Ultra High Temperature Thermionic Sensor

NETL Crosscutting Research Review Meeting
Scott Limb(PI), Scott Solberg, Arun Jose, Victor Liu
April 28, 2015

Funded under NETL Crosscutting Research: Development of Novel Architecture for Optimization of Advanced Energy Systems
DE-FE0013062
Program Manager: Barbara Carney

DISCLAIMER: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."
HEAT Sensor Project Goal

**Harsh Environment Adaptable Thermionics**

- Develop sensors that measure process parameters
  - Gasifiers -- harsh fuel, oxidizer and combustion product environment
  - High Temperature (750-1600 °C)
  - High Pressure (up to 1000 psi)

- Develop sensors that are wireless and self-powered
  - Generate their own energy to operate and wirelessly transmit data
  - Avoids wires that may be a reliability or inconvenience concern

*Source: GE Energy*

Thermocouple protection system for gasifiers (NETL website)
HEAT Sensor Project Concept

• Use Thermionic Materials as Sensors
  – Heat induced flow of electrons from a metal surface
  – Thermionic emissions occur at high temperature without need for external heater source

• Thermionic Technology
  – Diodes, Triodes, Tetrodes, etc…
  – Amplifier, Oscillators, Power Generation

The 1946 ENIAC computer used 17,468 vacuum tubes and consumed 150 kW of power.

70-watt tube audio amplifier selling for US$2,680[31] in 2011, about 10 times the price of a comparable model using transistors.[32]
HEAT Sensor Project Plan

• Model and Pattern Thin Film Thermionic Layers
• Develop Experimental System
• Develop High Temperature Hermetic Package
  – Use High Temperature Co-Fired Ceramics (99.9% pure alumina)
  – Adhesive and Hermetic Sealant Development
• Thermionic Measurements
  – Temperature Sensor
  – Pressure Sensor
  – Circuits and Power Generation
Richardson’s Law

\[ J = A_G T^2 e^{\frac{W}{kT}} \]
Pressure Sensor

Simulation

Differential Anode Current vs Pressure

- 800 deg C
- 1000 deg C
- 1200 deg C
- 1400 deg C
- 1600 deg C
Autonomous Power & Wireless Transmission

Wireless Transmission Circuit Example

Power Generation Concept

50 mA/mm² max current
# Vacuum Tubes vs HEATS Platform

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Vacuum Tubes</th>
<th>HEATS Platform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating vacuum level</td>
<td>Similar</td>
<td>Similar</td>
</tr>
<tr>
<td>Package hermetic sealing temperature</td>
<td>&lt;300 °C</td>
<td>&gt; 1300 °C</td>
</tr>
<tr>
<td>Package operating temperature</td>
<td>&lt;300 °C</td>
<td>&gt; 1300 °C</td>
</tr>
<tr>
<td>Package dimensions</td>
<td>~ cm</td>
<td>~ mm</td>
</tr>
</tbody>
</table>
Hermetic Seal Development

- Encouraging initial results using Alumina Paste
  - Fired @ 1350C
  - <3.4e-4 mbar base pressure
  - Our target is <1e-4 mbar

- Planned Improvements
  - Explore application method and firing procedure
  - Seal area and structure modification
  - Decrease paste particle size
  - Add CTE matched high temperature glass filler
Hermetic Seal Development

• Important parameters
  – CTE match (thin glue line)
  – Need melting component to fill in pores (sealing temperature)
  – Surface wettability during curing (additives and surface preparation)
  – Structural thermal stability of substrates

• Secondary importance
  – Paste particle size
  – Drying temperature

Slight separation between fired excess paste blob and disk.

A few obvious cracks

No obvious grain growth

Paste, fired at 1500°C.

Sample after sealing but before any drying

Sample after drying (<300 C bake) Delamination is clearly visible
Hermeticity Testing

- Multiple paste formulations tested by measuring Tungsten oxidation weight gain
  - Package tungsten powder using sealing paste
  - Bake in air for set period of time
- Failed paste formulations showed oxidation of W (yellow) and volume expansion
- Promising paste formulation showed minimal mass gain at prolonged 1200C temperature soaks
  - 1.463 gr W initially
  - 7 mg gain after 130 hrs
  - ~ 1 e-5 bar cc/s ; Spec -- < 1e-7 bar cc/s
- 1mm thick HTCC plates had some curvature after curing
Hermeticity Testing

- Used single layer alumina plate to minimize plate curvature during curing
- Soaked for over 2500 hrs at 1300C.
- Cycled to room temperature 3x and repeatedly cycled between 1000C to 1300C.
- Outgassing was further reduced by an high temperature cycle of 1400C.

![Graph showing hermeticity test results using PARC Paste Formulation @ 1300C.](image)

**Milestone Specification**

- Net Rate of Rise (bar*cc/s)
- Cumulative Soak Time

*After firing, can see that some of sealant material flowed*
Thermionic Oxygen Poisoning

• Thermionic material oxidized
• Determined background vacuum in MTI tube furnace was too high
  – Getters did not prevent oxidation
  – Reduced current emissions observed
• Could not hermetically seal a package without oxidation of the thermionic material
New Test Apparatus

- Converted bell jar evaporator for thermionic testing
- Background pressure – $1 \times 10^{-7}$ mbar vs $1 \times 10^{-4}$ mbar for MTI furnace
- Temperature control up to 1300C for now (will test to 1600C in future)
Data

Thermionic Measurement at 1200 °C

Current (uA) vs. Bias Voltage (V)

- Evaporator
- MTI Furnace
Data – Theory vs Actual

\[ J = A_G T^2 e^{\frac{-W}{kT}} \]

**Measured vs. Computed Device Current**

Cathode area = 1.77 cm\(^2\), gap = 0.15 cm

Current limited by emission (Richardson-Dushman).

Fitted values: \( W_f = 2.866 \text{ eV}, \text{ const} = 39 \text{ A/cm}^2/\text{K}^2 \)
Repeatability

![Graph showing Device Current (µA) vs. Bias Voltage (V) with data points for different temperatures: µA @1215C, µA @1166C.]
Repeatability

Current reading repeatability at selected temperatures

@1115C, 2nd
@1115C, 3rd

Current reading repeatability at selected temperatures

@1166C, 2nd
@1166C, 3rd
Temperature Measurement

Filled markers: device warming
Un-filled markers: device cooling

Re-heated after weekend
## Key Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Device Interconnect</th>
<th>Device Vacuum</th>
<th>Thermionic Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milestone 3</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Hermetic Seal @ Temp</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milestone 4</td>
<td>Zirconia wire</td>
<td>Active pumping</td>
<td>La</td>
</tr>
<tr>
<td>Temperature Sensor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milestone 6</td>
<td>Zirconia wire</td>
<td>Active pumping</td>
<td>La</td>
</tr>
<tr>
<td>Pressure Sensor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milestone 9a</td>
<td>Zirconia wire</td>
<td>Active pumping</td>
<td>La, BaO</td>
</tr>
<tr>
<td>Self powered and wireless</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Milestone 9b</td>
<td>None</td>
<td>Self-contained vacuum with getter</td>
<td>La, BaO</td>
</tr>
<tr>
<td>Self powered and wireless</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>