Low-Cost Integrated Composite Seal for SOFC: Materials and Design Methodologies
SECA Core Technology Grant  Oct 04 - Feb 06

Xinyu Huang, Kristoffer Ridgeway, Srivatsan Narasimhan, Yanhai Du, Ken Reifsnider
Connecticut Global Fuel Cell Center, University of Connecticut, Storrs, CT

Chin Ma
Inframat Corp., Farmington, CT

Fong Shu
Physical Acoustics Corporation, Princeton Jct., NJ
Outline

- Concept: integrated multi-layered composite seal
- Coating development: materials selection, fabrication, and screening tests
- Leak testing: methods and initial results
- Summary & future work
- Q & C
General requirements for SOFC seal

### Functional Requirements and Materials Selection Parameters [J. Stevenson]

<table>
<thead>
<tr>
<th>Mechanical</th>
<th>Hermetic (or near hermetic)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimal CTE mismatch (or ability to yield or deform to mitigate CTE mismatch stresses)</td>
</tr>
<tr>
<td></td>
<td>Acceptable bonding strength (or deformation under compressive loading)</td>
</tr>
<tr>
<td></td>
<td>Thermal cycle stability</td>
</tr>
<tr>
<td></td>
<td>Vibration and shock resistance (for mobile applications)</td>
</tr>
<tr>
<td>Chemical</td>
<td>Long-term chemical stability under simultaneous oxidizing/wet fuel environments</td>
</tr>
<tr>
<td></td>
<td>Long-term chemical compatibility with respect to adjacent sealing surface materials</td>
</tr>
<tr>
<td></td>
<td>Resistance to hydrogen embrittlement/corrosion</td>
</tr>
<tr>
<td>Electrical</td>
<td>Non-conductive</td>
</tr>
<tr>
<td>Fabrication</td>
<td>Low cost</td>
</tr>
<tr>
<td></td>
<td>High reliability with respect to forming a hermetic seal</td>
</tr>
<tr>
<td></td>
<td>Sealing conditions compatible with other stack components</td>
</tr>
</tbody>
</table>

Reference: Jeff Stevenson et al, SECA meeting presentation, PNNL
Integrated composite seal concept: IC to IC seal

- Adherends (e.g., stainless steel IC)
- Metallic bond coat
- Stable corrosion resistant oxide (Al2O3) layer formed naturally during APS coating
- Porous ceramic layer (top coat)
- Hermetic filler material (e.g., glass)

Large body of knowledge exists on producing robust ceramic coating, particularly thermal barrier coatings (TBC) on metallic substrates.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>filler infiltration &amp; curing</th>
</tr>
</thead>
<tbody>
<tr>
<td>t = 200 ~ 400 microns</td>
<td>Become an integrated structural unit after coating fabrication</td>
</tr>
</tbody>
</table>
Integrated composite seal concept: IC to ceramic seal

Adherends (e.g., stainless steel IC)

Metallic bond coat

Porous ceramic layer (top coat)

Hermetic filler material (e.g., glass)

Dense ceramic layer (e.g., electrolyte)

Stable corrosion resistant oxide (Al₂O₃) layer formed naturally during APS coating

Pressure

filler infiltration & curing

Pressure

Depending on filler materials, the seal structure can be made either rigid (hard, solid) or compliant (soft, wet)

\[ t = 100 \sim 200 \text{ microns} \]
Potential advantages

Ceramic coating is expected to have
- Good compatibility with filler materials (good wetting, long-term chemical stability)
- Good stability in oxidation and reducing environments
- Low electric conductivity, high dielectric strength
- A porous structure that help retaining low-viscosity filler materials
- Relax requirements on filler materials
  - Wetting stainless steel
  - Short-term and long-term chemically stability in contact with stainless steel
  - Low electric conductivity, high dielectric strength
- Multi-layered structure allows gradual transition of thermo-mechanical properties (functional gradients) from substrate → bond coat → top coat → hermetic filler
  - Higher resistance to mechanical failure
- Low cost fabrication method available
- Integrated design reduces stack assembly cost
Goal and phase I objectives

- The goal for this two-phase effort is to create a unique high-temperature composite solid oxide fuel cell (SOFC) seal and the associated design methodologies to support the SECA Industrial Teams in their efforts to design, manufacture, and market reliable SOFC power generation systems.

