SURFACE MODIFICATION FOR IMPROVED JOINING AND CORROSION RESISTANCE

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Presenter: Young Chae Lim

DOE-VTO AMR

Project ID # MAT225

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OVERVIEW

Timeline
- Start: *Oct 2021
- End: Sept 2023
- 10% Complete

Budget
- Project Funding $3.225 M (3 years)
- FY 2021: $1.075M
  - ORNL: $475K
  - PNNL: $550K
  - ANL: $50K

* Funding Received Jan 2021

Barriers
- Multi-Materials Systems: Engineered Surfaces (corrosion)
- Multi-Materials Systems: Predictive Modeling (corrosion)
- Multi-Materials Systems: High volume joining
- Lack of robust solutions to address materials incompatibilities when designing multi-materials vehicles
- Fundamental understanding and modeling tools for optimizing joining methods and interfaces for multi-material components

*2017 U.S. DRIVE MTT Roadmap Report, (currently being updated)

Partners
- Pacific Northwest National Laboratory (PNNL)
- Oak Ridge National Laboratory (ORNL)
- Argonne National Laboratory (ANL)
Objective: High-Quality, Corrosion-Resistant Joints with 3x Longer Lifetime with Surface Modification Treatment vs. Baseline Joints with No Surface Modification Treatment

- Develop novel surface modification techniques to optimize joint quality and adhesion, and provide electrical insulation to improve galvanic corrosion resistance
- Systematically understand (processing)-(interface chemistry)-(joining-corrosion) relationships
  - The potential of the surface modification(s) to improve adhesion and mitigate galvanic corrosion
  - The impact of these surface-modified phases on electric insulation, bulk corrosion resistance, joint quality, and mechanical behavior

Corrosion mitigation (general and galvanic corrosion) in the joints of dissimilar materials is a key technical challenge that must be overcome to successfully integrate candidate lightweight autobody structures from Al alloys, carbon-fiber reinforced polymer (CFRP) composites, and steels
**Selected materials**
- Al 5052-H32, 5083, 6061-T6, 6063, 7075, A356 (cast)
- PPA and PA66 carbon fiber composites
- Galvanized DP590 and 980

**OVERALL APPROACH:**
**SURFACE MODIFICATION-JOINING-CORROSION PERFORMANCE**

- Task 1.0: Surface Modification Process Development and Characterization (Laser, Plasma, Adhesives)
- Task 2.0: Joint Processing, Quality, and Adherence
- Task 3.0: Bulk Substrate and Macro-Galvanic Corrosion Assessment
- Task 4.0: Scanning Electrochemical Cell Microscopy (SECCM) for Micro-Galvanic & Interface Assessment
- Task 5.0: Modeling of Joint Corrosion Behavior
SURFACE MODIFICATION-JOINING STRATEGIES: ATTEMPT ELECTRIC INSULATION BY GROWTH OF OXIDES ON AL OR USE OF ADHESIVES

• Can the joining accommodate submicron oxide layers to reduce galvanic coupling?
  • Successfully demonstrated pre-formed surface coating rivet improved galvanic corrosion resistance for Mg-CFRP by friction self-piercing riveting process from Joining Core Program (JCP) Phase 1
• Collaboration with other thrusts in Joining Core Program Phase 2: MAT222, MAT223, MAT224
## MILESTONES

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Milestone/Deliverable Name/Description</th>
<th>End Date</th>
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</thead>
<tbody>
<tr>
<td>Q1</td>
<td>Complete baseline evaluation of general corrosion properties for monolithic (not joined) as-received materials (Al, steel, and/or CFRP) electrochemical testing</td>
<td>Month 3</td>
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</table>
| Q2      | • Develop a method for characterization of adhesive-CFRP and adhesive-Al (or galvanized steel) interfaces and interphase formation by microscopy  
• Utilize the corrosion model to provide a baseline corrosion potential without the surface treatment techniques in dissimilar joints                                                                                                                                                                           | Month 6         |
| Q3      | Evaluate and characterize electrochemical properties before and after laser and atmosphere plasma treatment at least one Al alloy type at the flat coupon level                                                                                                                                                                                               | Month 9         |
| Q4      | • Complete electrochemical resistance and corrosion properties assessment for laser and/or AP treated oxide surfaces of at least one Al alloy type  
• Demonstrate at the coupon level the surface energy and bonding improvements after the air plasma treatment on CFRP composite                                                                                                                                                           | Month 12        |
| Go/No-Go decision | • Document determination of targeted achievement of electrochemical resistance and/or corrosion properties at least 3x better than the baseline untreated Al surface  
• Perform lap shear tests to demonstrate a 20% increase in surface energy and an 10% increase in lap shear strength on CFRP composite with surface modification                                                                                                                                 | 9/30/2021       |
ACCOMPLISHMENTS: ATMOS. PLASMA TREATMENT OF AL ALLOYS (AA) AND DUAL PHASE (DP) 590 TO ENHANCE ADHESIVE BONDING

