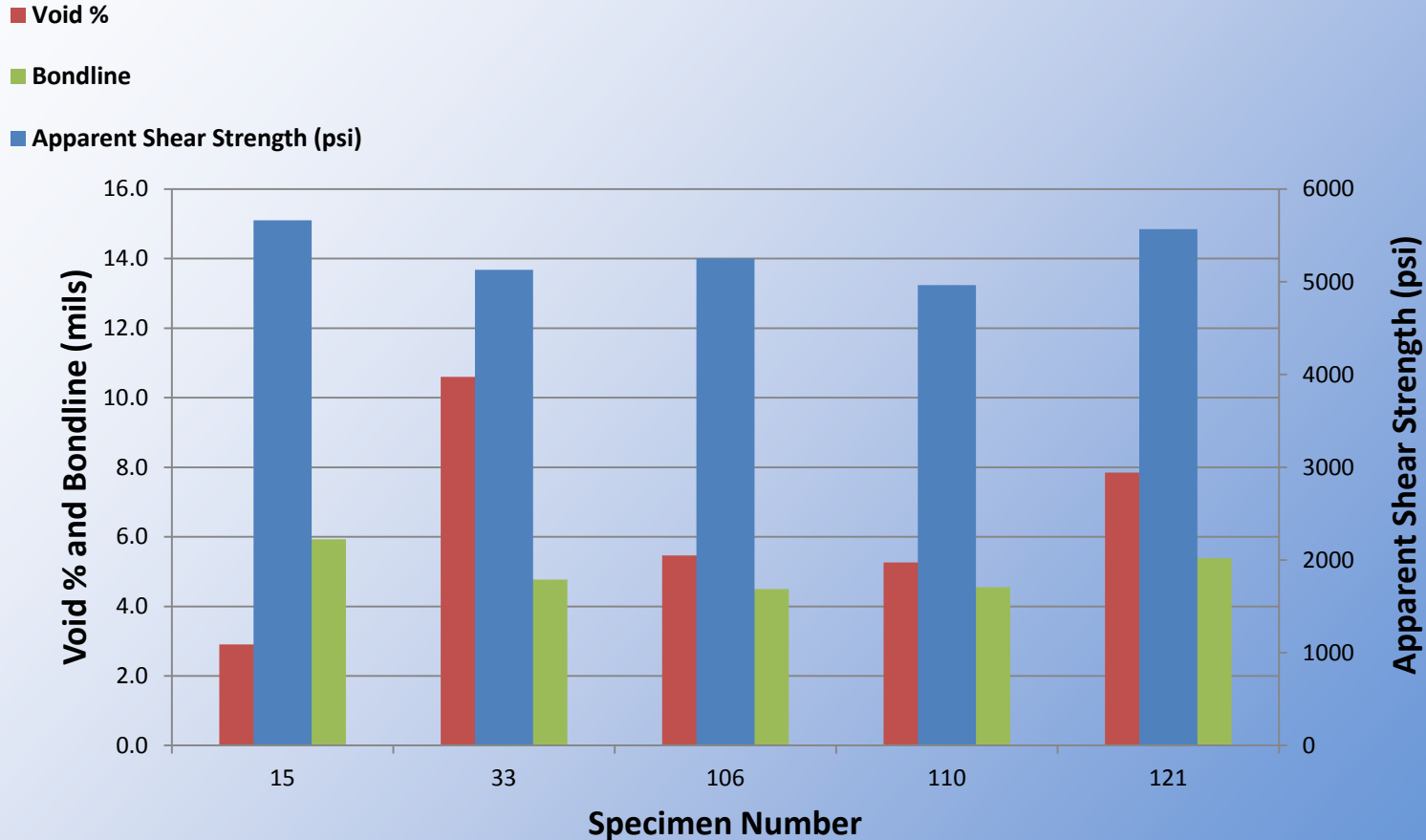
Separated specimens





Hygrothermal Aging Results, RT

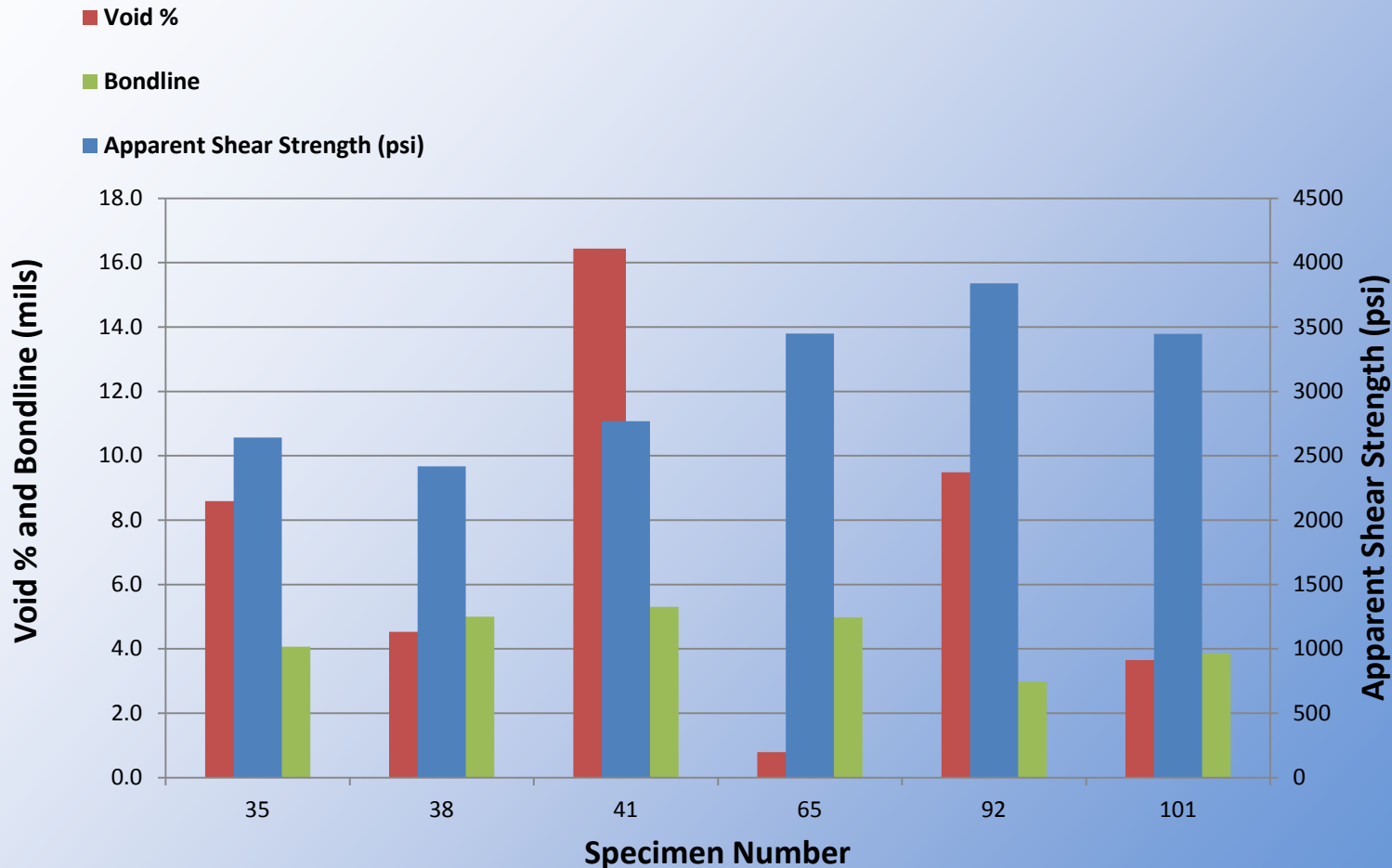
Control lap shear test results after 360 days, tested at RT





