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14. ABSTRACT
Thermoelectric generators offer the potential for effective waste heat recovery in combustion applications (e.g. engines). However, traditional manufacturing of TEGs involves assembly and integration processes which lead to performance degradation and high costs. Additive manufacturing methods of semiconductor energy conversion materials could lead to higher efficiency, cost-effective energy technologies. This project investigated additive laser sintering and melting of thermoelectric materials. The results advance semiconductor materials processing

15. SUBJECT TERMS
thermoelectric, additive manufacturing, selective laser melting, half-Heusler

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Report Title

Final Report: W911NF-12-R-0012-03: STIR: Next Generation Additive Manufacturing: Laser Sintering & Melting of Thermoelectric Materials

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Thermoelectric generators offer the potential for effective waste heat recovery in combustion applications (e.g. engines). However, traditional manufacturing of TEGs involves assembly and integration processes which lead to performance degradation and high costs. Additive manufacturing methods of semiconductor energy conversion materials could lead to higher efficiency, cost-effective energy technologies. This project investigated additive laser sintering and melting of thermoelectric materials. The results advance semiconductor materials processing knowledge to enable flexible manufacturing and device design of thermoelectric generators. The project resulted in the first-ever demonstration of selective laser melting on thermoelectric half-Heusler material. Challenges associated with thermoelectric material powder morphology were overcome to enable spreading of thin (~100 μm thick) layers. Multiple samples were produced in a layer-by-layer additive manufacturing approach. Changes in material phase occurred during laser processing. While the original half-Heusler phase could be regained through a post-processing annealing step, the phase change may indicate a critical challenge with selective laser melting of half-Heusler materials. Future work necessitates a comparison of phase changes in half-Heusler materials to other thermoelectric material in order to determine which materials may be most compatible with the selective laser melting process.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper
03/27/2017	1 Nicholas Batista, Ahmed El Desouky, Joseph Crandall, Shanyu Wang, Jihui Yang, Saniya LeBlanc. Powder metallurgy characterization of thermoelectric materials for selective laser melting, TechConnect World Innovation Conference & Expo. 15-MAY-17, Washington, DC. : ,
03/27/2017	2 Haidong Zhang, Ahmed El Desouky, Shanyu Wang, Michael Carter, Nicholas Batista, Joseph Crandall, Jihui Yang, Saniya LeBlanc. Selective laser melting of thermoelectric materials, International Conference on Thermoelectrics. 30-JUL-17, Pasadena, CA. : ,

TOTAL: **2**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received	Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Nicholas Batista	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Ahmed El Desouky	0.17
Shanyu Wang	0.22
Haidong Zhang	0.00
FTE Equivalent:	**0.39**
Total Number:	**3**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Saniya LeBlanc	0.11	
Jihui Yang	0.00	
FTE Equivalent:	**0.11**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Statement of Problem:
Thermoelectric generators offer the potential for effective waste heat recovery in combustion applications (e.g. engines). However, traditional manufacturing of TEGs involves assembly and integration processes which lead to performance degradation and high costs. Additive manufacturing methods of semiconductor energy conversion materials could lead to higher efficiency, cost-effective energy technologies [1]. This project investigated additive laser sintering and melting of thermoelectric materials. The results advance semiconductor materials processing knowledge to enable flexible manufacturing and device design of thermoelectric generators.

Summary of Most Important Results:
The project resulted in the first-ever demonstration of selective laser melting on thermoelectric half-Heusler material. Challenges associated with thermoelectric material powder morphology were overcome to enable spreading of thin (~100 µm thick) layers. Multiple samples were produced in a layer-by-layer additive manufacturing approach. Changes in material phase occurred during laser processing. While the original half-Heusler phase could be regained through a post-processing annealing step, the phase change may indicate a critical challenge with selective laser melting of half-Heusler materials. Future work necessitates a comparison of phase changes in half-Heusler materials to other thermoelectric material in order to determine which materials may be most compatible with the selective laser melting process.

