The Evaluation of High Temperature Adhesive Bonding Processes for Rocket Engine Combustion Chamber Applications

Daniel McCray, Jeffrey Smith, & Brian Rice
University of Dayton Research Institute (UDRI)
300 College Park
Dayton, OH 45469-0138

Dr. Kay Blohowiak & Robert Anderson
Boeing Phantom Works
800 North 6th St., 10-20 Bldg.
Renton, WA 98055

Dr. E. Eugene Shin, Linda McCorkle & Dr. James Sutter
NASA Glenn Research Center (NASA GRC)
21000 Brookpark Road, M/S 49-3
Cleveland, OH 44135

Abstract

NASA Glenn Research Center is currently evaluating the possibility of using high-temperature polymer matrix composites to reinforce the combustion chamber of a rocket engine. One potential design utilizes a honeycomb structure composed of a PMR-II-50/M40J 4HS composite facesheet and titanium honeycomb core to reinforce a stainless steel shell (Figure 1). In order to properly fabricate this structure, adhesive bond processes had to be developed for the titanium core, the stainless steel shell, and the PMR-II-50 composite.

Proper prebond surface preparation is critical in order to obtain an acceptable adhesive bond. Improperly treated surfaces will exhibit decreased bond strength and durability, especially in metallic bonds where interfaces are susceptible to degradation due to heat and moisture. Most treatments for titanium and stainless steel alloys require the use of strong chemicals to etch and clean the surface. These processes are difficult to perform due to limited processing facilities as well as safety and environmental risks and they do not consistently yield optimum bond durability. Boeing Phantom Works previously developed sol-gel surface preparations for titanium alloys using a PETI-5 based polyimide adhesive. In support of part of NASA Glenn Research Center, UDRI and Boeing Phantom Works evaluated variations of this high temperature sol-gel surface preparation, primer type, and primer cure conditions on the adhesion performance of titanium and stainless steel using Cytec FM 680-1 polyimide adhesive. It was also found that a modified cure cycle of the FM 680-1 adhesive, i.e., 4 hrs at 370°F in vacuum + post cure, significantly increased the adhesion strength compared to the manufacturer’s suggested cure cycle. In addition, the surface preparation of the PMR-II-50 composite was evaluated in terms of surface cleanliness and roughness. This presentation will
discuss the results of strength and durability testing conducted on titanium, stainless steel, and PMR-II-50 composite adherends to evaluate possible bonding processes.

**Figure 1: Honeycomb Panel for Rocket Engine Combustion Chamber Wall**
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Dr. Kay Blohowiak & Robert Anderson, Boeing Phantom Works
Dr. E. Eugene Shin & Linda McCorkle, Ohio Aerospace Institute
Dr. James Sutter, NASA GRC

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Jacksonville, FL

Background

- NASA GRC is currently evaluating use of High-Temp PMCs in the design of a rocket engine combustion chamber
- A potential design requires adhesive bonding processes for 3 adherend types:
  - PMR-II-50 composite
  - Stainless steel
  - Titanium
Proposed Bonded Structure

Stainless Steel Facesheet

Titanium Honeycomb Core

PMR-II-50 Facesheet

Cytec FM 680-1 Film Adhesive

Components of Adhesive Bonding Process

ADHESIVE PROCESSING

Main contributor to bond strength but can also affect durability

Function of:
- Cure Temperature
- Cure Pressure
- Postcure

PREBOND SURFACE PREP

Main contributor to environmental durability but can affect strength

- Titanium core
- Stainless Steel facesheet
- PMR-II-50 facesheet

Bond Durability

Bond Strength
Adhesive Processing

- Cytec FM 680-1 polyimide adhesive
  - 0.10 psf, fiberglass woven carrier
- Cytec's recommended cure cycle:
  - 2 hours at 600°F & 100 psi
  - Postcure for 2-16 hours at 600°F-700°F
- Cytec published mechanical data using adherends composed of both Ti-6Al-4V and Avamid N laminates
  - Grit-blast surface preparation

Limitations in using recommended cure
- Difficult to fabricate a vacuum bag on a complex part with Kapton film
- Large thermal stresses due to CTE mismatch between composite, Ti core, and stainless steel at specified cure temp

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FM 680-1 Adhesive Cure Evaluation

- Proposed alternate cure cycle for FM 680-1:
  - 4 hours at 370°F & 15 in Hg vacuum pressure
  - 16 hour freestanding postcure at 700°F
- Allows the use of low temperature bagging films and sealant tapes
  - Reduces cost
  - Easier to process

Effect of Alternate Cure on FM 680-1 on Ti-6Al-4V Adherends

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**FM 680-1 Alternate Cure Evaluation Summary**

- 370°F vacuum cure cycle provided results equivalent to Cytec's published data on grit-blasted Ti-6Al-4V
- Lower temperature cure allows for use of consumable materials with maximum use temperature of 400°F
  - Lower cost & easier process
  - Possible reduction in thermal stresses???