Hygrothermal Aging Results, RT

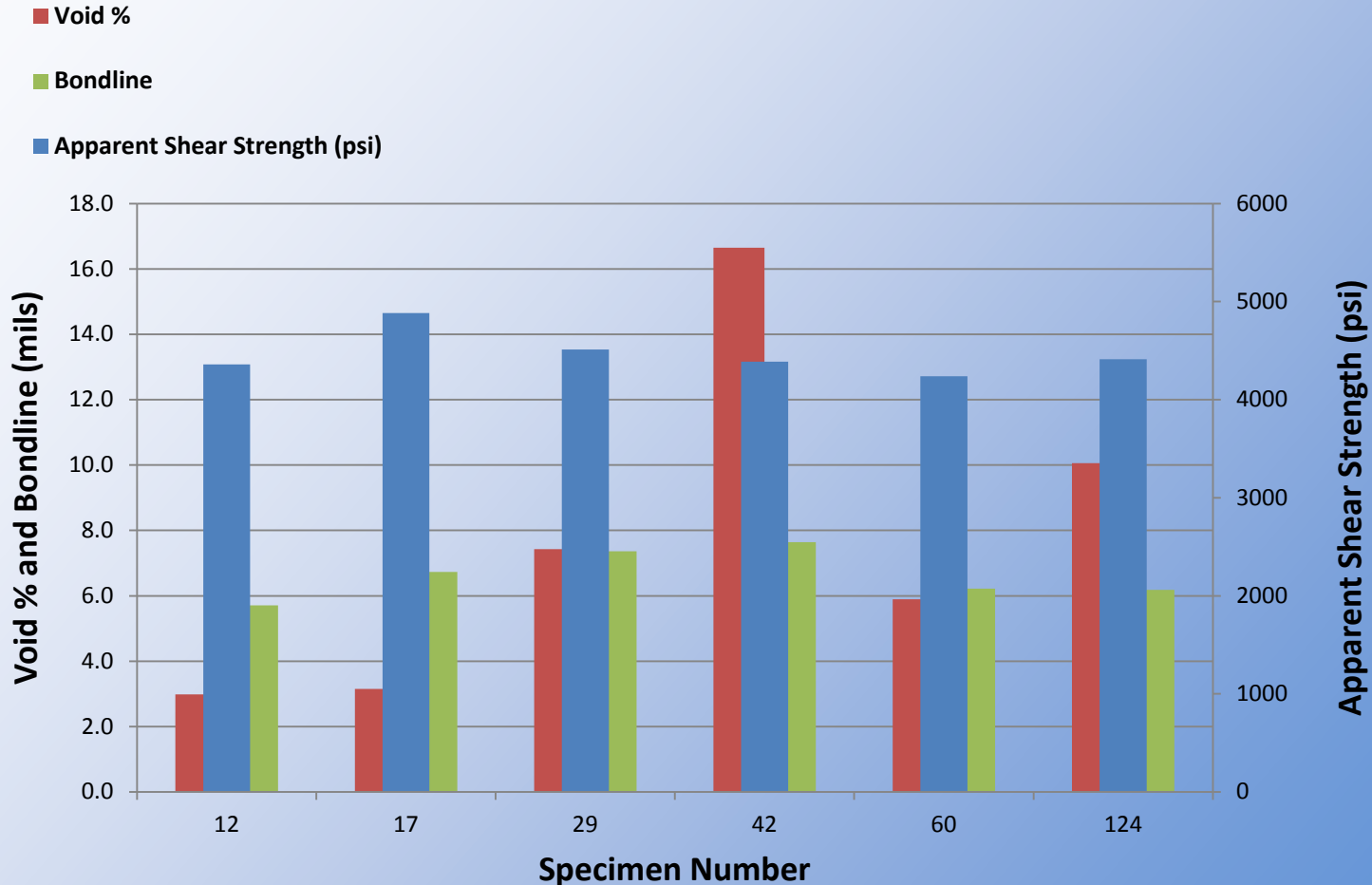
Aged lap shear test results after 540 days, tested at RT





