Integration of Advanced Materials and Interfaces for Durable Thermoelectric Automobile Exhaust Waste Heat Harvesting Devices

Y. Sungtaek Ju : PI

Bruce Dunn : co-PI

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Project ID: ACE069

Overview

Timeline

- Start – Oct 2010
- Finish – Sep 2013
- 12% complete

Budget

- Total project funding
  - NSF/DOE : $290K
- Funding received in FY 2011
  - $93K
- Funding for FY 2012
  - $95K

Barriers

D) Component/system durability
C) Themoelectric device/system packaging
B) Scale-up to a practical thermoelectric device
A) Cost

Partners

N/A

Project Objectives - Relevance

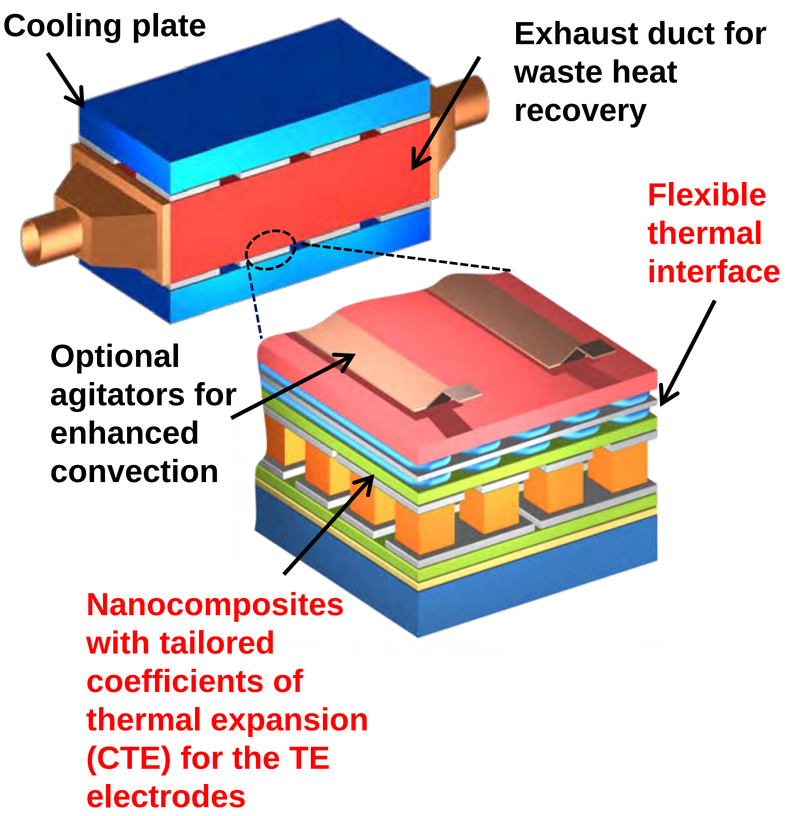
The interfaces between dissimilar materials provide the vital thermal and/or electrical links in TE modules.

The thermomechanical reliability of these interfaces presents a key technical challenge in the implementation of TE waste heat harvesting systems.

- **Develop metal-matrix composites with tailored coefficients of thermal expansion (CTEs) to provide significant design flexibility in minimizing the thermomechanical stress.**
- **Develop associated bonding techniques for the composite electrode layers and the thermoelectric elements.**
- **Develop flexible thermal interfaces to accommodate mechanical vibration and a large mismatch in CTE between exhaust duct walls and TE device cover plates.**

Technical Approaches (I)

- **Metal-matrix composites with tailored CTE**
  - ➢ **Tailor CTE by incorporating novel nanoscale fillers with *negative CTE*.**
  - ➢ **These composites will serve as electrode layers to help minimize thermomechanical stress at their interfaces with TE elements.**
- **Liquid-based flexible thermal interfaces**
  - ➢ **Allow us to achieve good thermal contact without requiring direct solid-solid contacts or large forces.**
  - ➢ **Flexible interfaces can accommodate mechanical stress due to vibration and mismatch in CTE between the exhaust duct wall and insulating TE module cover plates.**



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Technical Approaches (II)

- **Demonstrate the concept by synthesizing composites incorporating nano-fillers with negative CTE using Ag as an initial base matrix material.**
- **The composites will cover expected CTEs of silicides and other TE materials being developed by other teams.**
- **Characterize the thermomechanical and thermal/electrical transport properties of the composites.**
- **Identify low-cost metal matrices to substitute for Ag and optimize the composites.**
- **Develop low-cost bonding schemes for the composites and various TE elements.**
- **Develop designs for liquid-based flexible thermal interfaces and associated sealing/protection schemes.**
- **Explore candidate materials with suitable melting temperatures/ oxidation kinetics and perform early life testing.**

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Major Milestones

Month/Year	Milestone
Sep - 11	Fabrication and thermomechanical characterization of a complete series of nanocomposites that cover the expected range of CTE values for TE materials being developed by other teams. Identify candidate materials for the flexible thermal interfaces and complete a first-generation design for grooves and sacrificial rings through modeling and experimental validation. Design and construct a thermal interface life testing setup.
Sep - 12	Identify and down select low-cost metal (e.g., Al, Ni, or other) that can effectively substitute for Ag in metal-matrix nanocomposites with tailored CTE through material synthesis, microstructural, thermomechanical, and conductivity characterization. Complete preliminary life testing of first generation flexible thermal interfaces and refine the design and down select the interface material.