The results will be presented through oral presentations and papers at two conferences. An abstract titled “Powder Metallurgy Characterization of Thermoelectric Materials for Selective Laser Melting” has been accepted to the 2017 TechConnect World Innovation Conference and Exposition [2]. An abstract titled “Selective Laser Melting of Thermoelectric Materials” has been submitted to the 2017 International Conference on Thermoelectrics [3].

1. A. El Desouky, M. Carter, M.A. Andre, P.M. Bardet, S. LeBlanc, “Rapid Processing and Assembly of Semiconductor Thermoelectric Materials for Energy Conversion Devices,” Materials Letters, (2016).
2. N. Batista, A. El Desouky, J. Crandall, S. Wang, J. Yang, S. LeBlanc, “Powder Metallurgy Characterization of Thermoelectric Materials for Selective Laser Melting,” 2017 TechConnect World Innovation Conference and Exposition, Washington, DC, May 14-17. (abstract accepted for oral presentation, manuscript submitted)
3. H. Zhang, A. El Desouky, S. Wang, M. Carter, N. Batista, J. Crandall, J. Yang, S. LeBlanc, “Selective Laser Melting of Thermoelectric Materials,” 2017 International Conference on Thermoelectrics, Pasadena, CA, July 31-August 3. (abstract submitted)

Methods, Results & Discussions, Conclusions, and Figures are included in the attachment.

Technology Transfer

These results have been discussed with Dr. Patrick Taylor:

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US Army Research Laboratory
Sensors and Electron Devices Directorate
Power Components Branch
Attn: RDRL-SED-E (Taylor)
2800 Powder Mill Road
Adelphi, MD 20783
OFC: (301)-394-1475
FAX: (301)-394-0310

Project Title:

Next Generation Additive Manufacturing:
Laser Sintering & Melting of Thermoelectric Materials

Project Personnel:

Saniya LeBlanc, Assistant Professor
Ahmed El Desouky, Postdoctoral Scientist
Department of Mechanical and Aerospace Engineering
The George Washington University

Jihui Yang, Associate Professor
Shanyu Wang, Postdoctoral Scientist
Materials Science and Engineering Department
University of Washington

Project Dates: March 1, 2016 to November 30, 2016

I. List of Figures

II. Statement of Problem

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IV. Methods

The material used for this study was a half-Heusler, ZrNiSn. The ZrNiSn samples were prepared by arc melting followed by annealing. High purity Zr foil (99.95%, Alfa Aesar), Ni powders (99.999%, Alfa Aesar), and Sn shots (99.999%, Alfa Aesar) were used as raw materials. The Ni powders were melted into small shots with sizes of 1-5 mm using arc melting (SA-200, MRF Inc., USA). The Ni shots, Zr foils, and Sn shots were loaded into a water-cooled Cu crucible for arc melting under an Ar atmosphere (SA-200, MRF Inc., USA). The congealed melts were re-melted three times after turning them over to ensure homogeneity. The obtained ingots were vacuum sealed in quartz tubes, then annealed in a box furnace at 900 °C for 168 h. After annealing, the ingots were crushed, hand grounded into fine powders (<100 µm). The phase identity and purity of bulk samples were determined by powder X-ray diffraction (XRD, Bruker D8 Advance, Germany) using the Cu K_α radiation (λ = 1.5406 Å).

Selective laser melting relies on spreading thin (~50 µm thick) layers of powder in which the particles are close-packed; the spreading ability is influenced heavily by the powder particle morphology and size distribution. The ZrNiSn powder morphology and particle size distributions were analyzed. Particle size distribution was determined by imaging samples of the powder in a scanning electron microscope. The images were analyzed with ImageJ, an open-source image processing tool, to determine the particle size distribution. Powder spreading is analyzed by spreading powder in stainless steel plates with 100-300 µm deep depressions. Spreading is done with both a blade and roller.

