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Low-Cost Structural Thermoelectric Materials: Processing and Consolidation

by Mark A Tschopp, Kris A Darling, Mark A Atwater, Laszlo J Kecskes

ARL-TR-7167 January 2015

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Weapons and Materials Research Directorate, ARL

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14. ABSTRACT
The US Army requires the ability to generate electrical power on-the-move, operating in all environmental conditions and at all times of day. Waste heat from Army vehicles is a rich source of energy that usually is exhausted to the environment. Therefore, an opportunity exists to capture this waste heat and convert it into energy, thereby supplementing power generation and increasing output. The research objective of this seedling effort is to examine the feasibility of experimentally processing half-Heusler thermoelectric materials using existing powder processing capability at the US Army Research Laboratory. Two candidate low-cost half-Heusler thermoelectric materials were examined herein: Fe–Al–V and Ti–Ni–Sn. These materials were processed using conventional powder metallurgy techniques with equal channel angular extrusion (ECAE) processing used for consolidation. Two studies were pursued and showed that ECAE temperatures above 400–600 °C resulted in microstructure evolution that complicated the ECAE consolidation process. A copper canning material aided in the degree of powder consolidation, but further work is required to better understand the microstructure conditions that led to the poor consolidation in these alloys using ECAE consolidation.

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1. Introduction

The US Army requires the ability to generate electrical power on-the-move, operating in all environmental conditions and at all times of day. Waste heat from Army vehicles is a rich source of energy that usually is exhausted to the environment. Therefore, an opportunity exists to capture this waste heat and convert it into energy, thereby supplementing power generation and increasing output.

Thermoelectric (TE) materials are a class of materials that generate electricity in the presence of a temperature gradient. The disadvantage of the current technology is that these materials (e.g., bismuth and lead tellurides) typically consist of elements that are expensive, under foreign control, mechanically weak, toxic, and environmentally unfriendly. More recently, a new class of TE materials has surfaced based on alloys with a half-Heusler (HH) structure. Unlike TEs with rare constituent elements (e.g., Te in Bi_2Te_3 and Pb–Te), HH TEs comprise more common inexpensive elements with superior mechanical, tribological, and/or oxidation/corrosion properties (e.g., transition metals) but are less efficient at converting heat to electricity. There are several intermetallics that readily form HH structures. The proposed effort examines 2 intermetallics: 1) lower-cost, lower-performance intermetallics based on elements from IUPAC (International Union of Pure and Applied Chemistry) 5-8-13 groups (e.g., Fe–V–Al); and 2) higher-cost, higher-performance intermetallics based on IUPAC 4-10-14 columns (e.g., Zr–Ni–Sn) of the periodic table.

The challenge is how to optimize HH TEs to serve as a viable replacement of traditional materials in terms of both efficiency and cost while extending their utility toward more mechanically demanding structural roles. The necessary fundamental science is how to link the alloy chemistry/processing design with TE efficiency and strength using mechanical alloying (creating nanostructured or nanocomposite HH TEs). A current research thrust is augment experiments with statistical sampling techniques, artificial neural networks, metamodeling techniques, and design optimization to attain a high-temperature HH TE material with optimal properties. This advancement can provide the opportunity to increase vehicle efficiency, allowing for lightweight electrical systems, lower operational costs, and increased sustainability. Ultimately, the goal is to produce a material that incorporates the benefits of HH materials (e.g., low cost, sustainable, and mechanically superior) while extending the technology to be competitive with state-of-the-art materials (e.g., Bi_2Te_3, figure of merit ZT of 1) in terms of output and efficiency.

Developing the next generation of structural TEs requires integrating computational materials design techniques synergistically with laboratory-scale nanofabrication methodologies. There are 3 main aspects of such an effort: 1) to develop and experimentally process HH TE materials, 2) to measure the mechanical properties and TE efficiency of the developed HH alloys, and 3) to develop the computational infrastructure to guide further HH TE development. This type of effort ultimately requires a multidisciplinary approach with expertise in both the materials science and mechanics of TEs as well as knowledge about the properties and performance of TE materials.