Research Accomplishments – Summary

Task 1: Synthesis and Characterization of Metal-Matrix Composites with Tailored CTEs

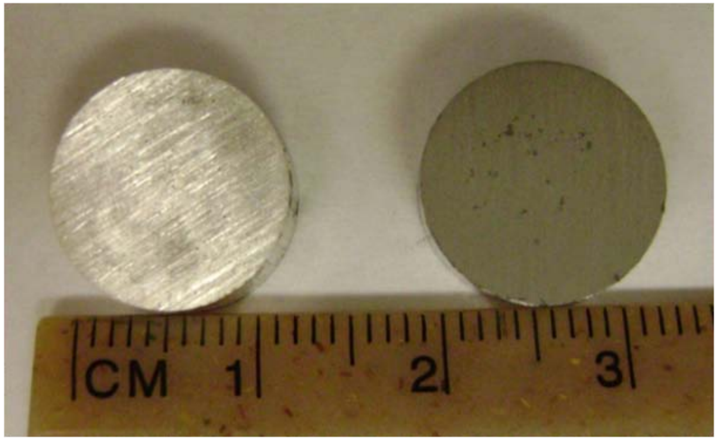
- **Successfully demonstrated a synthesis of ZrW_2O_8 with a negative thermal expansion coefficient.**
- **Successfully synthesized Ag-based composites with ZrW_2O_8 nanofillers and demonstrated initial feasibility for CTE tunability.**
- **Successfully demonstrated feasibility of synthesizing fully dense (< 1% open porosity) composites with CTE < 7 ppm/K and electrical/thermal conductivities ~ 30% of those of bulk Ag.**

Task 2: Development of flexible thermal interfaces

- **Identified potential candidate interface materials (Bi, Sn, salts)**
- **Developed a model and constructed an experimental setup to establish force – liquid morphology relations.**

Task 1 – Research Accomplishments (I)

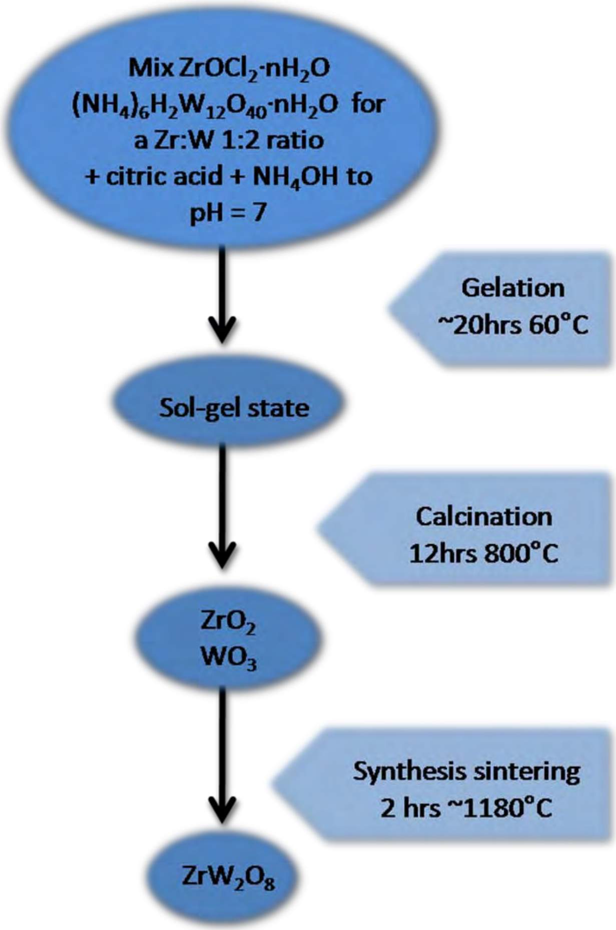
- Successfully synthesized nanoscale fillers of ZrW_2O_8 with negative thermal expansion coefficients (CTE < -10 ppm/C).
- Successfully synthesized Ag/ZrW_2O_8 composites and performed preliminary characterization of their properties.
- Silver (Ag) was selected as the metal matrix in our initial feasibility study due to its high conductivity and our experimental observation that the thermal stability of ZrW_2O_8 is higher in Ag (650 C) than in Cu (500 C).