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**Residual Stresses Due to CTE Mismatch**

- Bonded M40J/PMR-II-50 composite (12 plies) to 0.040" steel using FM 680-1 adhesive (11" x 1" strips)
  - 370°F, vacuum bag cure
  - 370°F, v.b. cure + 700°F P.C.
  - 600°F, autoclave cure
- Measured amount of curvature due to CTE mismatch
- **NO REDUCTION IN THERMAL STRESSES DUE TO ALT CURE!**

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370°F Cure

- Radius of curvature: ~37 inches
- Maximum displacement: 0.36 inches

370°F Cure with 700°F Postcure and 600°F cure

<table>
<thead>
<tr>
<th>Steel</th>
<th>M40J/PMR-II-50</th>
</tr>
</thead>
</table>

* Bond failed in adhesive due to excessive peel stress

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• Existing surface treatments require the use of strong chemicals and hazardous materials
  – Difficult to perform
  – safety & environmental regulations
  – Inconsistent results

• Boeing Phantom Works developed “Boegel” sol-gel coatings for adhesive bonding to metals
  – Water-based coating with pH around 8
  – Robust process proved under High Speed Civil Transport Program with NASA LaRC using PETI-5

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Molecularly Engineered Interfaces

~200 nm

Metal Part

organic interface
inorganic/organic hybrid layer
inorganic interface

Courtesy of Boeing Phantom Works
Boegel System

- Organic portion of coating tailored to match resin system
  - Aminopropyl and aminophenyl silanes evaluated
- Zirconium an integral part of the coating
  - Ties together functionalized silicon components
  - Improves hydrolytic stability
  - Better match to titanium and stainless steel interface
  - Free energy of Zr alloying into Ti part is higher than Si, Al, or Ti oxides

Sol-Gel Process Overview

Titanium only

- Degrease
- Nitric/HF Etch
- Turco 5578 Alkaline Etch

Steel only

- Grit-blast Pretreatment

Drench Coat with Sol-Gel Solution
Bake at 260°F
Prime

Courtesy of Boeing Phantom Works
Sol-Gel Surface Preparation Evaluation

Processing Variables

- Sol-Gel Chemistry
  - Boegel AM (Aminopropyl)
  - Aminopropyl + Aminophenyl silane (APS + APhS)
  - No sol-gel
- Bond Primer
  - Cytec BR 680
  - No bond primer
- Primer Cure Temps
  - 400°F or 600°F

Materials

- Adherends
  - Ti-6Al-4V
  - Stainless Steel
  - Cytec FM 680-1 Adhesive

Test Conditions

- Tensile Lap Shear ASTM D 1002
  - Room Temperature (RT)
  - 600°F dry
  - RT after 3 day water boil exposure

Ti-6Al-4V Lap Shear Results

- Specimens treated with both sol-gel chemistries exhibit higher strength @ RT than grit-blast controls
- APhS+APS sol-gel specimens (HT 6 & 7) exhibit better strength at 600°F than Boegel AM specimens (HT 1 & 2)
Evaluation of Ti-6-4 Failure Modes (30x)

Grit-blast & BR 680 (HT11)  Boegel AM & BR 680 (HT1)  APhS + APS & BR 680 (HT6)  APhS + APS no primer (HT8)

RT
1645 psi  3555 psi  3537 psi  4287 psi

600°F
1637 psi  825 psi  1129 psi  1326 psi

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Ti-6-4 Water Boil Failure Modes (30x)

Grit-blast & BR 680 (HT11)  Boegel AM & BR 680 (HT1)  APhS + APS & BR 680 (HT6)  APhS + APS no primer (HT8)

1447 psi  2232 psi  2041 psi  2300 psi

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Steel

- Addition of sol-gels improved RT strength
- APhS+APS sol-gel specimens exhibited better failure modes (higher % cohesive) than Boegel AM sol-gel specimens
- Specimens fell apart before testing when BR 680 primer was used without sol-gel (HT14)
  - Complete interfacial failure

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Evaluation of Steel Failure Modes (30x)

