Life testing of segmented high efficiency thermoelectric couples

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Government sponsorship acknowledged.
Outline

• **Introduction**
  – Evolution of RTG
  – High efficiency thermoelectric couple
  – Evaluating life time performance of thermoelectric couples

• **Component life test**
  – Sublimation life test
  – Thermoelectric properties life test
  – Contact resistance life test
  – Status of TE materials for high efficiency couples

• **Couple life test**

• **Summary**
The evolution of RTGs

**MHW-RTG**
- **TRL 9-10**
- 158 We
- 4.2 W/kg
- 6.6% Efficiency
- > 30 Year life demonstrated
  - LES 8/9, Voyager 1 & 2

**GPHS-RTG**
- **TRL 9-10**
- 283 We
- 5.1 W/kg
- 6.8% Efficiency
- > 18 Year life demonstrated

**SNAP-19**
- **TRL 9-10**
- 40 We
- 3 W/kg
- 6.2% Efficiency
- > 14 Year life
  - Pioneer 10&11, Viking 1 & 2

**MOD-RTG**
- **TRL 3-6**
- 330 We
- 7.7 W/kg
- 6.8% Efficiency (Si-Ge)
- > 14 Year life

**MMRTG**
- **TRL 5-6**
- 125 We
- 2.8 W/kg
- 6.3% Efficiency
  - MSL

**ARTG**
- **TRL 7-8**
- 6-8 W/kg
- > 10% efficiency

- Requires > 12% efficient couple technology

- Ulysses, Galileo, Cassini, New Horizons

Pre-decisional / NASA Internal Use Only

NOTE: Graphics not to Scale
High efficiency thermoelectric couple

Segmented high efficiency thermoelectric couple
(up to 15% efficiency, up to 1273 K hot side operation)
What controls RTGs Lifetime Performance?

1. Fuel decay (Reduced heat from GPHS)
   ~ 0.8%/year decrease in power output

2. Decrease in hot-junction as a result of decreasing heat input
   (smaller DT = lower Carnot efficiency)
   ~ 0.5%/year decrease in power output

3. Main other mechanisms dependent on time and temperature
   • Degradation of thermoelectric properties (lower ZT values)
   • Sublimation losses (increased TE leg electrical & thermal resistance)
   • Thermoelectric couple interfaces (increased electrical contact resistances)
   • Thermal insulation (reduced thermal efficiency)

Decrease in power output:
~ 0.3%/year
(~5% over 14 years)

Total Decrease in power output:
~ 1.6%/year total
(22% total over 14 years of operation)
Establishing life time performance

• **Component life test**
  - Subjects for component life test
    • Sublimation
    • Thermoelectric properties of materials
    • Bonding interfaces
  - Design, fabricate and test coupons to quantify each degradation mechanism and assess kinetics
  - Test duration will depend on kinetics
  - Develop models

• **Couple life test**
  - Steady state nominal and accelerated operating conditions
  - Prototypic single couple and multi-couple assembly

• **Update performance model (DEGRA) and validate predictions**
Component life test
(sublimation life test)
Sublimation suppression

• **Sublimation suppression goal**
  – 10% cross sectional reduction at the hot end of the leg after 14 years operation (2~3% reduction in power output)

![Graph showing sublimation rate vs. legs diameter](image)

- **Leg height**: 1.27 cm

• **Sublimation phenomenon**
  – Most of TE materials used in power generation have peak figures of merit at the temperature where sublimation is a non-negligible mechanism
  – Sublimation leads to reduction of effective cross section, which leads to decrease in power output
  – Sublimed species can condense on cold side, which can cause short circuit on the device.
  – State of practice power generation thermoelectric couples have always some measure of sublimation control.