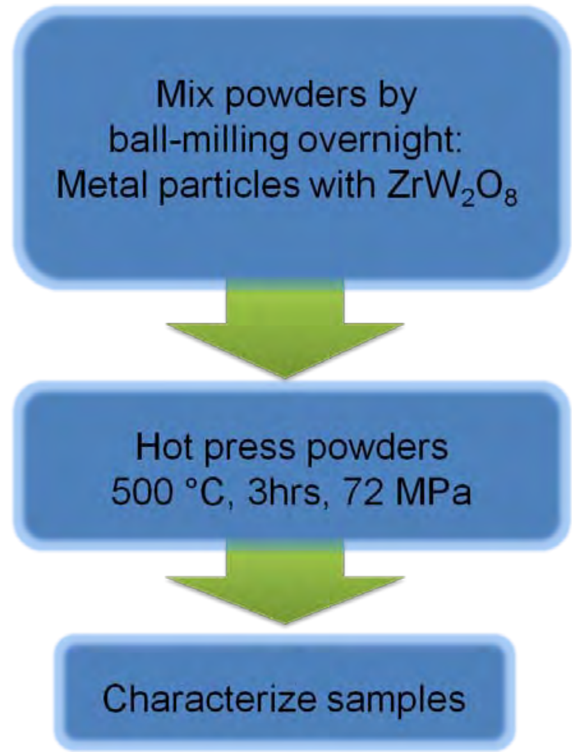
Photographs of pure Ag (left) and Ag/ZrW_2O_8 composite (right) prepared by uniaxial hot-pressing of either Ag powders or mixtures of Ag and ZrW_2O_8 nanopowders, respectively.

Task 1 – Research Accomplishments (II)

Synthesis Process for ZrW_2O_8
(De Buysser et al., 2007)

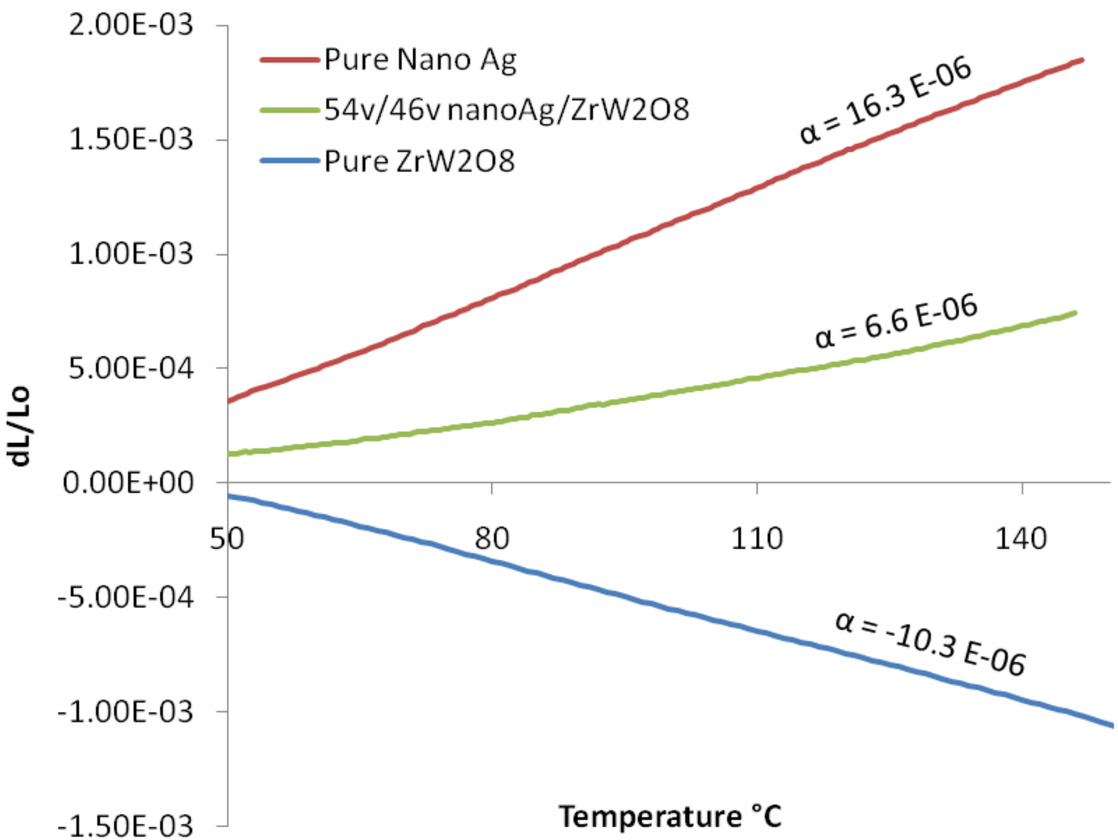


Metal matrix composite fabrication process



Task 1 – Research Accomplishments (III)