Experimentally, TE alloy samples can be generated by high-energy ball milling and subsequently consolidated by equal channel angular extrusion (ECAE). This combined processing route not only provides a means to quickly verify computational results, but also generates unique, nonequilibrium structures and compositions. High-energy ball milling coupled with ECAE is known to create and retain unique structures in materials. More specifically, mechanical alloying can even mix immiscible materials and produce a dramatically reduced grain size (less than 10 nm) in a short amount of time (less than 8 h). Similarly, low-temperature ECAE can densify powders without altering their metastable properties. Hence, the substantially reduced grain size can improve the TE performance by decreasing the thermal conductivity while simultaneously increasing the strength. This is due to the increased grain boundary volume fraction, which hinders the motion of dislocations (strengthens) and scatters phonons (decreased thermal conductivity). Though mentioned often in literature, this mechanism for TE improvement has been focused upon very little. There is even some indication that HH TEs benefit more from grain size reduction than traditional materials. Because HH TEs possess a large unit cell, their high power factor is due to the large carrier effective mass rather than the high carrier mobility.

Another promising avenue for designing next-generation TEs is to use state-of-the-art sampling, metamodeling, and design optimization techniques to guide compositional development. For instance, most studies examining the influence of alloying HH TEs are largely based on iteratively alloying and doping, i.e., x and y in $\mathrm{Hf}_x\mathrm{Zr}_{1-x}\mathrm{CoSn}_y\mathrm{Sb}_{1-y}$. An alternative approach is to use statistical sampling or design of experiment techniques to map the x–y design space, using Taguchi methods, fractional factorial experiments, or space-filling techniques such as Latin Hypercube sampling. In this manner, the x–y compositional space can be efficiently and methodically sampled to help guide the trial HH alloy compositions. Upon evaluating these alloys for performance metrics, we can use the responses to generate metamodels that describe the relationship between factors (such as x and y) and responses (such as TE figure of merit ZT and compressive strength). Metamodels can be simple (or complex) polynomial regression models, radial basis function models, Kriging models, or artificial neural network models. These predictive design models can then be used to guide the development of the HH TE alloys by

running virtual experiments, validating the models with subsequent experimental compositions, and combining these models with design optimization.

In turn, the mechanical and TE properties can be evaluated and included as a response for the particular alloy/process combination. The mechanical properties may include compressive, tensile, and shear strength, or creep resistance. As stated previously, the TE efficiency is strongly associated with the dimensionless figure of merit, defined as $ZT = (S^2\sigma/\kappa)\,T$, where S, σ, κ, and T are the Seebeck coefficient, the electrical conductivity, thermal conductivity, and the absolute temperature. However, prior to pursuing this level of effort, the processing methodology for generating HH TEs needs to be defined. In this first effort, the research objective is to examine the feasibility of experimentally processing HH TE materials using existing powder processing capability at the US Army Research Laboratory (ARL). Two candidate low-cost HH TE materials were examined herein: Fe–Al–V and Ti–Ni–Sn. These materials were processed using conventional powder metallurgy techniques with ECAE processing used for consolidation. Two studies were pursued and showed that ECAE temperatures above 400–600 °C resulted in microstructure evolution that complicated the ECAE consolidation process. A copper canning material aided in the degree of powder consolidation, but further work is required to better understand the microstructure conditions that led to the poor consolidation in these alloys using ECAE consolidation.

2. Experimental Methodology

2.1 Background

There are a number of excellent review articles on the subjects of generic properties of HH compounds,[1] TE materials,[2] low-dimensional TE materials,[3] nanostructured TEs,[4] and only very recently nanostructured HH TE compounds.[5] The best approach for optimizing HH TEs utilizes prior knowledge pertaining to HH TE systems and doping elements (focusing predominately on those elements abundant in nature), alloy processing knowledge, characterization methods of the microstructure, and methods for measurement of physical properties of the TE materials.