Hygrothermal Aging Results, 71°C

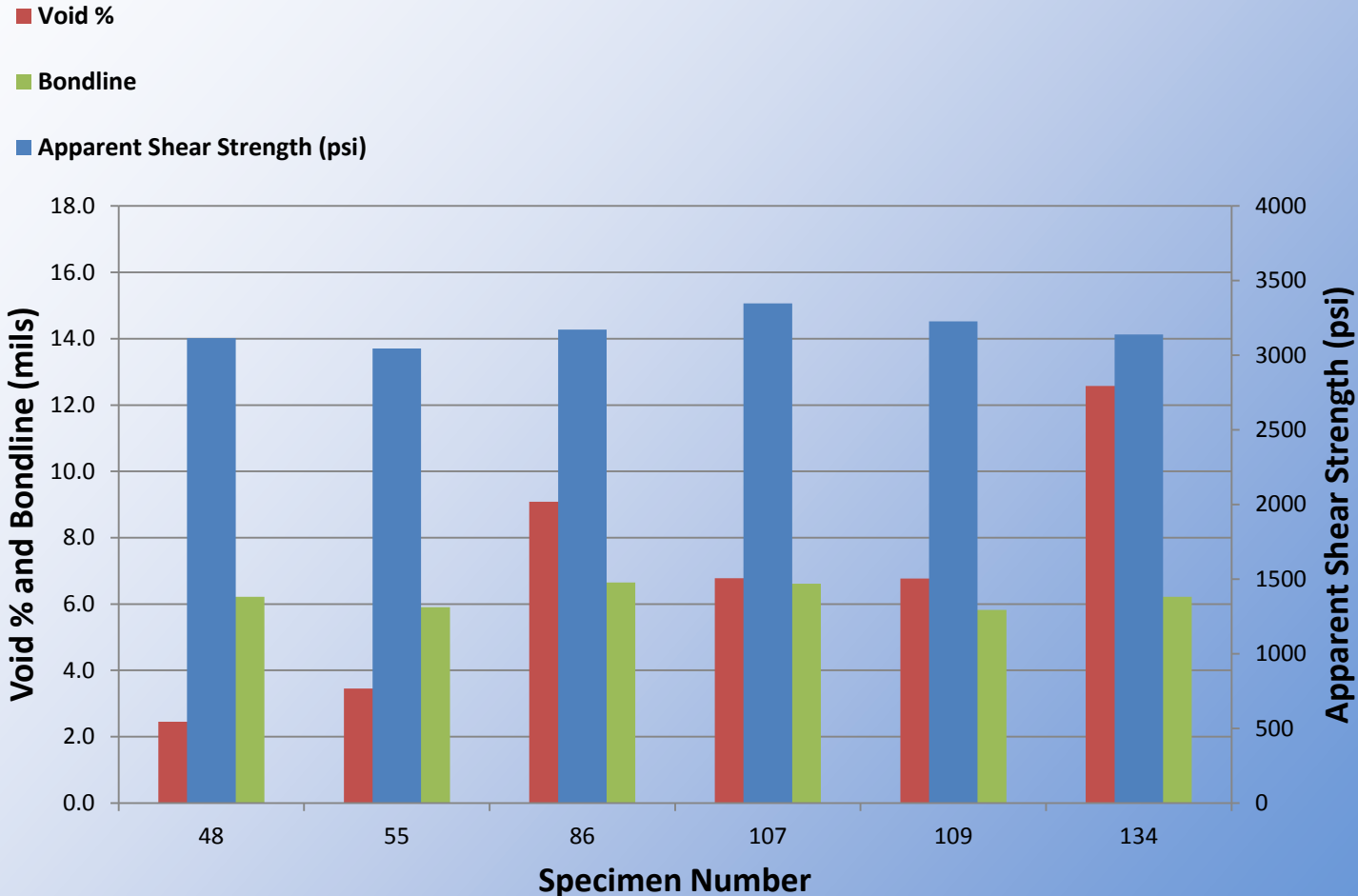
Control lap shear test results after 360 days, tested at 71°C





Hygrothermal Aging Results, 71°C

Aged lap shear test results after 540 days, tested at 71°C



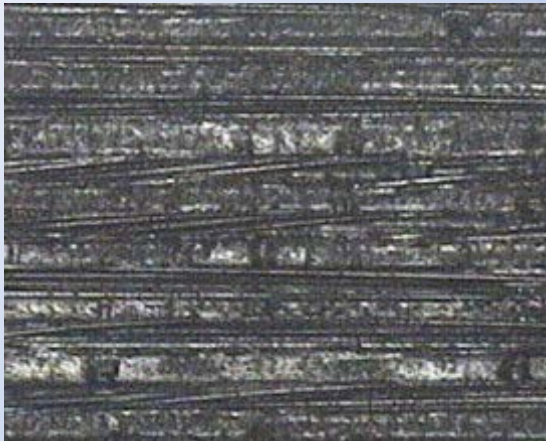
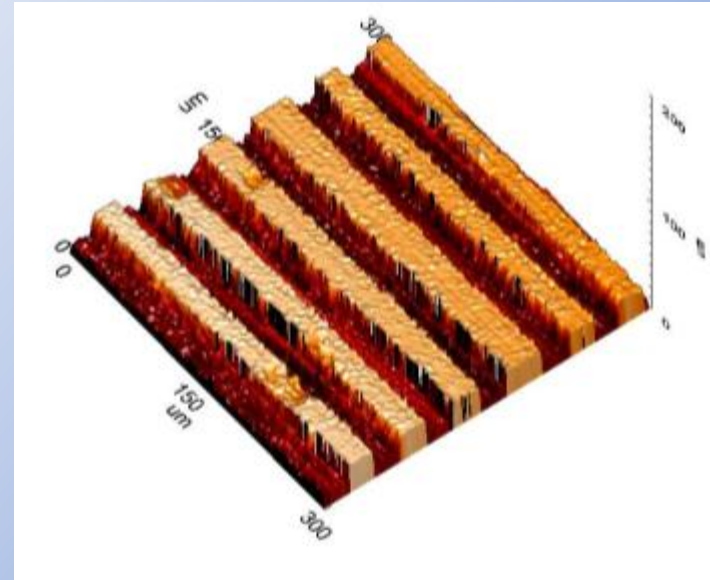
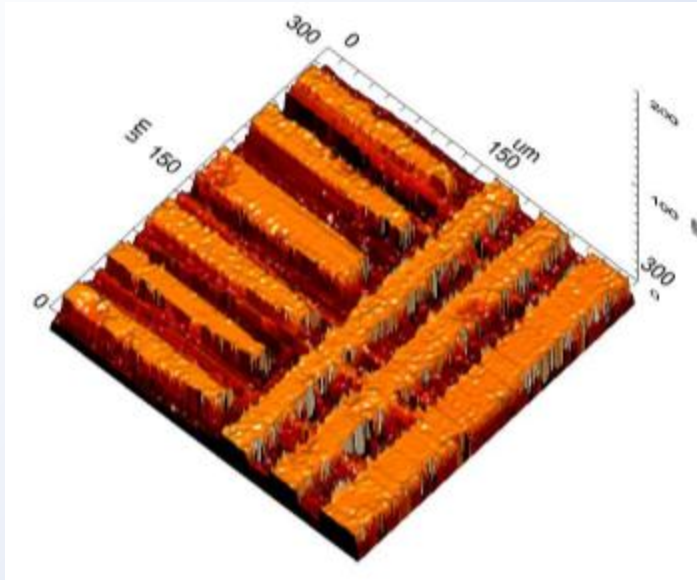


Fabrication of Control Specimens

- Used SoA techniques
- 16 plies of unidirectional T800H/3900-2 prepreg
- Wet peel-ply (Hysol EA9895) was co-cured at 90 to the prepreg fiber direction
- Cured at 177 C (350 F) for 2 hours at 690 Kpa (100 psi) in an autoclave with vacuum bag