Selective laser melting of the powders was conducted with a custom-built laser system. The LeBlanc Lab's in-house system is designed to work with small amounts of material since most new materials are only available in small quantities. (Commercial selective laser melting equipment requires large power quantities, thus precluding studies of new materials.) The system uses a continuous wave, ytterbium fiber laser (IPG Photonics YLR-100-AC-Y11; 1070 nm, 50 µm spot size) with variable power 0-100W. The laser is scanned using a mid-power scanner with an F-theta lens mounted on an adjustable height platform. The control system combined with the scanner allows control of the laser scan pattern, hatch distance, and scan speed. The samples are processed in inert gas.

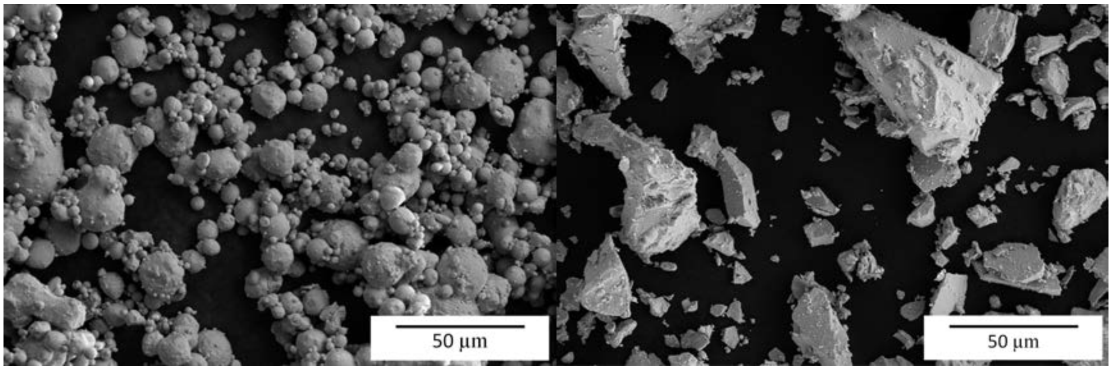
Fine powders (<100 µm diameter) were evenly spread inside a thin stainless steel ring which served as the sample container for one layer. The rings were stacked on top of each other to form a powder bed for the desired number of additive layers. The thickness for each layer was about 150 µm including the ring (50 µm) and the adhesive tape (~100 µm) between two rings. Each layer of powder was spread manually. The laser scanned the powder bed surface in a pre-designed pattern. In this proof of concept work, the pattern was a circle with a radius of 4 mm. The laser power was 30 W with 350 mm/s scan speed and 25 µm hatch distance. The parameters were chosen to thoroughly melt each layer but minimize the energy density, thus avoiding rough sample surfaces or sample bending. After each layer of powder was deposited, the laser repeated the scan; after 10 layers, a flat disk with a diameter of 8 mm and thickness over 1 mm was formed. The processing was done in an N_2 environment to reduce the likelihood of oxidation.

V. Results and Discussion

Powder characterization:

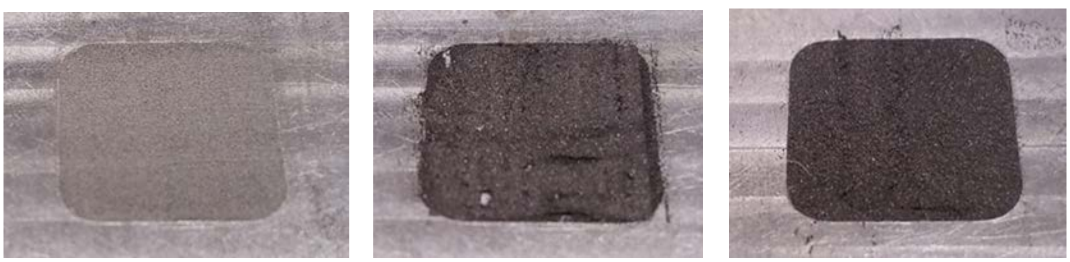
Typical laser powder bed fusion powders have particles with spherical morphologies. Irregular shaped powder with large particle size distribution can mechanically interlock during the spreading process, causing powder lift-off during spreading. On the other hand spherical shaped powder does not interlock. Friction also plays and important role as spherical particles have less particle-to-particle contacts which enhances the powder's ability to flow and spread. As shown in Figure 1, the ZrNiSn powder particles have irregular morphology with varying aspect ratios. The ZrNiSn has a large particle size distribution, and the majority of particles are smaller than 5 µm in diameter. The impact of these characteristics is shown in Figures 2 and 3. The ZrNiSn powder cannot be spread into a uniform layer unless the layer is at least 300 µm thick and spread with a roller. Even for thick layers, the powder had to be re-applied multiple times to fill in gaps. In the laser additive manufacturing process, thin (40-100 µm) layers are required.