2.1.1 Alloying and Doping in Half-Heusler Thermoelectrics

There are several ways that the TE efficiency for a particular TE system can be improved. For instance, minor element substitution (alloying and doping) in HH alloys has been shown to lead to dramatic increases in TE efficiency.[6–8] Most of the work has been limited to labor-intensive experimental adjustments since each alloy must be generated and its composition verified before determining its properties. Half-Heusler alloys consist of 3 interpenetrating face-centered cubic lattices that can each be tuned separately. By substituting elements on each of the sublattices, Shen et al. find that complex materials can arise (e.g., $Zr_{0.5}Hf_{0.5}Ni_{0.8}Pd_{0.2}Sn_{0.99}Sb_{0.01}$),[6] which can lead to increased TE efficiency (Fig. 1).

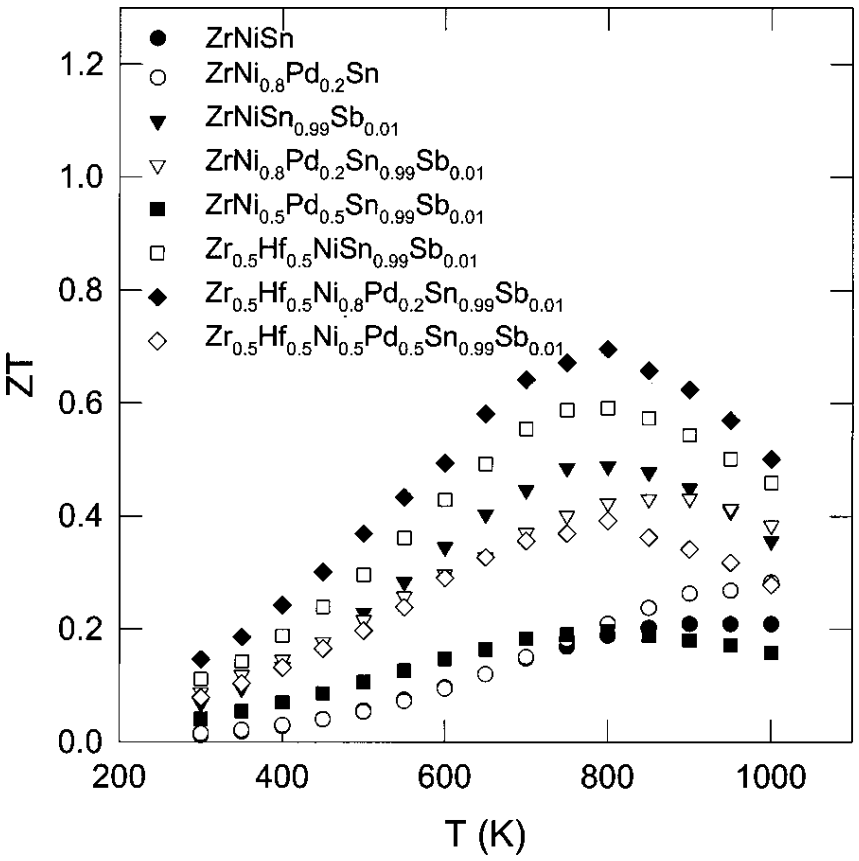

Fig. 1 TE figure of merit ZT for different element additions to a baseline Zr–Ni–Sn TE material between 300 and 1,000 K