Pattern Versatility





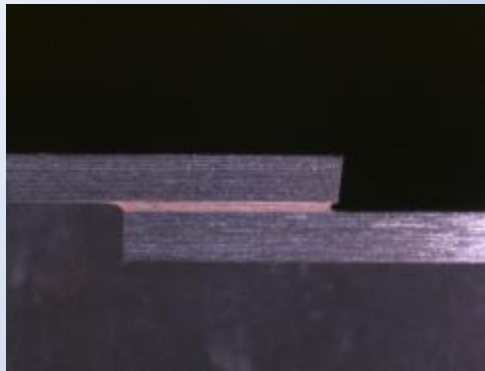
Adhesive Bonding

- Panels (10 cm x 20 cm) were bonded using a strip of AF 555M adhesive (1.6 cm x 20 cm).
- Bondline was shimmed to 0.02 cm (8 mils).
- Autoclave cured at 350°F for 2 hours.
- Bonded panels were trimmed and machined into seven single lap shear specimens (2.54 cm x 19 cm).
- Tested according to ASTM D3165-00.

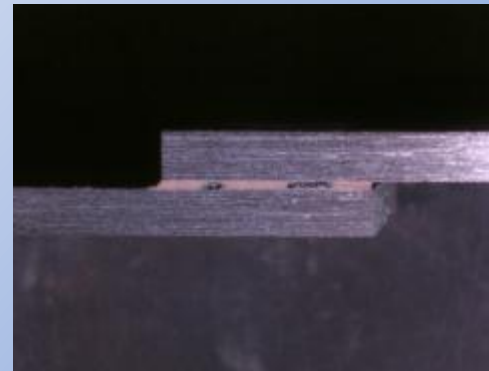


Quality Control of Bond Area

- Bond-line thickness and porosity measured
- Bond quality assessed by examining bond-line edges under a microscope
- Porosity of bond measured by X-ray CT



(a)

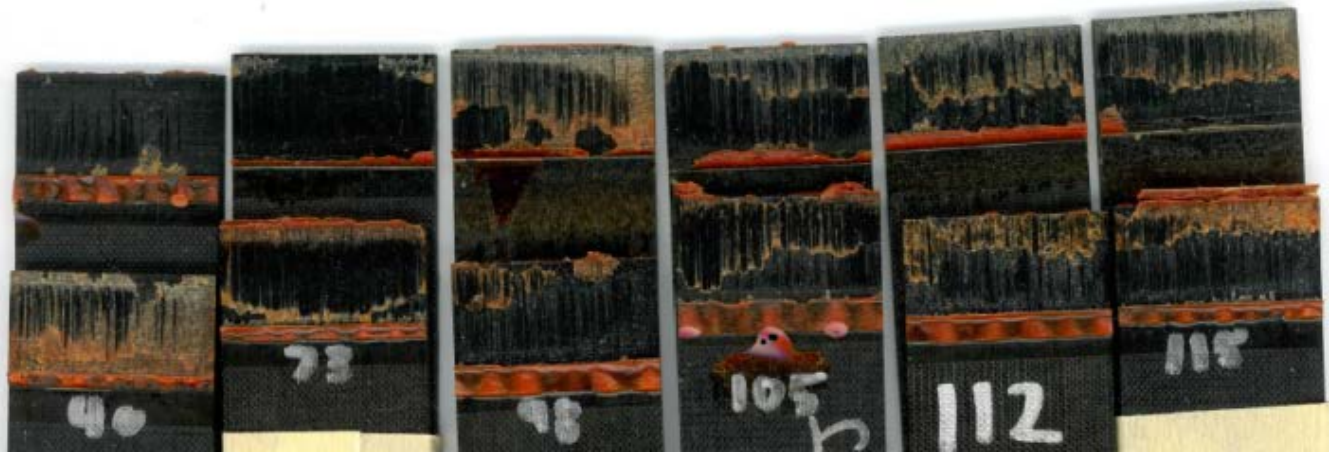


(b)

Bond lines without voids (a) and with voids (b)



SLS Failure Analysis after 360 Days Aging



**Aged 360 Days
Average RT
Strength
26.8^{+/-} 2.8 MPa**



**Aged 360 Days
Average 71°C
Strength
19.6^{+/-} 3.4 MPa**

- Predominant failure mode is fiber tear/light fiber tear (cohesion).
- Aged specimens from 1st generation laser surface treatment exhibited predominately adhesion failure (specimens 14, 25, 30 and 40).



Ti Wedge Test Matrix

- 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 | Bonding, Testing |
|--------------------|--------------------|--|------------|-----------------|-------|---------|-------------|------------------|
| | Nitric/HF preclean | Thermal Age | Laser Prep | BAC5667 Class 1 | | | Bond Primer | |
| | | | | 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).