These results demonstrate the need to engineering the ZrNiSn (or any new material) powder such that spherical particles are available for the laser processing step. Typically, the spherical morphology is achieved through gas or water atomization. However, the limitations of the atomization process make it undesirable for thermoelectric materials. A newer process, plasma spheroidization is more promising. **This work resulted in the formation of an industry collaboration which will allow the LeBlanc Lab to attempt plasma spheroidization of thermoelectric materials.** The white paper for this new endeavor is attached in the appendixes of this report.



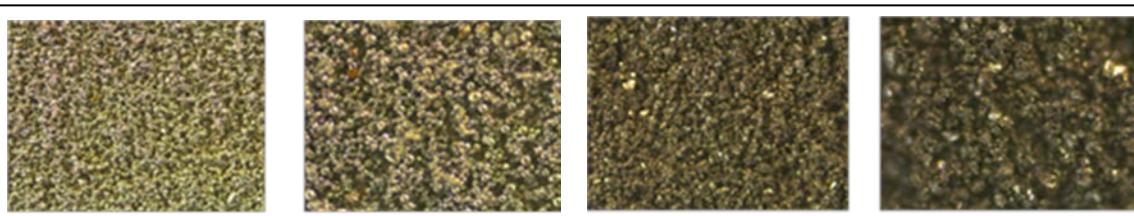
(a) (b)

Figure 1. Scanning electron micrographs of (a) standard stainless steel SS340 atomized powder used in typical laser powder-bed fusion and (b) half-Heusler ZrNiSn powder used in this study.



(a) (b) (c)

Figure 2. Camera images showing top surfaces of (a) standard stainless steel SS340 powder spread in a 100 µm layer, (b) half-Heusler ZrNiSn powder spread in a 100 µm layer, and (c) half-Heusler ZrNiSn powder spread in a 300 µm layer.

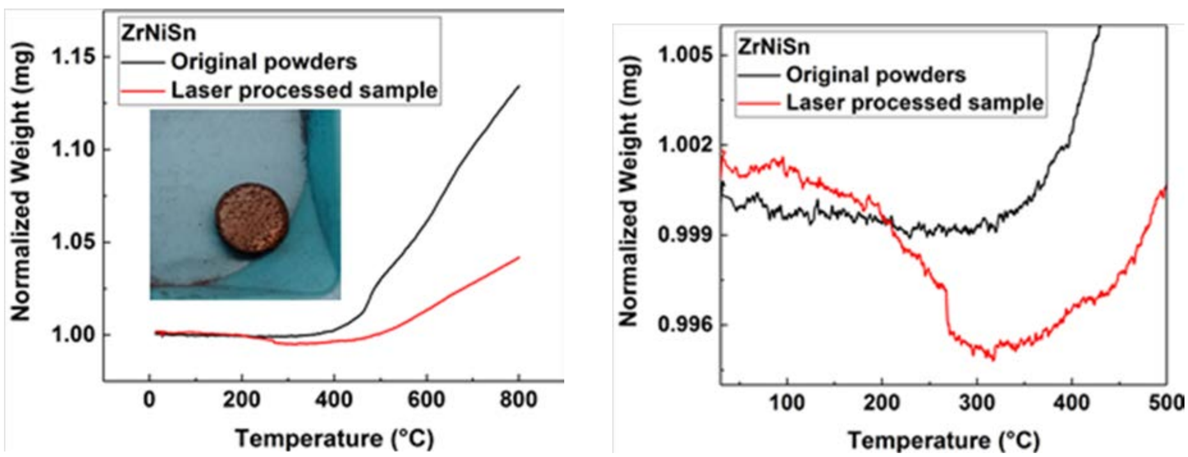


(a) (b)