2.1.2 Nanostructuring in Half-Heusler Thermoelectrics

There is also evidence that HH TEs benefit more from grain size reduction than traditional materials.[9] This "nanostructuring" of the grain size can lead to a remarkable decrease in the thermal conductivity of the TE alloy, thereby increasing the TE efficiency. For instance, in Fig. 2, Bhardwaj et al.[10] show a 70% increase in the temperature-dependent TE efficiency ZT in nanostructured $Zr_{0.25}Hf_{0.75}NiSn$ over its bulk counterpart. In this work, 2 processing techniques were used to produce the TE materials: 1) casting, annealing, and then consolidating the material; and 2) casting, annealing, powdering the annealed sample, ball milling for 10 h, and then consolidating the sample. In both cases, the consolidation technique used was spark plasma sintering. Their study shows that the nanostructure process results in a 70% increase over temperatures ranging from 325 to 775 K, which indicates that the nanostructured microstructure has some degree of thermal stability at these higher temperatures.

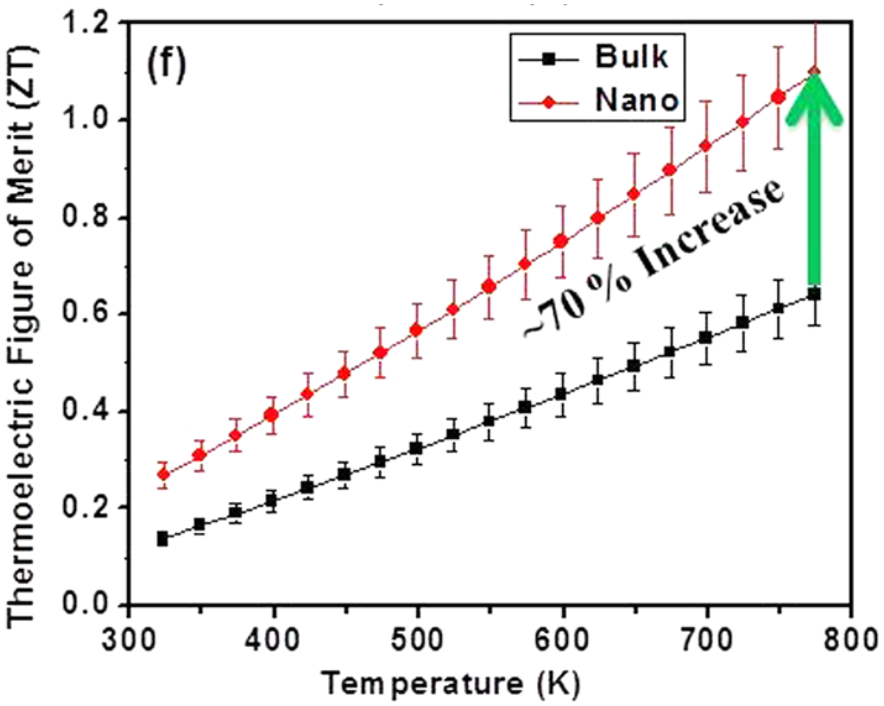

Fig. 2 Comparison of the temperature-dependent TE properties of normal bulk (black curves) and nanostructured (red curves) $Zr_{0.25}Hf_{0.75}NiSn$ for the TE figure of merit ZT

2.2 Powder Processing

Powder processing routes represent a readily scalable process for producing bulk nanostructured materials with dimensions much greater than 1 mm. Powder processing techniques are typically a 2-step process whereby nanostructured powders are first created and subsequently consolidated at elevated temperatures (greater than 50% of the melting temperature, T_m). ARL efforts have utilized powder processing for generating thermally stable nanocrystalline materials[11,12] and this research utilizes the existing powder processing infrastructure at ARL to explore nanostructured TE materials.