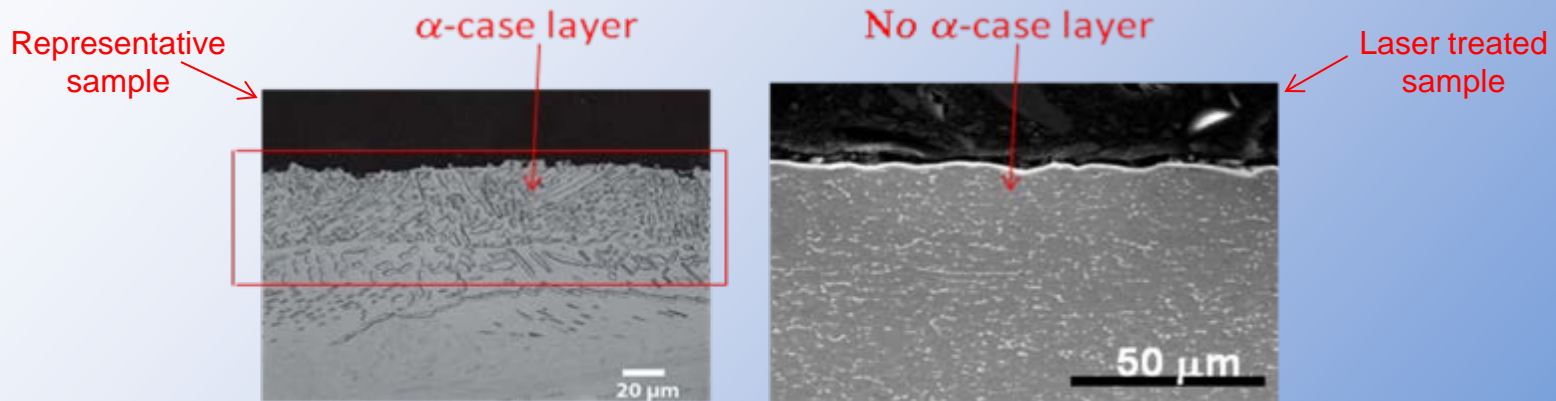
Test Plan

- 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



Alpha Case Inspection

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

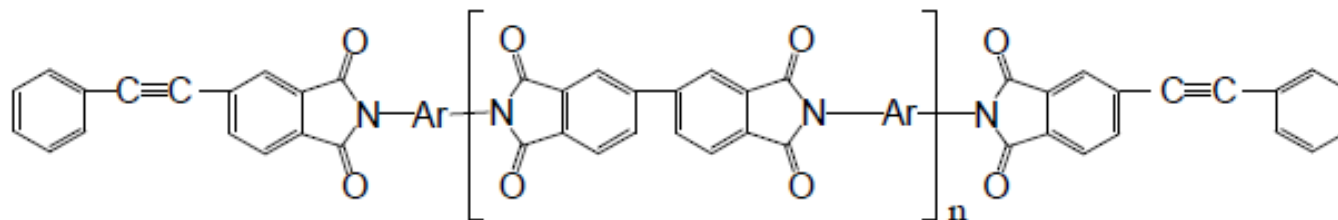


- The α -case layer is caused by oxygen diffusion into the surface and in an α/β alloy like Ti-6Al-4V results in hardening causing embrittlement.
- Microscopic analysis and nanoindentation experiments were conducted on laser etched coupons to determine if any α -case was observed.
- No indication of 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.



Adhesive Chemistry

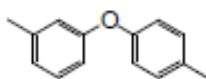
PETI-5



PETI-5

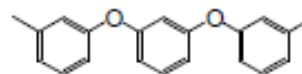
M_n : 2500 - 5000 g/mol

Where Ar =



85 mole %

and



15 mole %

Phenylethynyl Terminated Imide (PETI) Oligomer (2,500 g/mol)

- Ti bonding applicable to high-temperature applications
- Preparation and handling of the adhesive is well understood



Hygrothermal Aging Results, 71°C

- The control specimens after 540 days and testing at 71°C exhibited predominantly cohesion failure modes, but some adhesion type failures were observed. For hygrothermally aged specimens, the amount of cohesion failure began to decrease after 200 days.
- Detailed investigation of the failure modes of specimens at 200, 360 and 540 days revealed that only a few specimens exhibited high adhesion failures.
- All of the specimens that exhibited adhesion failures also had the lowest apparent shear strengths within their respective sample set.
- The heritage of all specimens that exhibited adhesion failure was traced through their fabrication steps and it was determined that they emanated from laser ablated panels that were part of the first generation of panels fabricated.
- Thus, the first generation laser treated specimens that received treatment when the laser was not operating properly are directly linked to the of loss mechanical properties and adhesion failures observed.



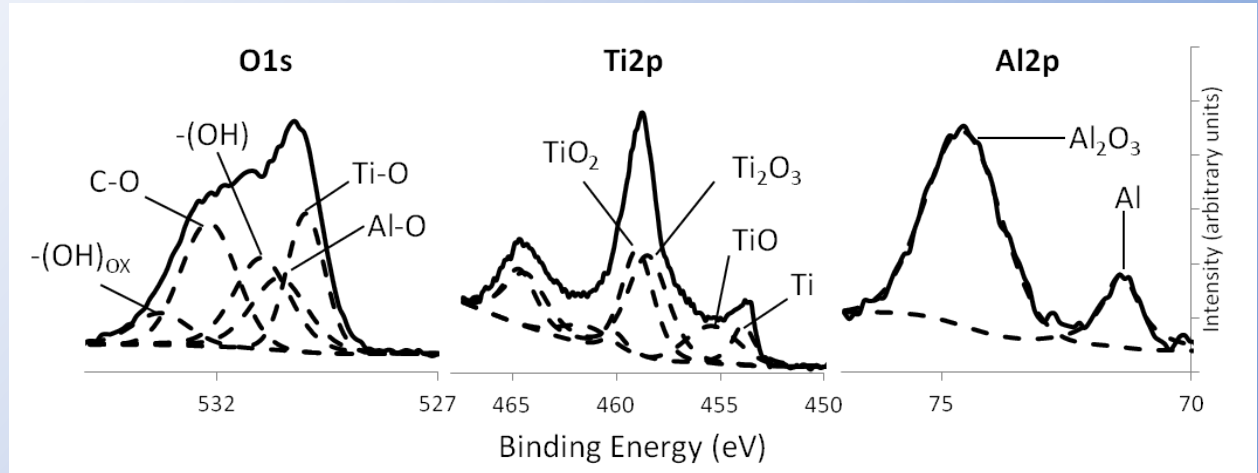
Bonding of Adherends

- Panels cut into six 61 cm by 10.8 cm (24" X 4.25") strips
- Peel plies were removed
- A strip of AF-555M was laid down on the exposed surface & a roller was used to remove trapped air
- Adhesive was then sandwiched between the second half of the adherend panel
- The specimen was bagged & cured in an autoclave at 177° C (350° F) for 2 hours under 310 KPa (45 psi)