Figure 3. Top view, optical microscope images (5x on left and 10x on right) of (a) stainless steel powder spread in 100 µm layer and (b) half-Heusler ZrNiSn powder spread in a 300 µm layer. The loss of focus in the far right image shows that the layer of powder is not entirely uniform, a result which is probably due to partial powder lift-off during the spreading process.

Laser processing characterization:

The laser processing resulted in a disk-shaped ingot with a flat and porous surface (see inset of Figure 4a). The ingot was gently ground into a powder and compared with the original unprocessed powders through thermogravimetric analysis (TGA). The result shown in Figure 4a demonstrates a similar trend for both powders. They started to gain weight from around 320ºC; the increase in mass suggests oxidation processes, indicating the processing environment was not O_2 free in spite of the N_2 purge steps. Nevertheless, the similarity in the two curves suggests composition was preserved for the majority of the laser processed powders. Figure 4b is a close-up view of the two curves from 30 to 500ºC. It shows the processed powders experienced a small mass decrease between 100 and 320ºC while the mass of the original powders was relatively stable in the same range. The TGA result suggests the processed sample has some impurity, indicating a small amount of decomposition due to the laser processing.



(a) (b)

Figure 4. Thermogravimetric analysis of laser processed material and starting material. (a) Comparison of the original, starting powder (black) and laser processed sample (red). Inset of (a) shows the optical image of the formed sample from laser-processed powder additive manufacturing. The sample has a diameter of ~8 mm, and a thickness over 1 mm. (b) Close-up showing laser processed sample weight decreased between 100 – 320ºC.

Phase characterization:

All the peaks in the X-ray diffraction (XRD) pattern corresponding to the as-fabricated ZrNiSn sample could be well indexed to the cubic half-Heusler with a space group F43-m (see Figure 5). There are small amounts of impurity phases, such as Ni_3Sn_4, which are normally observed in ZrNiSn samples even after long annealing times. After laser melting, the single-phase ZrNiSn decomposes into multiple phases including Ni_3Sn_4 and full-Heusler $ZrNi_2Sn$ due to the incongruent melting and complex phase diagram [4] shown in Figure 6. The solidification of ZrNiSn melt will first form the binary phases and then be followed by peritectic reactions. These results indicate the phase transformation could be completed if an annealing step were done after the laser melting process.

Further powder XRD analysis on the laser-processed and unprocessed (annealed) samples confirmed the TGA results, as shown in Figure 5. The laser processing was performed at different powers of 25 W, 35 W and 40 W with all other parameters held the same, and the powder XRD shows consistent results for all three powder levels. Figure 6 shows that the majority of the laser-processed powder is still in the original ZrNiSn phase after laser melting. After laser processing, the sample also consists of a small amount of decomposition phases

Ni_3Sn_4, Ni_3Sn_2, along with a ZrO_2 phase. The laser-induced decomposition reaction during the melting process therefore involves O_2 and can be described as: $6ZrNiSn+6O_2 \rightarrow 6ZrO_2+Ni_3Sn_4+Ni_3Sn_2$. These results are consistent with the TGA results: some oxidation occurred since the process was not in a strict O_2 free environment in spite of the N_2 gas purging.