- 150W air plasma torch: all four metal substrates increase in surface energy with the slowest speed.
- Increases in surface energy from exposed surfaces may be attributed to increased amounts of hydrated components (characterization in progress).
- Most of the epoxies are rich in hydroxyl groups and can provide better bonding characteristics with a hydroxyl-rich surface.
- Higher traversing speeds reduce surface energy indicated by lower polar component.

**Graphs:**
- **AA 6061**
  - Torch Velocity (cm/m): 19, 38, 76
  - Surface energy: Total and Polar
- **AA 7075**
  - Torch Velocity (cm/m): 19, 38, 76
  - Surface energy: Total, Polar, Tip Height 12.5 mm
- **AA 5052**
  - Torch Velocity (cm/m): 19, 38, 76
  - Surface energy: Total, Polar
- **DP590 steel**
  - Torch Velocity (cm/m): 19, 38, 76
  - Surface energy: Total, Polar

SE: surface energy
ACCOMPLISHMENTS: INITIAL LASER SURFACE PROCESSING OF 7075 AL SHOWED ENHANCED CORROSION RESISTANCE IN 3.5 WT.% NACL

- The impedance values were greater in laser-treated A7075 than untreated material.
- Surface characterization in progress.

Electrochemical Resistance Data

- Corrosion Resistance: 600 grit < 1.6 J < 1.2 J ≈ 1.4 J
Model Setup - High Velocity Riveting

<table>
<thead>
<tr>
<th>Material</th>
<th>Eq Potential (V)</th>
<th>Electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA5083</td>
<td>-0.44</td>
<td>Cathode</td>
</tr>
<tr>
<td>AA5052</td>
<td>-0.59</td>
<td>Cathode</td>
</tr>
<tr>
<td>AA6063</td>
<td>-0.68</td>
<td>Cathode</td>
</tr>
<tr>
<td>AA6061</td>
<td>-0.72</td>
<td>Cathode</td>
</tr>
<tr>
<td>AA7075 (Rivet Material)</td>
<td>-0.76</td>
<td>-</td>
</tr>
<tr>
<td>AA5182</td>
<td>-1.05</td>
<td>Anode</td>
</tr>
</tbody>
</table>

Ran simulations for \( h_{rivet} = 1\text{mm}, 0.5\text{ mm} \) and flushed

7075 Rivet material with different top sheet aluminum alloys were modeled

**Results**

- AA6063 as a top sheet has greatest corrosion current when coupled with 7075 rivet and will lead to the corrosion of the rivet
COLLABORATION AND COORDINATION

- Teams meet and virtually present monthly
- The exact same batches of materials are being used by all teams at each lab across the JCP
- Oak Ridge National Laboratory Team:
  - Materials Joining, Deposition Science & Technology, Corrosion Science & Technology, and Carbon & Composites Groups
- Pacific Northwest National Laboratory:
  - Solid Phase Processing- Joining, Materials Performance, Electrochemical Sciences Groups
- Argonne National Laboratory: X-ray, synchrotron beam characterization of surfaces
- Tri-national lab team formed to support joining, characterization, corrosion, and modeling tasks
- Periodic interactions with other thrusts within JCP with close coordination/ ties to automotive industry
- L&L Products: provide adhesives
PROPOSED FUTURE WORK