Experimental Dilatometry Data



Pure Nano Ag with high CTE

Pure ZrW_2O_8 with negative CTE

Ag/ZrW_2O_8 composite with tuned CTE

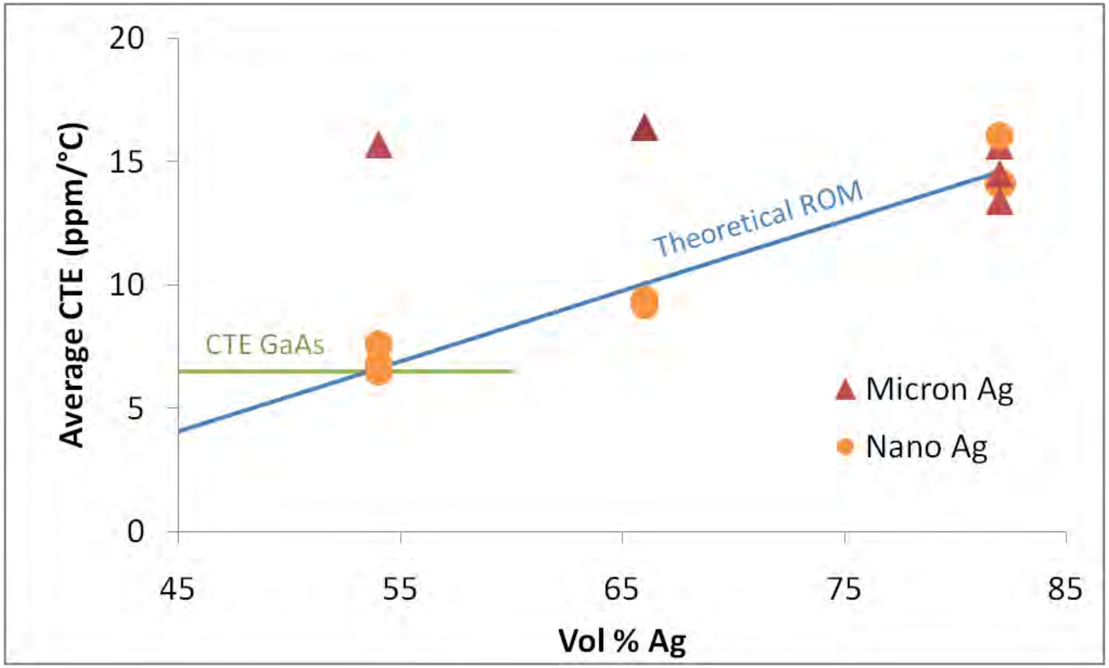
Well-behaved linear thermal expansion behavior.

We will extend the measurements to 400 C.

Task 1 – Research Accomplishments (IV)

Tuning the CTE through Composite Composition

- **The CTEs of Fe- and Mg-based silicides, examples of new low-cost materials being developed in the DOE/NSF program, range 6 ~ 10 ppm/C.**



The measured CTEs of the composites made from Ag and ZrW_2O_8 nanopowders agree with the predicted values from the rule of mixture (ROM).

The composites made from commercial microscale Ag powders contain significant voids and did not show CTE reduction.

Task 1 – Research Accomplishments (V)

Nano-sized powders improve composite properties significantly compared with commercial micrometer-sized powders

- **Lower CTE and lower open porosity**
- **Higher thermal/electrical conductivity**

		Composites made with commercial Ag micropowders		Composites made with commercial Ag nanopowders	
Vol % Ag/ZrW_2O_8	Theoretical CTE (x 10^{-6}/°C)	Measured CTE (x 10^{-6} /C)	Average open porosity (%)	Measured CTE (x 10^{-6} /C)	Average open porosity (%)
54/46	6.6	15.7	18.0	6.9	5.1 ± 3.9
66/34	10.0	16.4	9.9	9.3	0.2
82/18	14.6	14.6 ± 1.1	1.0 ± 0.0	15.1	0.9
100/0	19.7			21.8	0.7

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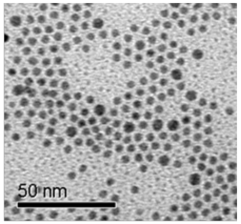
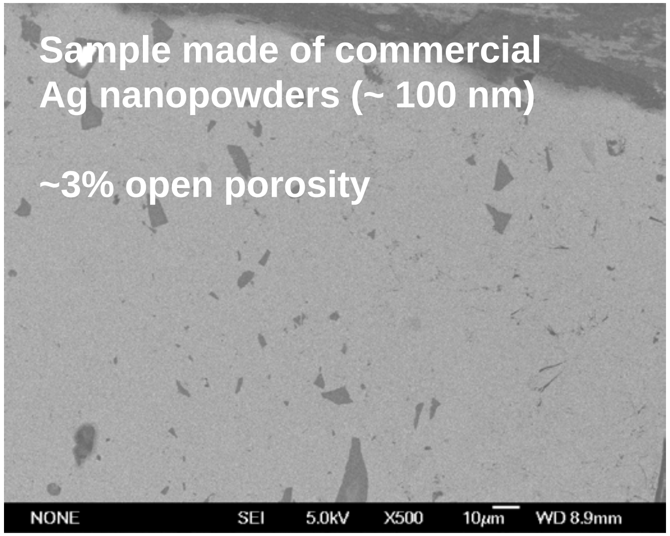
Task 1 – Research Accomplishments (VI)