The process of utilizing mechanical alloying to produce bulk nanocrystalline materials is shown in Fig. 3. There are a number of different types of mills ranging from laboratory-scale shaker mills (e.g., SPEX 8000 mill, discussed herein) that are able to produce 10–20 g of powder to commercial-scale mills that are able to produce thousands of grams of powder at a time. Additionally, these are often classified into low-energy or high-energy mills, depending on the frequency and amplitude of the milling media impacts. The material flow path starts with loading commercially-available powders (in the appropriate proportions, for alloys) and grinding media (typically steel balls) in the right proportion into a vial. This is then loaded into a high-energy shaker mill, whereby the back-and-forth shaking motion imparts kinetic energy to the grinding media. The kinetic energy acquired by the balls due to the agitation is imparted to the powder particles, thereby subjecting the powder particles to severe mechanical deformation between the balls. With increasing milling time, there is better mixing/dispersion within the elemental/alloy powders and a refinement in the grain size within the powders. Upon completion of the mechanical alloying stage, the resultant powder often contains a sufficiently small grain size (less than 100 nm). The powder microstructure can be characterized using scanning electron microscopy, transmission electron microscopy or X-ray diffraction techniques. Subsequent kinetic studies and characterization is often necessary to optimize consolidation processing parameters by understanding the evolution of the microstructure/grain structure with time and temperature. In some cases, second phase particles or additional phases may manifest in the microstructure at elevated temperatures. Last, consolidation of the nanostructured powder into bulk form utilizes various powder metallurgy consolidation processes: spark plasma sintering, ECAE, flash sintering, hot isostatic pressing, etc. These processes use high pressures, elevated temperatures (typically above 50% T_m), and time to compact and sinter the powders into a fully dense bulk nanostructured part.

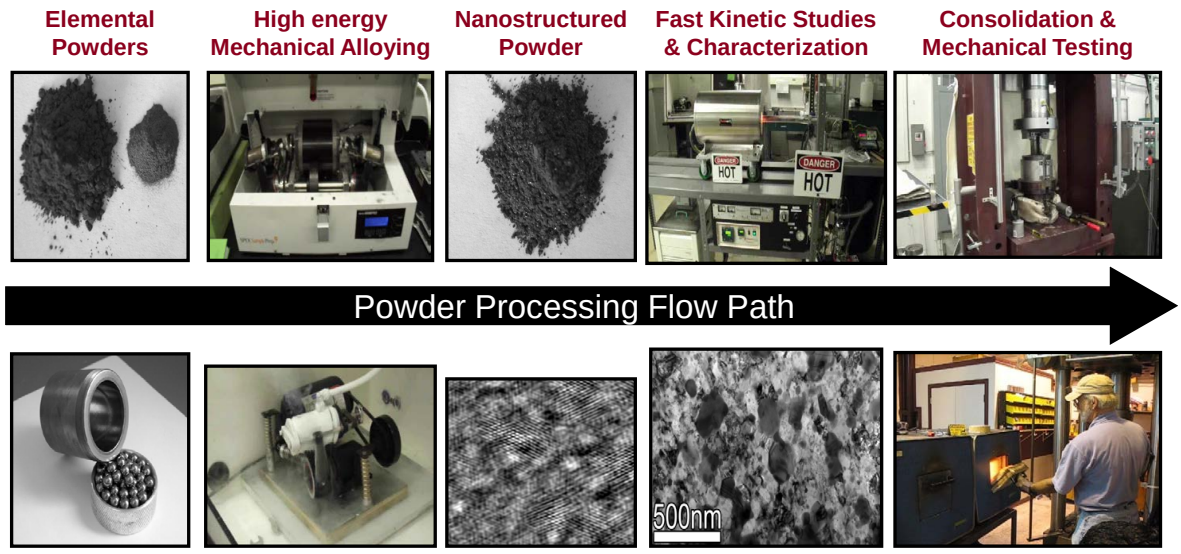

Fig. 3 Images of different stages utilized in ARL's powder processing of TE materials

The following subsections describe how the nanostructured TE materials were generated using mechanical alloying (Section 2.2.1), consolidated using ECAE (Section 2.2.2), and tested for microstructure and mechanical properties (Section 2.2.3).

