Novel Bonding Methodologies Toward the Attainment of Primary Bonded Aircraft Structure

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ARMD Seedling Project
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Innovation

• 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

• 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

• 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

- 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

- 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

Finishing a 2" x 3" field
Accomplishments

Duty Cycle (D) = 0.001”/pitch x 100%
Accomplishments

• 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

- Microhardness characterization results correlate with SEM data
Accomplishments

- **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

- 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

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$_2$O$_3$
- Oxidized hydroxyl species are removed at low power
Accomplishments

• 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

- 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.
Accomplishments

• 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

- 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)

- 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

- 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 $2 	imes 10^7$
  - Test duration: 5 months on two test stands (estimated cost $60-85K$)
Composite Ablation & Bonding

- 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
Summary of Phase I Results

- The potential formation of $\alpha$-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

Backup Charts
Motivation for Bonding

- 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

- 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

Grit blast and mechanical abrasion creates non-uniform surfaces, leaves loose debris, generates waste.
Laser Ablation Surface Preparation

- 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

Pattern concepts developed using CAD software

Example: Checkerboard pattern.

Laser Ablation Processing

Pulsed Laser Beam
Volatilized/Ejected Material
- Photochemical
- Photophysical
- Photothermal

Substrate
System Specifications:
Laser Type – Frequency tripled Nd:YAG
\[ \lambda = 355 \text{ nm} \]
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.
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
Metallographic cross-section and hardness depth profiles by indentation were examined for signs of an α-case formation.
Microhardness Profile and X-Section Images

Vickers Hardness Profile

- 1mm from interface (ablated)
- 3mm from interface (ablated)
- 12mm from interface (ablated)
- 1mm from interface (unablated)

Knoop Hardness Profile

- No α-case!

Metallographic x-sections

α-case

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, ½” overlap

**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

**Bonding Method**
Heated Press
Open air
1hr @ 700 °F (371 °C)
Active cooling
Effect of Pitch on Lap Shear

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
At an ablation power $\geq 600$ 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.

**Effect of Power on Lap Shear**

- Higher Power = **Apparent Shear Strength Increases**
- **Adhesive Failure Decreases**
Lap Shear Preparation

PETI-5 adhesive tape preparation

Lay-up in bonding jig

Separated specimens

Bonding in heated press