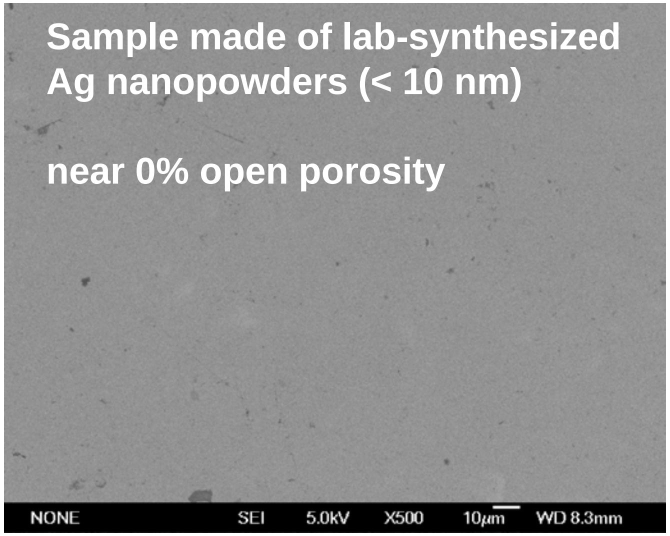
Lab Synthesized Ag Nanopowders

- **Further improvement in composite properties is achieved using lab-synthesized Ag nanosized powders (< 10 nm)**



SEM Images of Metal Matrix Composites (54/46 v/v Ag/ZrW_2O_8)





X 500

Task 1 – Research Accomplishments (VII)

Characterization of the Thermal and Electrical Conductivities

- The conductivities of the composite with CTE of 6.6 x 10^{-6}/K are approximately 3.5x smaller than those of bulk Ag samples.
- Part of the reduction in the conductivities may be due to small grain sizes (next slide).
- Further process optimization and thermal treatments will be pursued.

	Thermal Conductivity (W/m K)		Electrical Conductivity (S/cm)	
Vol% Ag/ZrW_2O_8	Commercial Ag nanopowders (< 100 nm dia.)	Lab Synthesized Ag nanopowders (< 10 nm dia.)	Commercial Ag nanopowders (< 100 nm dia.)	Lab Synthesized Ag nanopowders (< 10 nm dia.)
54/46	76	120	1.1 x 10^5	2.0 x 10^5
100/0	160	220		

*Standard electrical conductivity of pure bulk Ag is 6.8 x 10^5 S/cm

*Standard thermal conductivity of pure bulk Ag is 428 W/m·K

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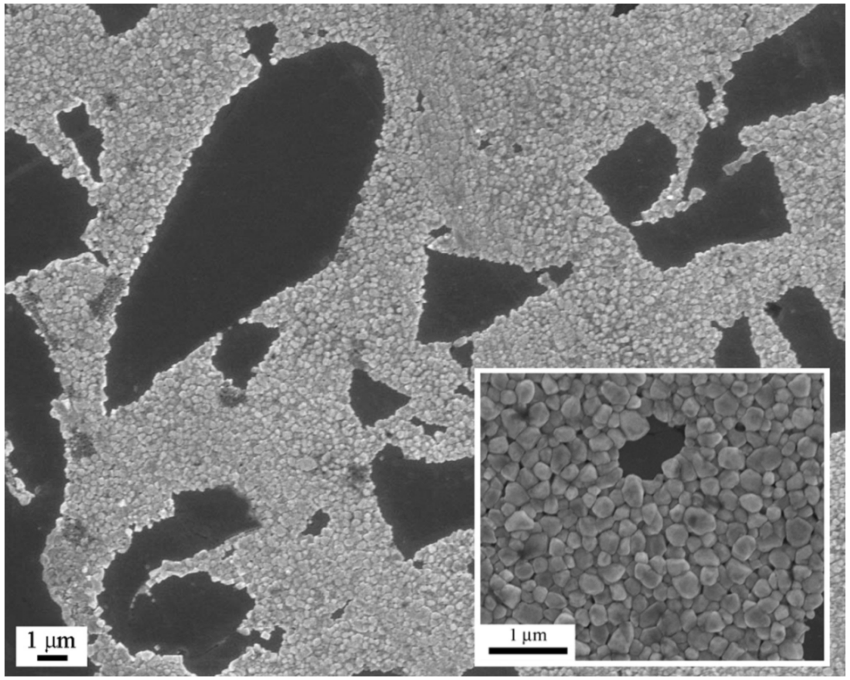
Task 1 – Research Accomplishments (VIII)

High Resolution SEM Characterization

High resolution SEM images of cross-sectioned 54/46 vol% Ag/ZrW_2O_8 composite having 3 % open porosity.

Dark phases are segregated oxide within the Ag matrix.

The average Ag grain diameter is 0.25 ± 0.06 µm.