• **Background on previous sublimation suppression methods**
  – SiGe technology employed $\text{Si}_3\text{N}_4$ thin films
  – $\text{PbTe}$/TAGS technology employed an inert cover gas and solid insulation
  – Skutterudite technology uses opacified aerogel

• **Requirements for sublimation suppression barriers**
  – Chemical stability against TE materials
  – Thermal stability at the operating temperature
  – Withstanding stress during thermal cycling
  – No significant effect on system performance
Beginning of life sublimation rate of bare TE materials in vacuum

Initial baseline sublimation rates of bare TE materials under vacuum

- n-SKD (CoSb$_3$) at 873K
- p-SKD (CeFe$_3$RuSb$_{12}$) at 873K
- Yb$_{14}$MnSb$_{11}$ at 1273K
- La$_{3-x}$Te$_4$ at 1273K
- n-Si$_{0.8}$Ge$_{0.2}$ at 1273K

- All the thermoelectric materials for RTG require some measure of sublimation suppression scheme (need 10$^{-6}$ to 10$^{-7}$ g/cm$^2$/hr)
**Yb\textsubscript{14}MnSb\textsubscript{11} sublimation life test with porous alumina layer at 1273K and 1323K**

- **Nominal**
  - Sublimation rate continuously met the goal during 18 month coupon test.
  - **Accelerated**
    - Accelerated test at 1323K also confirmed sublimation suppression of Yb\textsubscript{14}MnSb\textsubscript{11} with alumina paste layer.
    - In spite of several thermal cycles, sublimation rates remained unaffected.
    - Successfully demonstrated life time control of sublimation of Yb\textsubscript{14}MnSb\textsubscript{11}
Skutterudite sublimation life test with aerogel at 873K

- Sublimation rate continuously met the goal during 6 month coupon test.
- In spite of several thermal cycles, sublimation rates remained unaffected.
- **Successfully demonstrated** life time control of sublimation of skutterudite
Component life test
(TE properties life test)
Stable TE properties for Yb$_{14}$MnSb$_{11}$

5000hr – nominal and accelerated operating conditions (1273 K and 1323K)

All the three TE properties of Yb$_{14}$MnSb$_{11}$ (Seebeck coefficient, electrical resistance, and thermal conductivity) remained unchanged
Stable TE properties for $\text{La}_{3-x}\text{Te}_4$

1500hr – nominal and accelerated operating conditions (1273 K and 1323K)

All the three TE properties of $\text{La}_{3-x}\text{Te}_4$ (Seebeck coefficient, electrical resistance, and thermal conductivity) remained unchanged.
Stable Figure of Merit of $\text{Yb}_{14}\text{MnSb}_{11}$ and $\text{La}_{3-x}\text{Te}_{4}$

- Figure of merit was maintained after aging at either 1273K or 1323K.
- There is no degradation on TE properties of $\text{Yb}_{14}\text{MnSb}_{11}$ and $\text{La}_{3-x}\text{Te}_{4}$ after aging at either 1273K or 1323K.
- Further life test is in-progress.
Component life test
(Contact resistance life test)
A Yb$_{14}$MnSb$_{11}$/Mo/Yb$_{14}$MnSb$_{11}$ coupon showed no measurable contact resistance after 1500 hr at 1273K.
### Status of TE materials for high efficiency couples

<table>
<thead>
<tr>
<th></th>
<th>n-type Skutterudite</th>
<th>p-type Skutterudite</th>
<th>Yb$<em>{14}$MnSb$</em>{11}$ (Zintl)</th>
<th>La$_{3-x}$Te$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum operating temperature</td>
<td>873K</td>
<td>873K</td>
<td>1273K</td>
<td>1273K</td>
</tr>
<tr>
<td>Average ZT</td>
<td>1.01 [873 to 473K]</td>
<td>0.78 [873 to 473K]</td>
<td>0.98 [1273 to 773K]</td>
<td>0.88 [1273 to 473K]</td>
</tr>
<tr>
<td>TE Properties life test</td>
<td>&gt;10,000 hrs at 873 K (from couple test)</td>
<td>&gt;5,000 hrs at 1273K and 1323K</td>
<td>&gt; 1,500 hrs at 1273K and 1323K</td>
<td></td>
</tr>
<tr>
<td>Sublimation suppression</td>
<td><strong>Demonstrated with aerogel</strong> (5× 10^{-7} g/cm$^2$/hr for 6000 hrs at 873K)</td>
<td><strong>Demonstrated with alumina paste</strong> (2× 10^{-6} g/cm$^2$/hr for &gt;15,000 hrs at 1273K)</td>
<td>Not required up to 1173K</td>
<td></td>
</tr>
<tr>
<td>Contact Metallization</td>
<td>&gt;1500 hr aging at 873 K</td>
<td>&gt;1500 hr aging at 1273K</td>
<td>&gt;1000 hr aging at 1273K</td>
<td></td>
</tr>
</tbody>
</table>
Couple life test
Couple Fabrication and Assembly