2.2.1 Mechanical Alloying

High-energy cryogenic mechanical alloying was used to synthesize the Fe–Al–V and Ti–Ni–Sn TE powders. For each of the compositions, appropriate amounts of powders (–325 mesh, 99.9% purity, 5 g total) were loaded into hardened steel vials along with milling media (440C stainless steel balls) with a ball-to-powder ratio of 10-to-1 by weight, and then sealed inside a glove box in an argon (Ar) atmosphere (oxygen and moisture are less than 1 ppm). Ball milling was carried out in a SPEX 8000M shaker mill at cryogenic temperatures (verified to be approximately –196 °C) using liquid nitrogen. This was accomplished by placing the steel vial in a thick polymer sleeve that was fixed in the high-energy mill with a provision for liquid nitrogen flow around the vial via inflow and outflow vents. The vial was equilibrated for 20 min to reach a temperature around –196 °C and then milling was started. A milling time study was performed and it was found that alloying took 8 h at a minimum; based on this finding, all of the TE powders were milled for 8–10 h. After completion of the milling cycle, vials were opened inside the glove box and the powders were stored therein. This process was repeated, until a total powder charge of 40–60 g for each composition was attained. Cryogenic mechanical milling resulted in an un-agglomerated powder mass with a particulate size range of 20–100 μm.

2.2.2 Equal Channel Angular Extrusion Consolidation

Recent demonstrations of novel processing methods involving temperature, high shear, and high pressure have shown promise for bonding high-strength particulate materials. The ECAE process subjects a billet to a pure state of shear as material flows around an "L" shaped channel (Fig. 4). ECAE can be performed at elevated temperatures for any number of passes and the billet can be rotated between passes to provide precise texture control for the material.[13–15] This method, which induces severe plastic deformation at elevated temperatures, has demonstrated its effectiveness in consolidating metastable powders that have a very narrow processing window and cannot be easily consolidated using conventional methods. The addition of high shear can significantly reduce the temperature required to achieve full density and allow the consolidation of metastable microstructures.[16] Another benefit of these severe plastic deformation methods is that the material samples retain the same basic geometry and cross section as the starting piece, thus allowing for relatively simple scale-up.