<table>
<thead>
<tr>
<th>Method</th>
<th>RT 1444 psi</th>
<th>600°F 1031 psi</th>
<th>86 psi</th>
<th>961 psi</th>
<th>3401 psi</th>
<th>0 psi</th>
<th>3440 psi</th>
<th>1093 psi</th>
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<tbody>
<tr>
<td>Grit-blast &amp; no primer</td>
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<tr>
<td>Grit-blast &amp; BR 680</td>
<td>1444 psi</td>
<td>0 psi</td>
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<tr>
<td>(HT14)</td>
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<tr>
<td>Boegel AM &amp; BR 680</td>
<td>86 psi</td>
<td>1031 psi</td>
<td>961 psi</td>
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<td></td>
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<tr>
<td>(HT4)</td>
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</tr>
<tr>
<td>APhS + APS &amp; BR 680</td>
<td>3401 psi</td>
<td>0 psi</td>
<td>961 psi</td>
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2/11/03
Steel Water Boil Failure Modes (30x)

<table>
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<tr>
<th>Method</th>
<th>Pressure (psi)</th>
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<tr>
<td>Grit-blast &amp; no primer</td>
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<tr>
<td>(HT15)</td>
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<tr>
<td>Grit-blast &amp; BR 680</td>
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<tr>
<td>(HT14)</td>
<td>(Before water boil exposure)</td>
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<tr>
<td>Boegeal AM &amp; BR 680</td>
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<tr>
<td>(HT4)</td>
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<tr>
<td>APhS + APS &amp; BR 680</td>
<td>1798</td>
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<tr>
<td>(HT9)</td>
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</tr>
</tbody>
</table>

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Sol-Gel Testing Summary

- Use of sol-gel coatings significantly increased bond strength & durability
- Addition of aminophenyl silane to sol-gel improved lap shear strength at 600°F
- Use of BR 680 primer did not improve bond performance in lap shear test
  - Primer needed for shipping and storing treated parts
- No difference in primer cure temperature (400°F & 600°F)
- Use of “grit-blast/BR 680” process on stainless steel produced extremely weak bonds
- Sol-gel interface is susceptible to thermal degradation at 600°F

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Main objective is to remove the release ply imprint & contaminates while roughening the surface without exposing or damaging fibers.

Existing surface preparations for PMCs include:
- Abrasion with sandpaper
- Grit-blasting

Evaluated process was grit-blasting with 50 micron Al₂O₃ grit.
Effect of Grit-Blasting (50μ Al₂O₃ @ 60 psi) on M40J/PMR-II-50 Composite (30X)

NASA GRC Microscopy
M40J/PMR-II-50 Composite

Solvent wiped @ 40x
Grit-blasted @ 40x
Grit-blasted @ 125x

Solvent wiped @ 80x
Grit-blasted @ 80x
Remnant of lint-free wipe @ 200x

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X-Ray Photoelectron Spectroscopy (XPS)

- Purpose was to verify removal of Teflon-coated peel ply from composite bonding surface
  - Compared grit-blasted to non-grit-blasted
- Increase in % Al, Na, & O in grit-blast sample
  - Due to remnant grit
- F/C ratio decreased after grit-blasting
  - Could be due to removal of Teflon or exposing fibers
- Additional data analysis underway

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XPS Survey Spectra

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<thead>
<tr>
<th>Atomic Percent</th>
<th>Neat Resin</th>
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<tr>
<td>F/C</td>
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<td>0.44</td>
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Lap Shear Strength Using Best Performing Processes

- APhS+APS sol-gel used with Ti & steel specimens
  - BR 680-1 cured at 400°F
- Cytec FM 680-1
  - 4 hrs @ 370°F & 15 in Hg
  - Postcured for 16 hrs at 700°F
- PMR-II-50 RT specimens failed in laminate
  - Bond stronger than composite

Effect of Adherend on FM 680-1 Lap Shear Strength

Summary of Results

- Lower temp, nonautoclave cure identified for FM 680-1
- Use of sol-gel coatings significantly increased adhesive bond performance on stainless steel and Ti-6Al-4V
- Addition of Aminophenyl silane to sol-gel solution significantly increased lap shear strength @ 600°F
- Grit-blasting PMR-II-50 composite with 50μ Al₂O₃ @ 60 psi had mixed results
  - Induced damage into M60J laminates
  - Worked very well on M40J laminates
Future Work

- Fabricate full-scale combustion chamber
- Improve thermal resistance of sol-gel coating
  - Improve failure modes at 600°F

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Acknowledgements

- James Mazza & Brett Bolan, AFRL/MLSA
  - Technical input
- Ken Combs, UDRI (AFRL/MLSC)
  - Performing 600°F testing
- Molly Brown, SOCHE (AFRL/MLSA)
  - Fabrication of CTE strips and RT testing

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