- Evaluate laser and atmosphere plasma processes to controllably form insulating submicron oxide/ceramic surfaces on Al to increase corrosion resistance and reduce Al-steel joint galvanic coupling
  - Can such surfaces still be joined? Do they appreciably impact corrosion resistance?
- Evaluate atmosphere plasma processes to enhance adhesive bonding
  - Al-CFRP: joint quality and reduced galvanic coupling
  - Al-steel: joint quality and reduced galvanic coupling
- Collaboration with other thrusts in Joining Core Program Phase 2 to explore multiple joining processes
- Characterization
  - Surface/cross-section (x-ray photoelectron spectroscopy, electron microscopy, x-ray diffraction, radiography, tomography)
  - Extensive bulk and local electrochemical evaluation of bulk and joined materials
- Model and validate the effect of deformation, gaps, adhesives, surface treatment and crevice on the corrosion behavior of multi-material joints

*Any proposed future work is subject to change based on funding levels
SUMMARY

- Identified and procured selected materials (Al alloys, CFRP, and steel) in collaboration with other thrusts in the joining core program phase 2 to ensure consistent, comparable findings.
- Atmosphere plasma surface treatment on Al and steel metal surface increased surface energy compared with the untreated material to enhance adhesive bonding performance.
- Initial laser surface treatment on AA7075 improved the corrosion resistance and electrochemical resistance compared with the untreated material.
- COMSOL modeling of sheet/rivet interaction impacts on galvanic coupling initiated to guide materials surface modification and joining strategies.
TECHNICAL BACKUP SLIDES
TECHNICAL BACK-UP: IMPEDANCE DATA FITTING EXAMPLES

Zview (Scribner INC.) was used for computer-assisted impedance spectra fitting of all electrochemical impedance spectroscopy (EIS) data. Some examples of impedance fitting (as snapshots) are shown below.

**Al 7075 (0.83 cm²) 600 grit finish**

- Red: measured impedance data
- Green: model fit from a circuit model

- $R_2 \approx 7984$ ohm·cm²

**Al 7075 (0.83 cm²) 1.6 J laser-treated**

- $R_2 \approx 5673$ ohm·cm²
- $R_3 \approx 10357$ ohm·cm²
- Sum: 16030 ohm·cm²
Advantage of laser process
- Non-contact
- High precision, selective area, less distortion, environment friendly
- Applicable to complex, three-dimensional geometry by robot or CNC motion stages
- Amenable to Scale up

Laser Process parameters
- Laser power, pulse repetition rate, pulse duration, wavelength
- Focusing optic/beam shaping
- Scan speed
- Shielding gas (e.g., oxygen, nitrogen): forms Al$_2$O$_3$ or AlN

Improve adhesive bonding strength
Improve corrosion resistance of material and joint
### A7075 (2”x2” & 1”x1” coupons) EIS results

<table>
<thead>
<tr>
<th>Ohm∙cm²</th>
<th>600 grit (baseline)</th>
<th>Laser 1.6 J</th>
<th>Laser 1.4 J</th>
<th>Laser 1.2 J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitted R values</td>
<td>$R_2$ only</td>
<td>$R_2 + R_3$</td>
<td>$R_2 + R_3$</td>
<td>$R_2 + R_3$</td>
</tr>
<tr>
<td>Run 1</td>
<td>3777</td>
<td>16030</td>
<td>30741</td>
<td>42082</td>
</tr>
<tr>
<td>Run 2</td>
<td>7043</td>
<td>11641</td>
<td>19515</td>
<td></td>
</tr>
<tr>
<td>Run 3</td>
<td>7984</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 4</td>
<td>8123</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 5</td>
<td>9591</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avg.</td>
<td>7304</td>
<td>13836</td>
<td>30741</td>
<td>30799</td>
</tr>
</tbody>
</table>

### Resistance rank (tentative)
- Baseline < 1.6 J < 1.4 J~1.2 J

**Post-corrosion surface of 7075 after EIS + anodic polarization + anodic constant potential**

- Pitting but no visible substrate dissolution

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**POST-EXPOSURE SURFACE IMAGES**

1. [Image of 7075 post-corrosion surface after EIS + anodic polarization + anodic constant potential.]
   - Pitting but no visible substrate dissolution

2. [Image of another post-exposure surface image.]
   - Pitting but no visible substrate dissolution