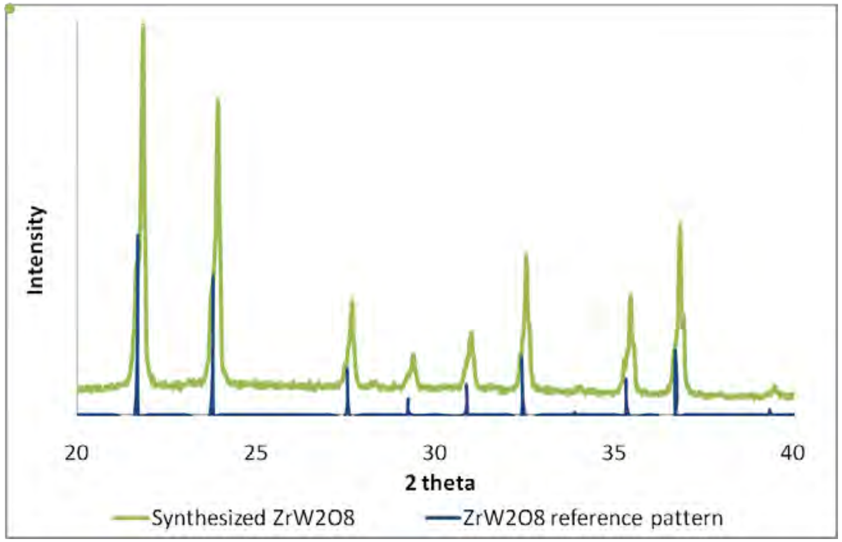


Task 1 – Research Accomplishments (IX)

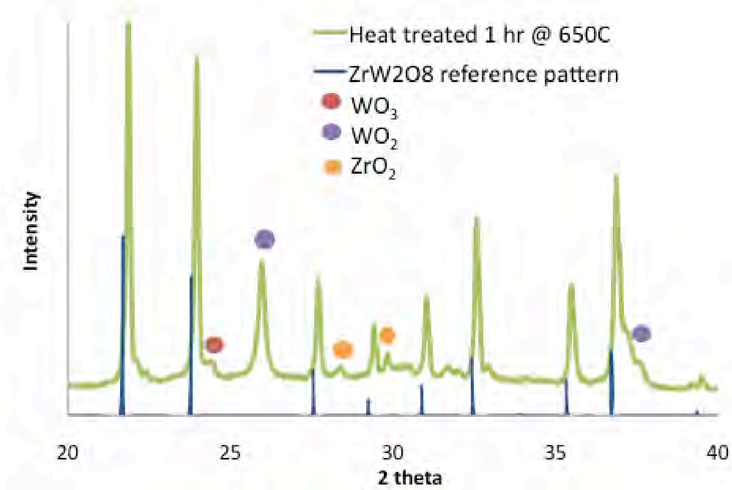
Preliminary Thermal Stability Testing

- The Ag/ZrW_2O_8 composites exhibit an onset of thermal decomposition at approximately 650 C into tungsten oxides and ZrO_2.
- This may be acceptable given the appreciable temperature drop between the exhaust gas and the TE module top plate.
- We will pursue substituting Mo to further increase the thermal stability of the nanofillers.

XRD peak patterns of as synthesized ZrW_2O_8 powder



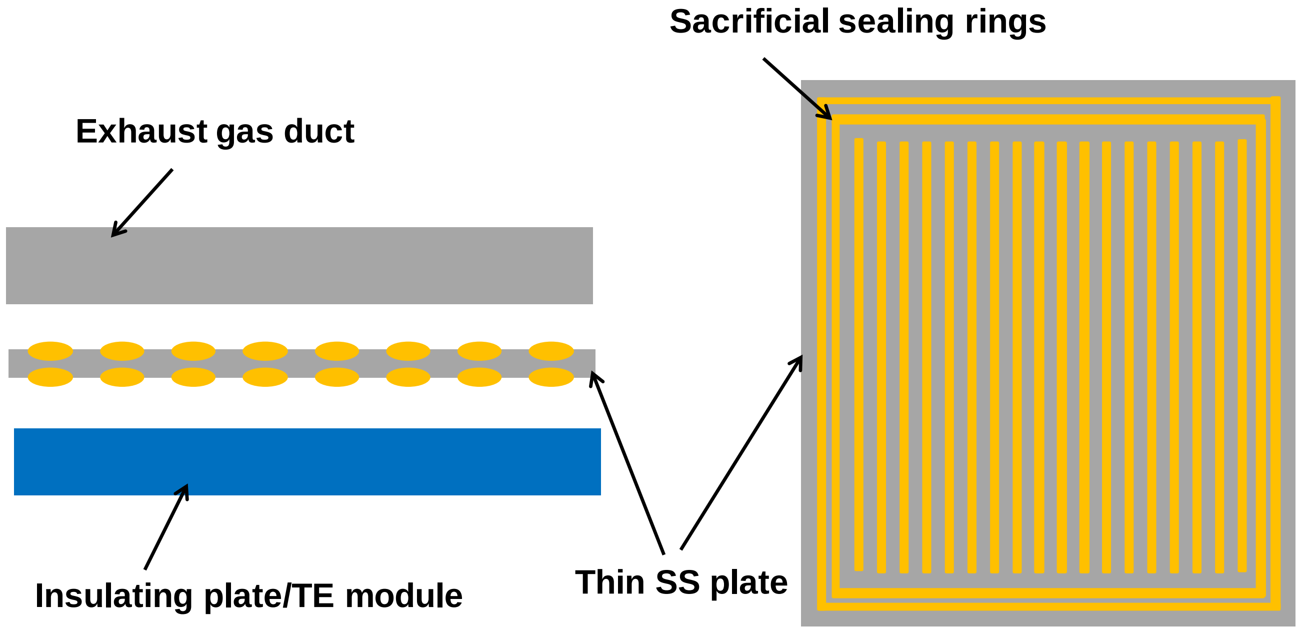
After heat treating at 650 C for 1 hr.