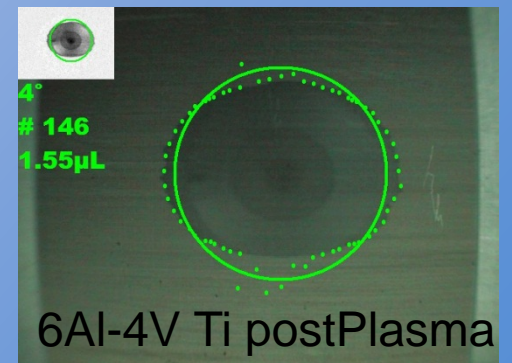
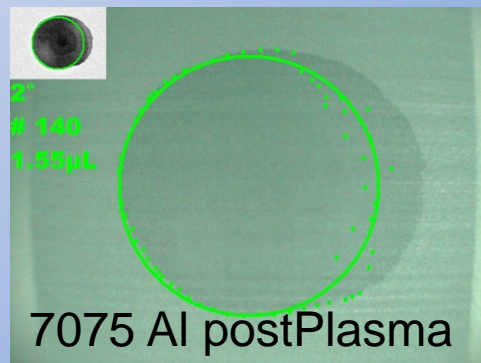
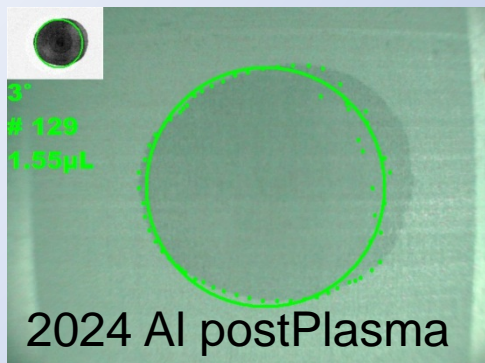
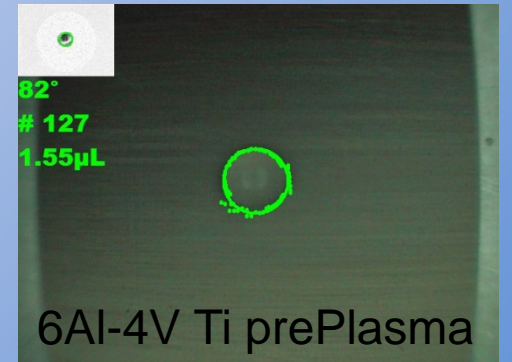
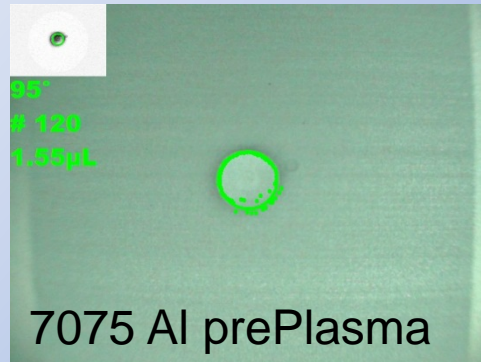
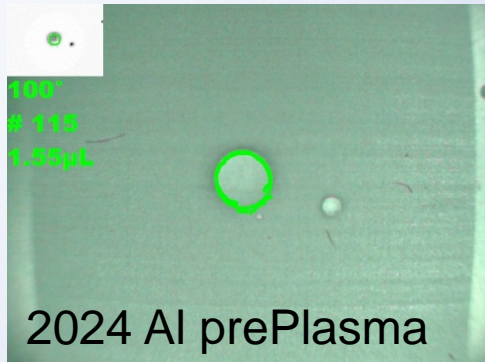
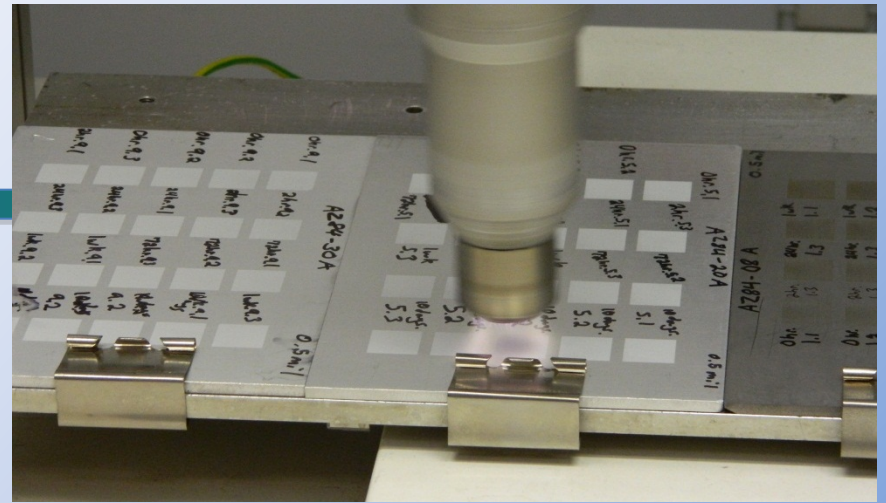
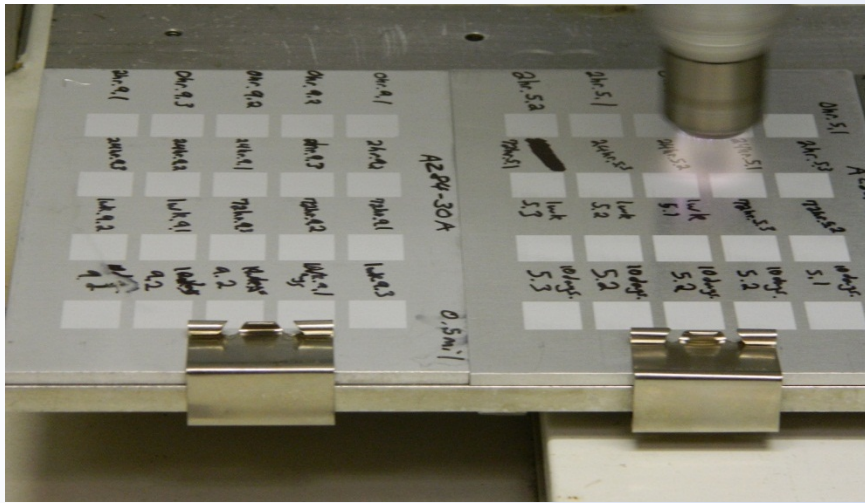