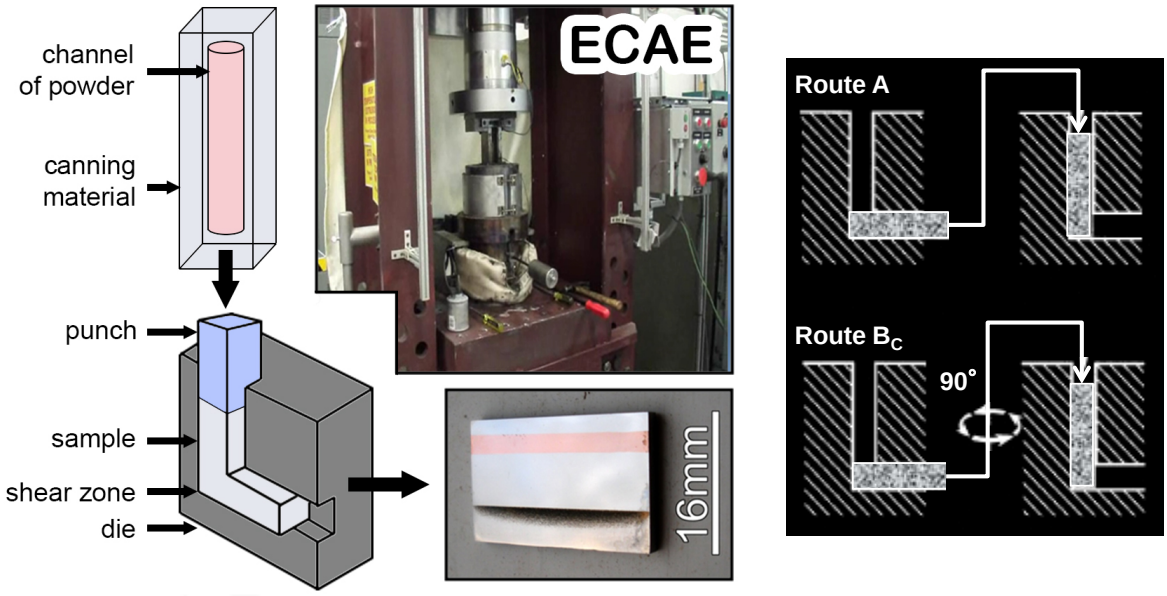

Fig. 4 The ECAE process for consolidation of nanostructured TE powders. The powders are inserted into a nickel canister, heated to an appropriate temperature, and processed using a particular ECAE processing route (e.g., route A or route B_c) to fully consolidate the powder material.

For the ECAE consolidation experiments, the as-milled powders were placed into nickel cans and sealed inside the glove box. The nickel cans were created by taking billets of Nickel 201 alloy with dimensions of 25.4 mm × 25.4 mm × 90 mm and drilling a 6- to 8-mm-diameter hole (approximately 50 mm long) along the long axis of the billet. The as-milled TE powders were placed into this powder chamber, which was then sealed shut. Prior to ECAE, the die assembly

was heated to 350 °C. The nickel cans loaded with as-milled powders were equilibrated (for 40 min) in a box furnace purged with pure Ar cover gas at 700 and 900 °C, respectively. The equilibrated cans were then quickly removed from the furnace, dropped into the ECAE tooling, and extruded at an extrusion rate of 25.5 mm s^{-1}. This procedure was repeated 4 times following route B_c (i.e., $4B_c$).[11,15] The ECAE tooling had a channel angle of 90°. The four consecutive extrusions resulted in a total strain of approximately 450%. The extruded cans were then serial sectioned to determine the degree of consolidation and to mechanically test. Multiple TE and temperature combinations with a nickel can were explored: Fe–Al–V at 600, 800, and 1,000 °C; and Ti–Ni–Sn at 800 and 1,000 °C. The poor consolidation results prompted one last sample: a copper canning material with Ti–Ni–Sn at 600 °C.

2.2.3 Property Assessment

X-ray diffraction profiles were performed on the as-milled TE powders (Fe–Al–V and Ti–Ni–Sn) at room temperature. Additionally, some of the TE powder was annealed at temperatures ranging from 200 to 1,000 °C (in increments of 100 °C) for 1 h. This annealing step is used to simulate the thermal conditions that the powder is exposed to during the ECAE consolidation step. Following the annealing treatment, the samples were cooled to room temperature and the 2θ X-ray diffraction profiles were performed on all samples. These profiles indicate the degree of mixing of the elements following mechanical alloying as well as the any phase precipitation caused by the annealing temperature (ECAE consolidation temperature). This assessment is an important characterization tool for determining the appropriate temperature for the consolidation process. Moreover, the full width half maximum (FWHM) of various peaks within the 2θ profile can be used to ascertain the evolution of the grain size with annealing temperature using the Scherrer analysis. Last, standard Vickers microhardness measurements were also performed on a Wilson Hardness Tukon 1202 equipped with a 1,000× lens system and performed under ambient conditions with a load of 50 gf and a loading time of 10 s.

3. Results

3.1 X-ray Diffraction Profiles

The X-ray diffraction 2θ profile for the Fe–Al–V TE material is shown in Fig. 5. The different temperatures to the right of the curves refer to the subsequent annealing temperature for the as-milled powder. The intensity measurements as a function of 2θ have been artificially increased to show the evolution of the intensity profile with annealing temperature. First, the samples were measured on a tungsten foil, which can be ignored in the present analysis. The broad peak at approximately 42°–45° for the as-milled powder indicates that a solid solution with a predominant Fe crystal structure exists. As the annealing temperature is increased, the width of the Fe peak decreases, which indicates an increase in the grain size for the Fe–Al–V TE material. The fact that the as-milled powder contains some amount of an Fe peak may indicate that further milling time (or larger scale, higher energy mechanical alloying) may be required to fully disperse the elements into a solid solution.

