## Overview

### Timeline
- **Start date:** September 1, 2013
- **End date:** August 30, 2017
- **Percent complete:** 25%

### Budget
- **Project budget:** $595,520
  - **Budget Period 1:** $144,860
  - **Budget Period 2:** $149,167

### Barrier
- Joining and assembly. High-volume, high-yield joining technologies for lightweight and dissimilar materials need further improvement.

### Project Partners
- Dr. Karsten Woll (former postdoc) – now with Karlsruhe Institute of Technology, Karlsruhe, Germany
Relevance – Project Objectives

**Overall Objective:** Develop and characterize novel reactive foils based on reduction-oxidation (Redox) reactions for use in bonding dissimilar materials

**Achievements for FY2014:**

- Mechanically fabricated 23 Cu-based and Ni-based Redox Foil systems representing 11 unique chemistries
- Determined baseline strengths for bonding aluminum 6061, magnesium AZ31, aluminum coated boron steel (ACBS), and hot stamped boron steel (HSBS) with Al:CuO-based, Al:Cu$_2$O-based and Al:NiO-based Redox Foils, that were fabricated using initial techniques.
- Minimized mass ejection from Redox Foils more than 10x through dilution
## Milestones

<table>
<thead>
<tr>
<th>Target Date</th>
<th>Milestones and Go/No-Go decisions</th>
<th>Status</th>
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<tbody>
<tr>
<td>9/30/2015&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>Optimize Redox Foil chemistries and dilutions</td>
<td>On Track</td>
</tr>
<tr>
<td>9/30/2015&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Optimize microstructures of Redox Foils</td>
<td>On Track</td>
</tr>
<tr>
<td>3/31/2016&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Optimize mechanical fabrication of Redox Foils</td>
<td>On Track</td>
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<tr>
<td>9/30/2016&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>Determine critical applied pressure for bonding</td>
<td>pending</td>
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<tr>
<td>9/30/2016&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>Identify range of acceptable Redox Foil thickness</td>
<td>pending</td>
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<tr>
<td>12/31/2016&lt;sup&gt;a,c&lt;/sup&gt;</td>
<td>Optimize surface preparation methods</td>
<td>pending</td>
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<tr>
<td>12/31/2017</td>
<td>Determine bond strengths and failure modes</td>
<td>pending</td>
</tr>
<tr>
<td>9/30/2017</td>
<td>Determine corrosion behavior of optimized bonds</td>
<td>pending</td>
</tr>
<tr>
<td>12/31/2017</td>
<td>Determine microstructure/degradation near bonds</td>
<td>pending</td>
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<sup>a</sup> Represents Go/No Go Decision; <sup>b</sup>10 MPa bond strength is needed; <sup>c</sup>20 MPa
Approach – Existing Technology

- Reactive joining has been commercialized with Al/Ni formation reactions.
  - NanoBond™ process
  - NanoFoil™ (Ni/Al Foils)
  - Local heat source
  - No thermal damage
- Requires pre-wet solder layer
- Expensive due to vapor phase processing of foils
Approach – Propose Technology

• Joining with Redox Foil
  – Exothermic reaction creates its own braze
  – Little thermal damage (HAZ)
  – Propagates ~0.1 m/s
• Can bond dissimilar metals
  – Ex. Steel to Mg
• Mechanical Fabrication
  – Cheaper than vapor phase processed reactive materials
  – High volume production of Redox foils can be enabled

\[ Al + MO + \text{dilution} \rightarrow Al_2O_3 + (M + \text{dilution}) + \text{heat} \]
Technical Progress: Fabrication

- Redox Foils fabricated by consolidating and processing (swaging and rolling) micron sized powders

![Graph showing reactants and mass percent](image)

**Reactants**
- Ni
- NiO
- Al
- Oxide
- Diluent

**Diameter reduction during**
- As-swaged mixture in jacket
- As-rolled mixture in jacket

**Redox Foil Fabrication**
- **Redox Foil**
- **10 mm**
Technical Progress: Bonding Parameters

• Constant pressure
  – 13 MPa
  – Maintained by spring
• 400 μm thick foils
• Foils spark ignited outside of bond area
• Base components
  – Al 6061
  – Mg AZ31
  – Al coated boron steel (ACBS)
  – Hot stamped boron steel (HSBS)
Technical Progress: Bond Strengths

- Copper appears to wet bonding substrates
- Too much flow of material from the bond area
- Flow will be reduced in large bond areas

**Graph:**
- **System:** Al 6061, ACBS, HSBS
- **Shear Strength (MPa):**
  - Al:CuO:40%Cu (400 µm thick)
  - Tested in Tension

**Image:**
- Al:CuO:40%Cu on Al 6061
Technical Progress: Bond Strengths

- Lower bond strength than copper foils
- Nickel braze does not wet substrates well

![Graph showing bond strength comparison](image)

- Al: NiO: 10% Ni (400 µm thick)
- Shear Strength (MPa vs. Base Metal)
- Shear Strength (psi vs. Non-wettable braze)

![Micrograph of bond interface](image)
Technical Progress: Fracture Surfaces

- The CuO/Cu$_2$O-based foils eject more material but have better wetting.
- The NiO-based Redox Foils eject less material but have poor wetting.
- **Strategy:** dilute to minimize mass ejection and then alloy to maximize wetting and minimize corrosion.