XPS Results

Peak Identification



Carbon signal not included in analysis



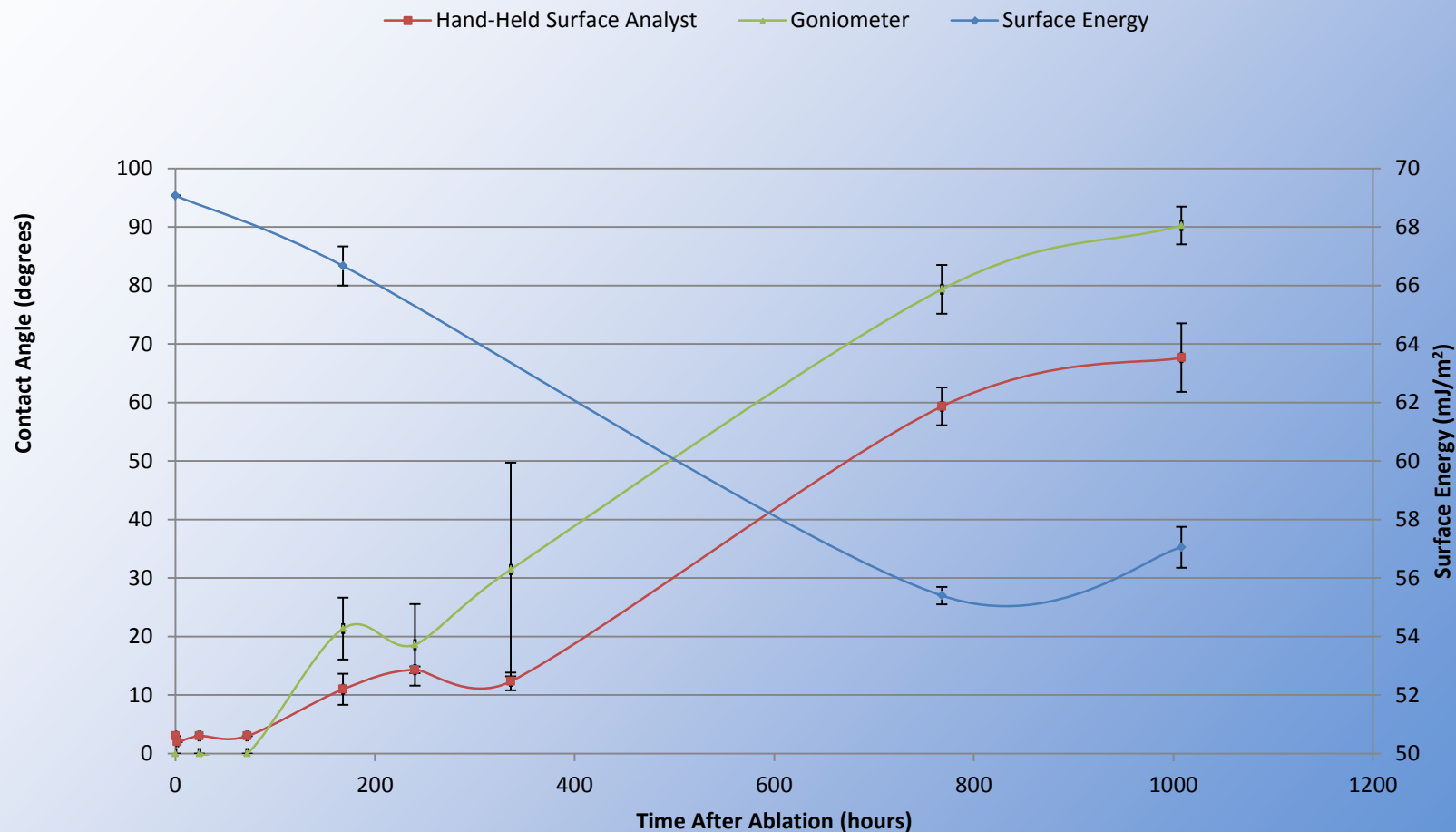


Out Time Study

- Titanium panels ablated with ½” squares
- Contact angles measured on isolated squares
- Two ablation patterns tested
 - 4 mil crosshatch, 0.5 mil lines
- Specimens stored at RT and 20% to 40% RH
- Contact angles 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
- Brighton Technologies Surface Analyst
 - Ballistic drop
 - Receding contact angle

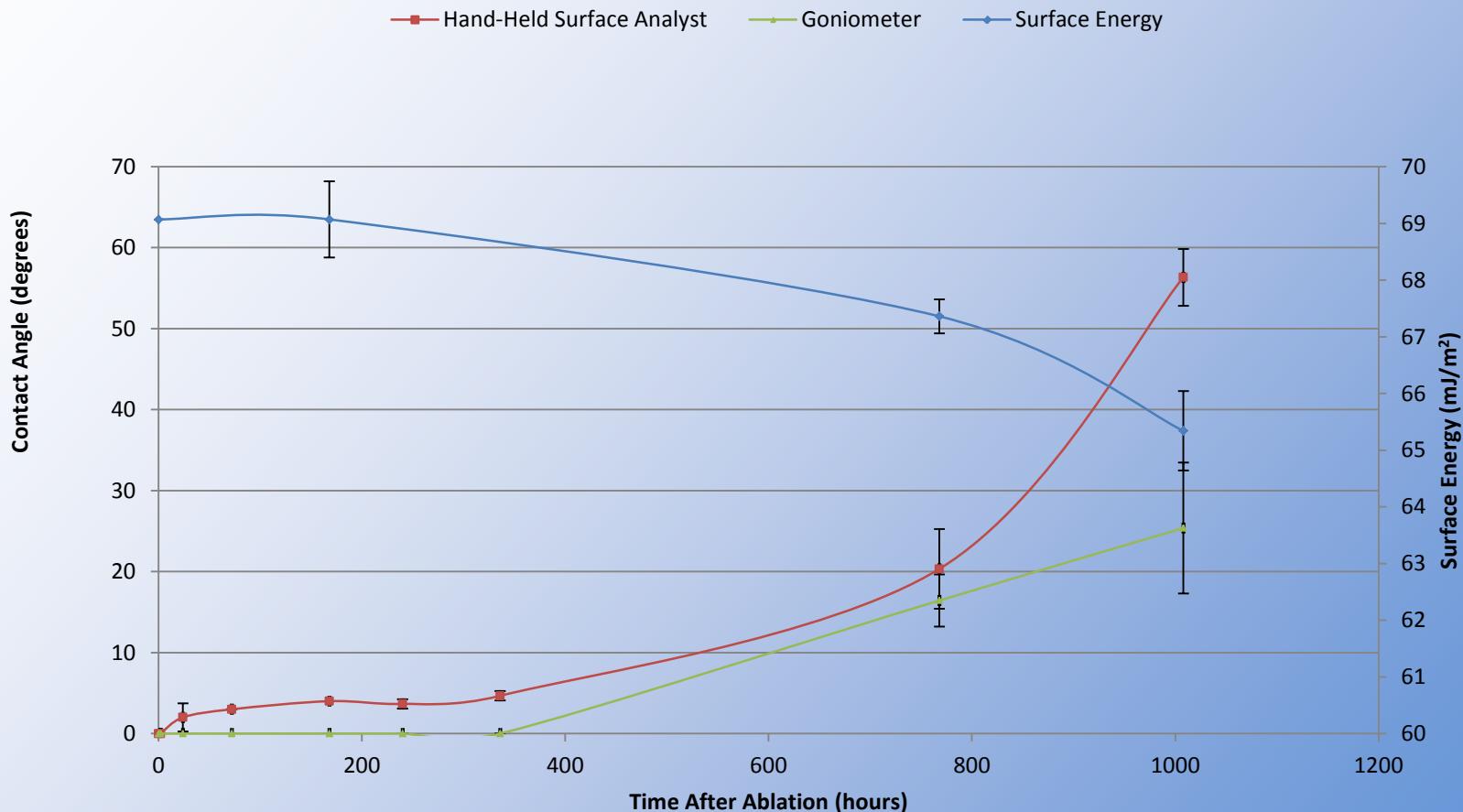


Out Time Study Results (44% Duty Cycle)





Out Time Study Results (200% Duty Cycle)





Summary

- 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.