- The objectives of the Phase I work are to prove a conceived composite structure and to demonstrate a design methodology using subscale samples.
Our approach

Fabrication

Microstructure & Material properties evaluation

Adherence (e.g., stainless steel)
Metallurgical bond coat
Stable corrosion resistant oxide layer
Hemispheric filler material
Porous ceramic top coat

Mechanical robustness

Seal performance
Outline

- Concept: integrated multi-layered composite seal
- Coating development: materials selection, fabrication, and screening tests
- Leak testing: method and initial results
- Summary
- Q & A
Materials selection

- Stainless steel interconnect and YSZ disks
  - Allegheny Ludlum AL453, Crofer22 APU
  - CoorsTek

- Ceramic coating materials
  - Bond coat (MCrAlY, Ni5Al)
  - Top coat (alpha-Al2O3 + partially stabilized ZrO2)

- Filler glass composition and properties
  - Alkaline earth aluminosilicates
  - Glass property requirements: matching CTE, low softening point, chemically stable, low crystallization rate
  - Coordinates with other CTP efforts on glass formulation: U. Missouri Rolla, U. Cincinnati, and Sandia National Lab.
Thermal expansion curves

![Thermal expansion curves graph](image-url)
Sample size and geometry

- Use 1”~2” button samples for Phase I work
  - Coated button samples for obtaining basic material properties studies, such as wetability, bond strength, oxidation resistance, etc.
  - Thermal cycling, thermal shock, mid-term aging test
  - Electrical conductivity studies
  - Glass infiltration studies
  - Leak testing

- Avoid complex geometry
  - Circular disks to avoid complexity due to sharp corners
Ceramic coating produced via atmospheric plasma spray (APS)

- Relatively low cost (compared to LPPS, VPS, EB-PVD)
- High throughput
- One step fabrication (no additional sintering step required)
- Coating has excellent thermal mechanical robustness
- Amenable to produce functional gradient coating structure

(Picture courtesy of Dr. China Ma, Inframat Corp.)
XRD of APS top coat

SECA coating type 3 (higher Al2O3 contents)

SECA coating type 4
XRD peak identification
Microstructure of APS top coat

Particle flying direction
Mercury intrusion porosimetry (Quantachrome Poremaster 6000)

- Measures distribution of pore volume over a range of pore sizes (0.003-200 microns)
- Based on Washburn equation
  \[ D = \frac{4 \gamma \cos \theta}{P} \]
  where
  - \( D \) = pore diameter
  - \( \gamma \) = surface tension of wetting fluid
  - \( \theta \) = contact angle
  - \( P \) = applied pressure
- Sample is exposed to mercury at increasing pressure up to 60,000 psi
- Volume of mercury that goes into pores in sample measured
Dense substrate attached
Interparticle porosity: 12.5%

Intraparticle porosity: 18.82%
Material screening test

- Basic thermal cycle resistance & high temp aging test to evaluate thermo-mechanical robustness of coating
- Electric resistance of coating/Pt/coating structure using DC or AC method
- Wetting behavior of selected glass and ceramic compositions

Water quench test from 800 °C
High temperature electric conductivity: ceramic coating

800 °C in air, ASR=9.25~320.7 kΩ·cm²
920 °C in air, ASR=2.61~189.1 kΩ·cm²

Increasing YSZ contents
Glass infiltration and curing

- Natural wicking or vacuum/pressure assisted infiltration
  - Porosity before and after glass infiltration
  - Interface morphology

- Curing schedule
  - Maximum temperature limited by furnace and substrate materials
  - Adjust heating/cooling rate and high temperature dwell to suite particular glass: maximize viscosity and avoid excessive crystallization
  - Apply pressure
Glass pellets on coated button sample