Al:CuO:40%Cu spreads on both surfaces, fracture within braze.

Substrate visible after fracture in bond interface.

Al:NiO:10%Ni leaves porous braze, fracture at substrate interface.
Technical Progress: Dilution

- Dilute foils enough to bring temperature of reaction below boiling points of products (and reactants)
- Dilution provides additional braze material
Technical Progress: Propagation

• Mass ejections and propagation velocity depend on chemistry and dilution

```
Al: NiO: 10% Ni

81 ms

Al: Cu₂O: 10% Cu

27 ms
```
Technical Progress: Foil Characterization

- As dilution increases, normalized mass ejection and velocity decrease
- Can mass ejection be eliminated without quenching?
Technical Progress: Quenching in Bonds

• Foils must generate heat faster than heat is dissipated into surroundings or else the reaction will quench

\[ \dot{Q}_{RX} > \dot{Q}_L \]

Sum of heat losses, including into substrate, foil, and atmosphere

Redox Foil ignition

Quenched reaction stops at interface

Bond propagates through entire foil

Pressure

Propagation

Top

Bottom

Ignition

Reacted Areas

Al:Cu$_2$O:10%Cu Aluminum 6061

Bottom base substrate after foil ignition and quenching
Technical Progress: Quenching in Bonds

- Large dilutions in NiO and Cu$_2$O systems lead to quenching in a bond (indicated by open symbols and dashed lines)
- Increase reactivity so foils can still propagate within a bond
Technical Progress: Quenching in Bonds

- Large dilutions in NiO and Cu$_2$O systems lead to quenching in a bond (indicated by open symbols and dashed lines)
- Increase reactivity so foils can still propagate within a bond
- Larger dilutions will yield larger quantities of braze

![Graph showing quenching in bonds with dilutions of NiO and Cu$_2$O systems]
Technical Progress: Enhancing Reactivity

- Decrease reactant spacing via alternative methods (ball milling)
- Incorporate ball milled powder into Redox Foil

Conventional Swaged/Rolled Material

Reactant spacing 1-3 micron

Ball Milled Powder

Reactant spacing < 1 micron
Response to Previous Year Comments

• This project started in October 1, 2013 but was not reviewed in 2014.
Collaborations

• **Severstal** – Material supplier
  Supplied aluminum-coated boron steel and hot-stamped boron steel for testing

• **Dr. Karsten Woll** – Former postdoc
  Now at Karlsruhe Institute of Technology
Remaining Challenges and Barriers

Challenge: Mass ejection & large volume fraction of alumina
Solution: Increase dilution to minimize ejection and increase braze

Challenge: High dilution can lead to quenching
Solution: Decrease average reactant spacing to enhance reactivity

Challenge: Molten braze from Redox reaction wets poorly
Solution: Alloy best braze(s) with reactive elements

Challenge: Best braze(s) may lead to corrosion
Solution: Alloy braze systems to minimize corrosion
Future Work

• Minimize reactant spacing and enhance reactivity so as to maximize dilution

• Identify optimum dilutions for the NiO and Cu$_2$O systems
  – wt% dilution as well as chemistry
  – Maximize wetting, minimize ejection

• Identify optimum means for combining diluent with reactive particles.

• Create statistically signification datasets for shear strengths of bonds and determine the modes of failure in the joint.
Summary

• Several Ni- and Cu-based Redox systems have been fabricated and studied while varying the level of dilution.
  – Velocity and mass ejection decrease with increasing dilution
  – The amount of braze available to the bond increases with dilution

• Preliminary bonding data suggests that moderate bond strengths can be obtained and depend strongly on foil chemistry and the materials being bonded.

• Further microstructural refinement is needed to promote propagation of the Redox reaction through the bond interface in heavily-diluted foils.
Technical Back-Up Slides

(Note: please include this “separator” slide if you are including back-up technical slides (maximum of five technical back-up slides). These back-up technical slides will be available for your presentation and will be included in the DVD and Web PDF files released to the public.)
Technical Backup: Fabrication

**Cold Press Powders** - thermite mixtures
(25 °C max)

Powders mixed and added to tube

Powders compacted

**Rolling** - create planar foil
(25 °C)

**Swaging** - radial reductions of tube
(100 °C max)

File Jacket leaving foil

Redox Foil

Steel Jacket
Technical Backup: Quenching Limits

![Quenching Limit Diagram]

- **Al:NiO:Ni**
- **Al:Cu₂O:Cu**
- **Al:CuO:Cu**

**Quenching Limit**

- Mg AZ 31
- Al 6061
- Propagate
- Quench
- No Ignition

Dilution (wt %)
Technical Backup: Alternative Diluent

![Graph showing the relationship between braze volume percentage and average normalized mass ejection fraction.](chart1.png)

![Graph showing the relationship between dilution weight percentage and velocity (m/s).](chart2.png)