Task 2 – Research Accomplishments (I)

Liquid-Based “Flexible” Thermal Interface

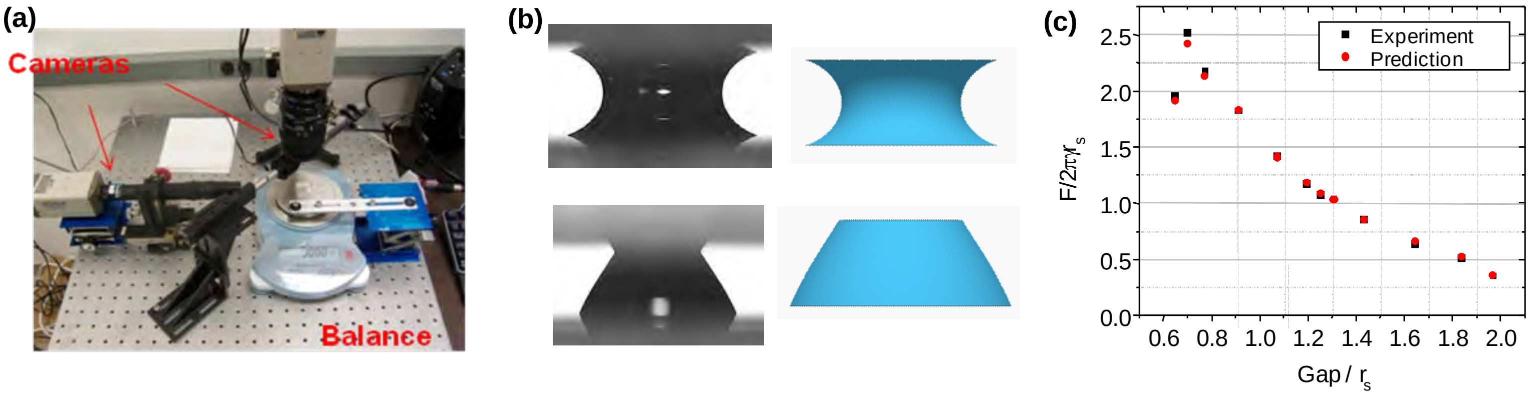
- Formulated a general approach to implementing a flexible thermal interface.
- Parallel grooves are etched into a stainless steel (SS) plate.
- Wires of a soft low-melting-point metal (Bi, Sn, etc) are placed on them.
- At elevated temperatures, the wires melt and form liquid interfaces.
- Sacrificial sealing rings protect the inner metal from oxidation and mass loss.
- Solidified metal may crack but can be perfectly healed when re-melted.



Task 2 – Research Accomplishments (II)

Clamping Force – Liquid Morphology Relations

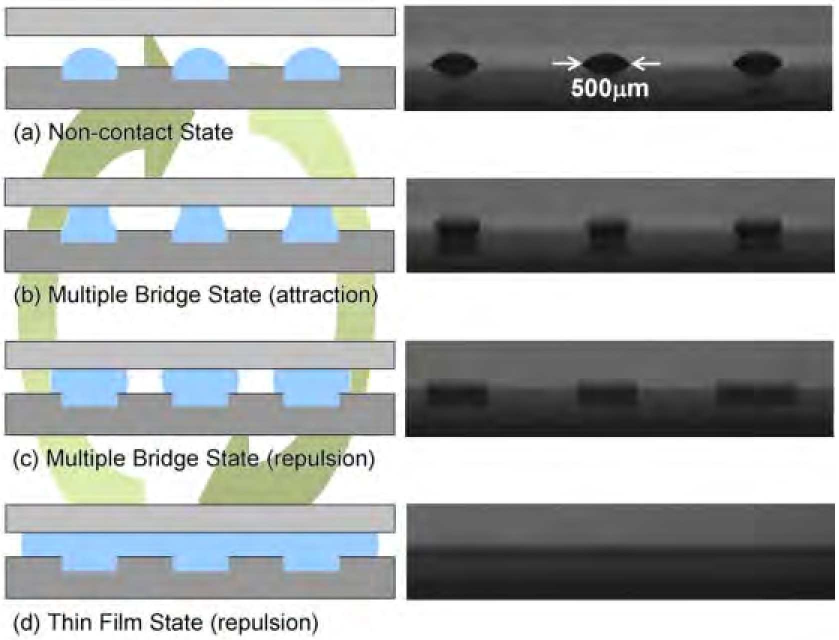
- Implemented an experimental setup to establish the relationships between the applied loading pressure and liquid morphology.
- Video microscopes and an analytic balance are used to simultaneously measure the applied force and liquid morphology.
- As an initial test, water/glycerin mixtures were used as a test liquid.
- The measured force-gap relation and liquid morphology agree well with predictions obtained using the surface energy minimization algorithm.