796 °C  890 °C  948 °C

1028 °C  1060 °C  1090 °C
Glass ceramic interface

Pictures of glass/ceramic interface shows good wetting
Outline

- Concept: integrated multi-layered composite seal
- Coating development: materials selection, fabrication, and screening tests
- Leak testing: method and initial results
- Summary
- Q & A
Sealing performance: leak rate testing

Objective: measure gas leak rate (sccm) per bond line length (cm) per unit pressure difference (psig)

- Facilitate the study of aging and thermal cycle effect on seal performance:
  - Leak rates v.s. # of thermal cycles
  - Leak rates v.s. hrs of aging time

- Reference: ASTM F 37-00 with controlled temperature and gas environment
Leak rate testing method

Direct leak flow rate measurement
- Measure flow rate of gas supply into sealed chamber
- Allow continuous monitoring of leak rate

Pressure leak-down test
- Sealed chamber initially pressurized, pressure decay recorded
- Effective in ultra-low leak rate regime

- Helium leak detector (mass-spec)
- Electrochemical method
  - monitoring OCV
UConn SOFC seal leak test stand

Figure 2 – SOFC Seal Test Stand Cross-sectional

Figure 3 – Seal Area Cross-Sectional View
UConn SOFC seal test stand

Temperature range: RT to 1100°C
Sample size: up to 5” in dia
Dynamic range (direct flow): 0.01~125 sccm
Mica leak rates generated with UConn SOFC seal test rig

0.1mm Muskovite Paper Mica Leak Rate - CGFCC

Standardized Leak Rate (sccm/cm)

Helium Differential Pressure (psi)

- 100 psi Compression
- 300 psi Compression
- 500 psi Compression
- 700 psi Compression
Room temperature leak test results

Gas leaks primarily through the interfacial path; leak rate through the bulk is about 4 order of magnitudes lower!!
Interparticle porosity 12.5%

Intraparticle porosity 18.82%

Pores do not form connected in-plane leak path

Pores do form connected in-plane leak path

May not need to infiltrate hermetic fillers into the bulk!
High tem leak test : 1” sample, hard glass (4460), matched CTE

Leak found to be insensitive to Compression!
High temp leak test: 2” sample, hard glass (Brow#27), mismatched CTE

INCONEL
16~17 ppm/C

Coated AL453
12~13 ppm/C

Glass may have over crystallized

Leak rate (sccm/100)
Diff pressure (psi)
Temperature C/400
DBae

2.88 sccm/cm
0.25 sccm/cm
As one of the layers in the proposed composite seal structure, a tough APS coating on Fe-Cr stainless steel based low-cost raw materials has been developed and tested.

- The unique micro-cracking pattern/pore structure in the top coat seems to contribute to the superior thermal shock resistance without forming leak paths.

- A flexible SOFC seal testing system has been designed, manufactured, and applied to evaluate composite seal leak performance.
  - Composite seal made with hard glass show brittle failure during thermal cycling.
  - Composite seal made of soft filler glass is being evaluated.
  - Future work: try other oxides and compounds with low melting points.

- At room temperature, the interface is the major leak path.
Summary & future work

Further mechanical testing and modeling work are being planned:

- Crack initiation and propagation resistance: strength and toughness
  - Pull-out test @ RT
  - Three/Four point bend test on a composite beam @ RT
- Localized material properties
  - Vicker’s indentation test
- FEM modeling of simple seal geometry

Ke An, PhD Dissertation, ESM Dept, Va Tech 2002
Acknowledgements

- Travis Shultz, Program Manager, NETL
- Gary Yang, Prabhakar Singh, PNNL
- Eric Jordan, ME Dept., UConn
- Richard Brow, U Missouri Rolla
- Raj Singh, U Cincinnati
- Ronald Loehman, SNL
- Pinakin Patel, Peng Huang, and Dana Kelly, FCE
- James Rakowski, ATI Alleheny Ludlum
- Grover Coors, CoorsTek
Questions and comments?