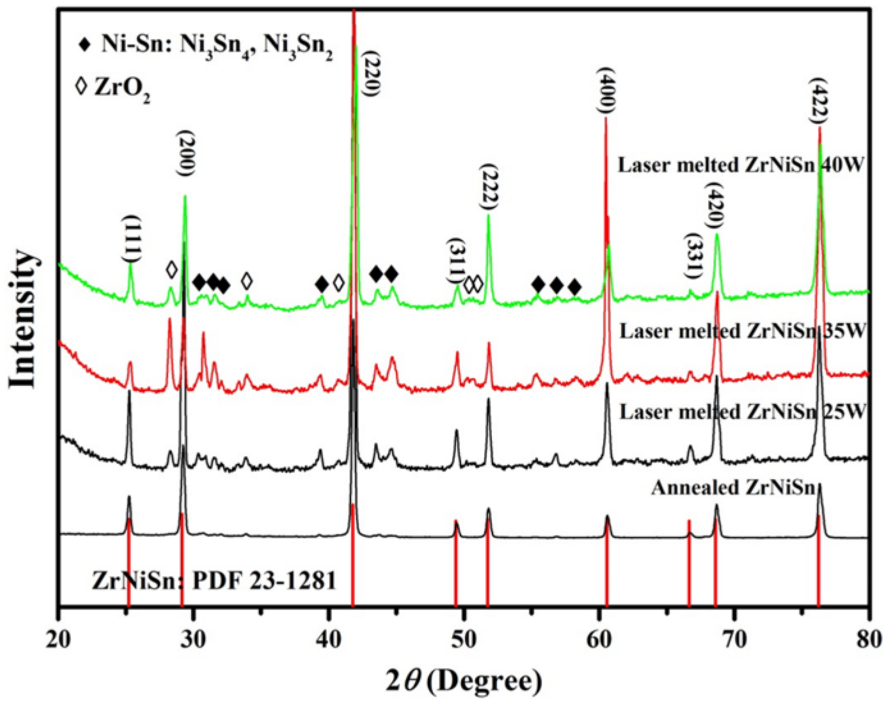


Figure 5. Powder XRD for the laser-processed samples at 25 W, 35 W, 40 W, along with the unprocessed powders.

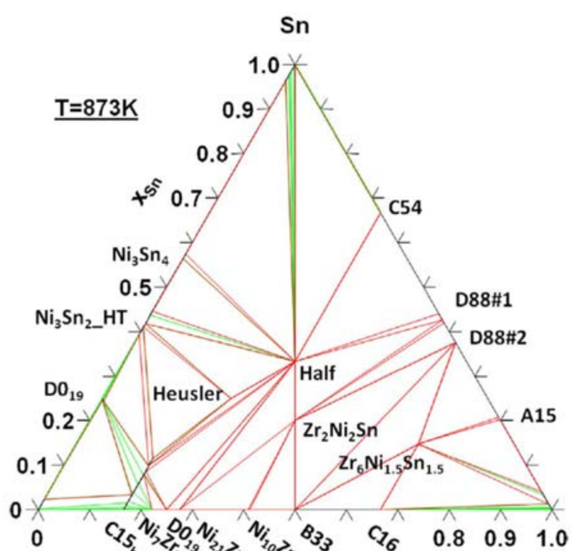


Figure 6. Ternary phase diagram of Zr-Ni-Sn reproduced from [4].

VI. Conclusion

This Army Research Office Short-term Innovative Research award resulted in the first-ever demonstration of selective laser melting on thermoelectric half-Heusler material. The results indicate additive manufacturing of mid- to high-temperature thermoelectric materials is indeed feasible. Using this approach, the geometry of thermoelectric generators could be tailored to maximize performance in waste-heat recovery applications.

VII. Bibliography

1. A. El Desouky, M. Carter, M.A. Andre, P.M. Bardet, S. LeBlanc, "Rapid Processing and Assembly of Semiconductor Thermoelectric Materials for Energy Conversion Devices," *Materials Letters*, (2016).
2. N. Batista, A. El Desouky, J. Crandall, S. Wang, J. Yang, S. LeBlanc, "Powder Metallurgy Characterization of Thermoelectric Materials for Selective Laser Melting," 2017 TechConnect World Innovation Conference and Exposition, Washington, DC, May 14-17. *(abstract accepted for oral presentation, manuscript submitted)*
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