Task 2 – Research Accomplishments (III)

Reversible Changes in Liquid Morphology (Prior Work)

- **Our prior work demonstrated reversible changes in the morphology of a liquid confined in microchannels.**
- **As the gap between the two parallel plates are reduced, the liquid transforms from discrete droplets, to discrete liquid bridges, and finally to a continuous liquid film.**
- **Our on-going work investigates how solidification-melting processes influence such morphology transitions under constant clamping pressure.**



Cha and Ju, Applied Physics Letters (2009)

Task 2 – Research Accomplishments (IV)

Candidate Materials for Flexible Thermal Interfaces

- **We have performed a literature survey to identify promising candidates (at present, Bi, Sn, and mixtures of nitrates of Na, K, and Ca).**

- **Evaporation Loss:**

  - **The vapor pressure of Bi and Sn at 700 K is << 1 mPa (Geiger et al., 1987; Massey et al., 2004).**
  - **The evaporation rate estimated using the kinetic theory is $<5\times10^{-11}$ m^3/m^2 s. This is equivalent to the loss of a liquid ring of width <1 mm at 100 μm thickness over 15-year period (2-hr driving each day).**

- **Oxidation: Based on the existing oxidation kinetics data (Tahboub et al., 1979), we estimate the total thickness of oxide formed to be < 200 μm over the 15-year life span.**

- **We project that we may effectively address evaporation and oxidation by using sacrificial rings. We will perform a life testing to make preliminary assessment for further development.**

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Collaborations

- **Jet Propulsion Laboratory, NASA:**
  - **On-going collaboration on nanostructured TE materials.**
  - **Technical guidance on the bonding and reliability testing of interfaces between the nanocomposites and TE elements.**
  - **Technical guidance/discussion on the design and testing of flexible thermal interfaces.**
  - **Will obtain TE element samples for later bonding technique development in FY12-13.**

- **HRL/GM:**
  - **Initiated discussions to identify potential collaboration opportunities for technology transfer on thermal energy harvesting and storage.**

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Proposed Future Work (II)

Task 1: Metal Matrix Nanocomposites with Tailored CTE

- **Synthesize and characterize a complete set of Ag-based composites that cover a wide range of CTE values expected of new TE materials and firmly establish the technical feasibility.**
- **Replace the relatively expensive Ag with other metals such as Al or Ni.**
- **Building on the current work on Ag-based composites, fabricate and characterize composites with these substituted metals for down selection.**
- **Improve conductivities through optimization of processing conditions and thermal treatments**
- **If necessary, evaluate substitution of Mo for W into ZrW_2O_8. The resulting compound, $ZrMo_xW_{2-x}O_8$, is expected to have better thermal stability than ZrW_2O_8.**

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Proposed Future Work (II)

Task 2: Flexible Thermal Interfaces

- ❖ Complete literature survey and select 2~3 candidate materials for preliminary life testing
- ❖ Construct life testing set up (automated thermal cyclers integrated with force clamps and video microscopes)
- ❖ Expand the models to predict the morphology and thermal interface resistance of flexible interfaces made of the selected materials as a function of loading pressure.
- ❖ Experimentally validate the models and use them to optimize design parameters (the length and width of grooves, gap between the duct wall and TE module cover plate).

Summary

Relevance: Composites with tailored CTEs and flexible thermal interfaces will offer significant design flexibility in thermomechanical design of TE modules.

Approach: The metal matrix composites incorporate nanofillers with negative thermal expansion to achieve widely tunable CTEs to match various TE materials. The flexible thermal interfaces utilize low-melting-point metal or salts to minimize thermo-mechanical stress due to CTE mismatch between duct walls and TE module cover plates.

Accomplishments: Successfully demonstrated the synthesis of fully-dense Ag-based nanocomposites with CTE < 7 ppm/K and characterized their properties. Identified material candidates for flexible interfaces and constructed a model/experimental setup to establish load-morphology relations. Journal publications and technical presentations are planned.

Collaborations: Initiated/continued technical interactions with JPL, a leading research organization for TE energy harvesting.

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