**Fixturing for Couple Component Fabrication**

**Couple Fabrication – HT stage and LT segments**

Zintl \( La_{3-x}Te_4 \)

p-SKD

n-SKD

**Couple assembled in test fixture**

Sublimation coating applied & thermal insulation installation
Extended testing performed on several segmented couples

~95% of BOL power output was maintained after 5000 hr operation of 800C segmented couples.

Performance decrease with time is highly dependent on maximum operating temperature

Hot side interfaces are main root cause

- Especially significant for Zintl p-leg
Hot Side Interface Stability Challenges

- Hot shoe interface degradation limits lifetime of current couple configurations operating above 1073K hot side temperatures
- Development of diffusion barriers to protect metal/TE contacts is required

Hot shoe metal poisoning in p-Zintl leg of unsegmented couple after > 1000 hour operation at $T_h \sim 1273$ K (composite view)
Hot Side Diffusion Barrier Development

- Several promising candidates have been identified
- Currently doing extended testing at the coupon level
- Planning on integrating diffusion barriers in next series of couples
Extended Testing of 800C and 700C Segmented Couples

- 700C and 800C segmented couples maintained most of BOL power output during extended couple testing
  - 800C segmented couples: ~95% of BOL power output after 5000 hr operation
  - 700C segmented couples: ~97% of BOL power output after 3000 hr operation
- Degradation of p-leg (Zintl) from hot shoe metal poisoning is alleviated when the couples are operated at lower temperature.
# Segmented Couples – Current Status

<table>
<thead>
<tr>
<th>Upper segments</th>
<th>p-Yb$<em>{14}$MnSb$</em>{11}$ Zintl/n-La$_{3-x}$Te$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower segments</td>
<td>p-SKD/n-SKD (Filled Skutterudites)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hot/cold side temperature (K)</th>
<th>1273/473</th>
<th>1173/473</th>
<th>1073/473</th>
<th>973/473</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T$_{SKD}$-interface ~ 873K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| BOL predicted couple efficiency | 13.7% | 12.5% | 11.2% | 10.0% |

<table>
<thead>
<tr>
<th>Comments</th>
<th>Validated at BOL (14.8%) (1500 h to date)</th>
<th>Not fabricated to date</th>
<th>Validated at BOL (11%) Maintained ~95% of BOL power output after 5000hrs</th>
<th>Validated at BOL (10%) Maintained ~97% of BOL power output after 3000hrs</th>
</tr>
</thead>
</table>
Summary

• Component life demonstrated that Skutterudites, Yb$_{14}$MnSb$_{11}$, and La$_{3-x}$Te$_4$ are acceptable for long life operation
  – Vacuum or inert gas operation
  – Life test results to date indicate that these TE materials are ready for couple technology development (further verification is in-progress with extended life tests).

• Developed effective sublimation suppression methods
  – Porous coating on Yb$_{14}$MnSb$_{11}$
  – Aerogel on skutterudites
  – Assessment of sublimation kinetics indicates that the sublimation rate is likely to remain unchanged for the desired life time.

• Segmented couple test demonstrated achieving predicted BOL efficiency

• Lower temperature segmented couples maintained BOL power output during life test
  – 800°C segmented couple: ~ 95% of BOL power output after 5000hr operation
  – 700°C segmented couple: ~ 97% of BOL power output after 3000hr operation

• On-going and future coupon and couples performance life tests will be used to verify degradation rates
Acknowledgements

This research was performed at the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Administration (supported by the NASA Radioisotope Power System Program Office / Technology Advancement Program).