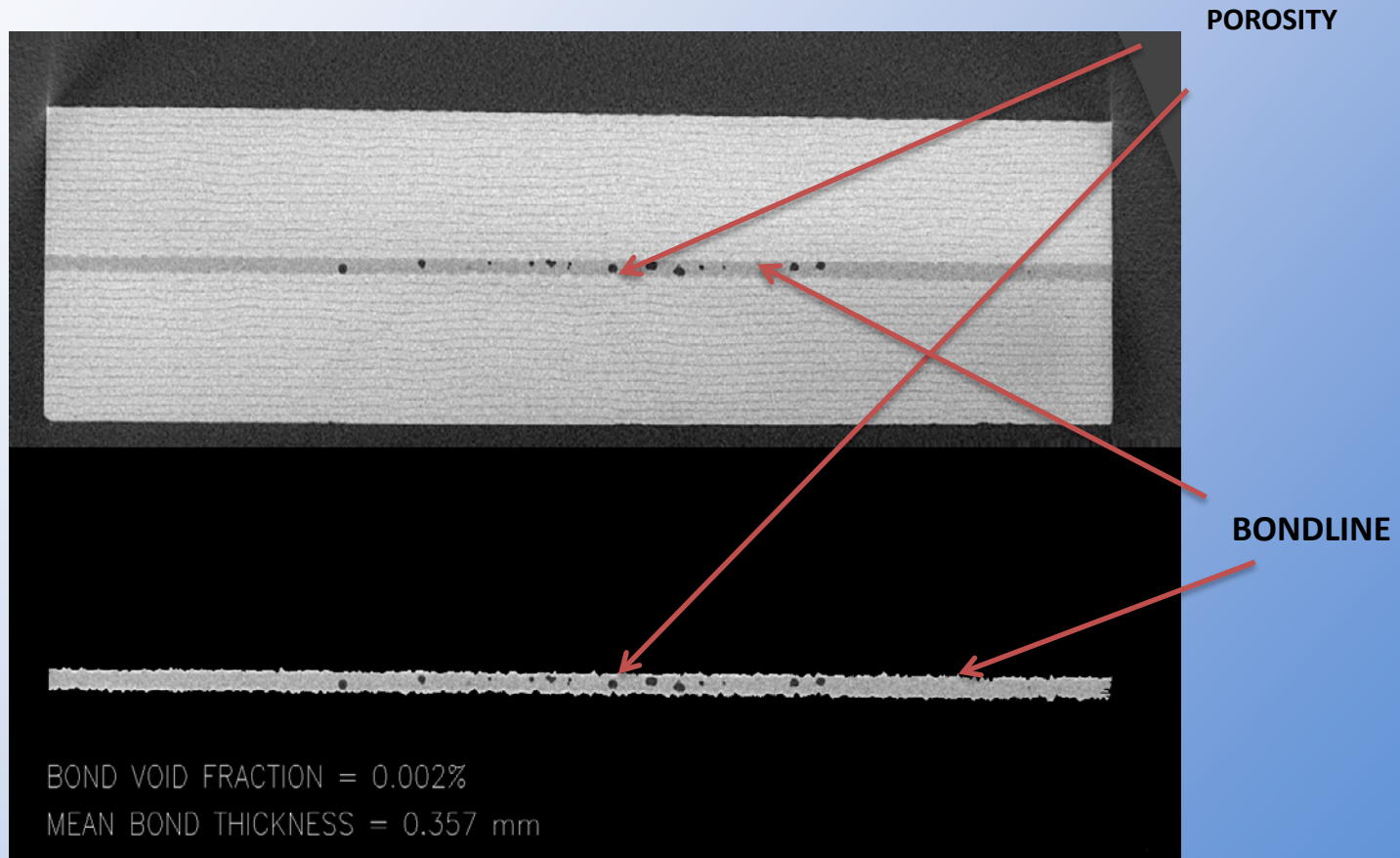
Objectives for CFRP

- To demonstrate laser ablative surface preparation that...
 - matches SoA bond performance.
 - uses green processes.
- Process must enable...
 - improved process control.
 - improved bond reliability.



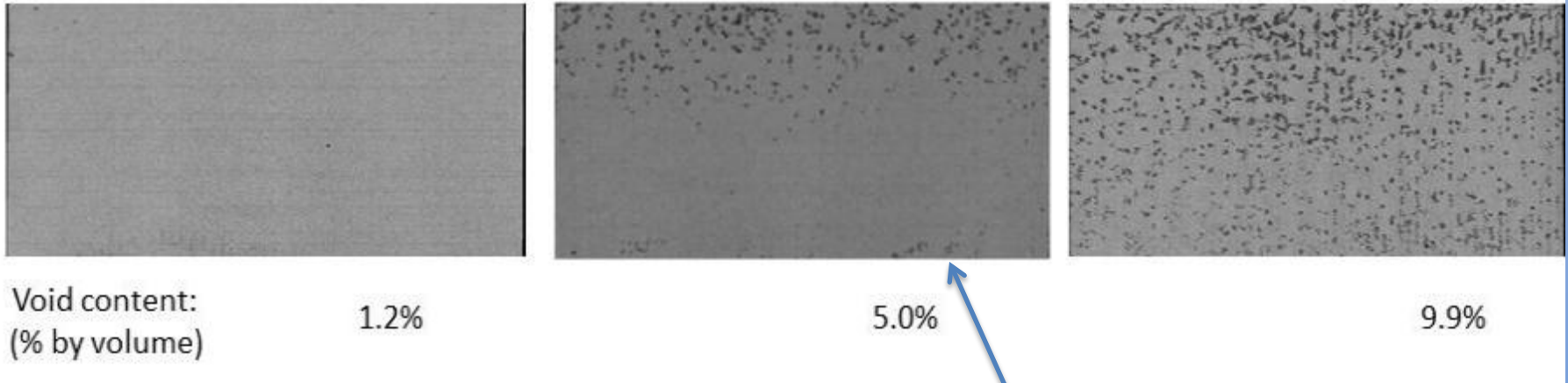
Bondline Analysis

X-ray CT Scan





CT Scan of Adhesive Bonds



Representative radiographs of lap shear specimen bond areas