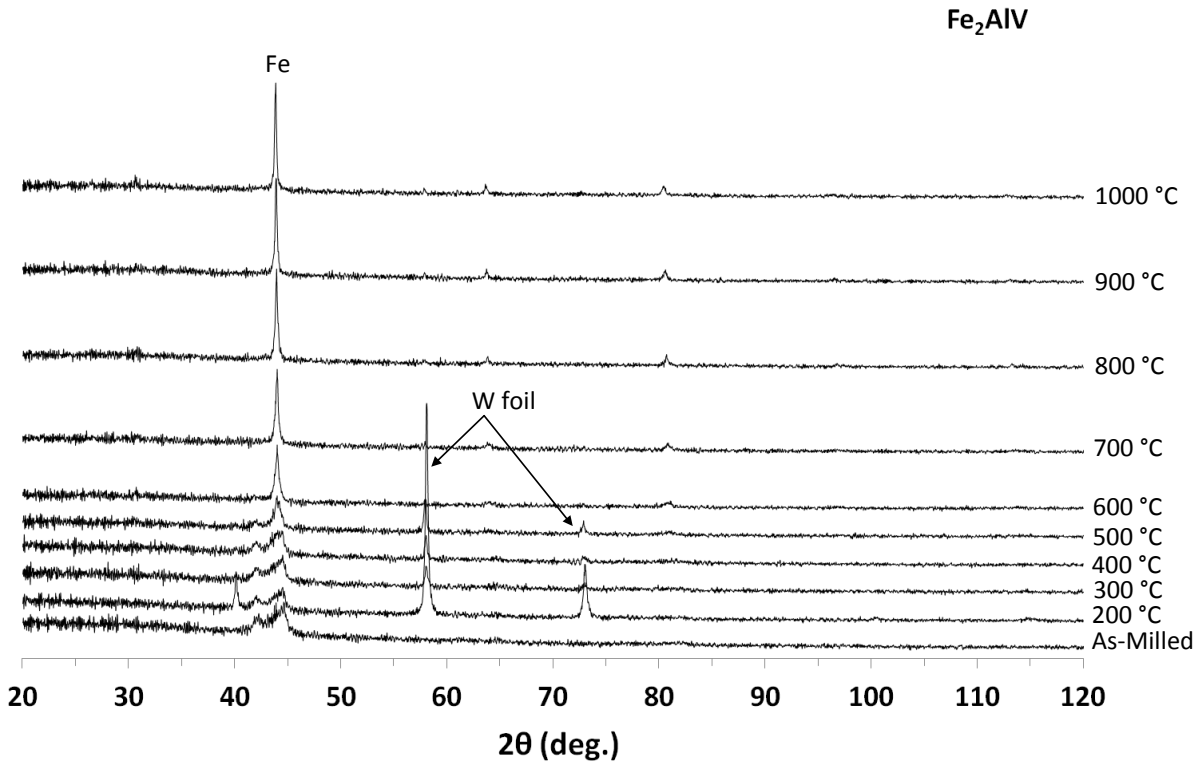

Fig. 5 X-ray 2θ profiles of the Fe–Al–V TE material

The X-ray diffraction 2θ profile for the Ti–Ni–Sn TE material is shown in Fig. 6. This plot was attained in a similar manner to that in Fig. 5 except with the Ti–Ni–Sn powder. The X-ray diffraction profile indicates a solid solution with a minor Ti peak in the as-milled powder after mechanical alloying. Similar to the Fe–Al–V TE material, the Ti–Ni–Sn TE material has a Ti crystal structure that develops in samples that were annealed at higher temperatures (greater than 500 °C) and the decreasing FWHM values with increasing annealing temperature indicates that the nanostructured grain size is increasing. Again, milling times beyond 10 h may be required to more effectively force all the elements into solution.

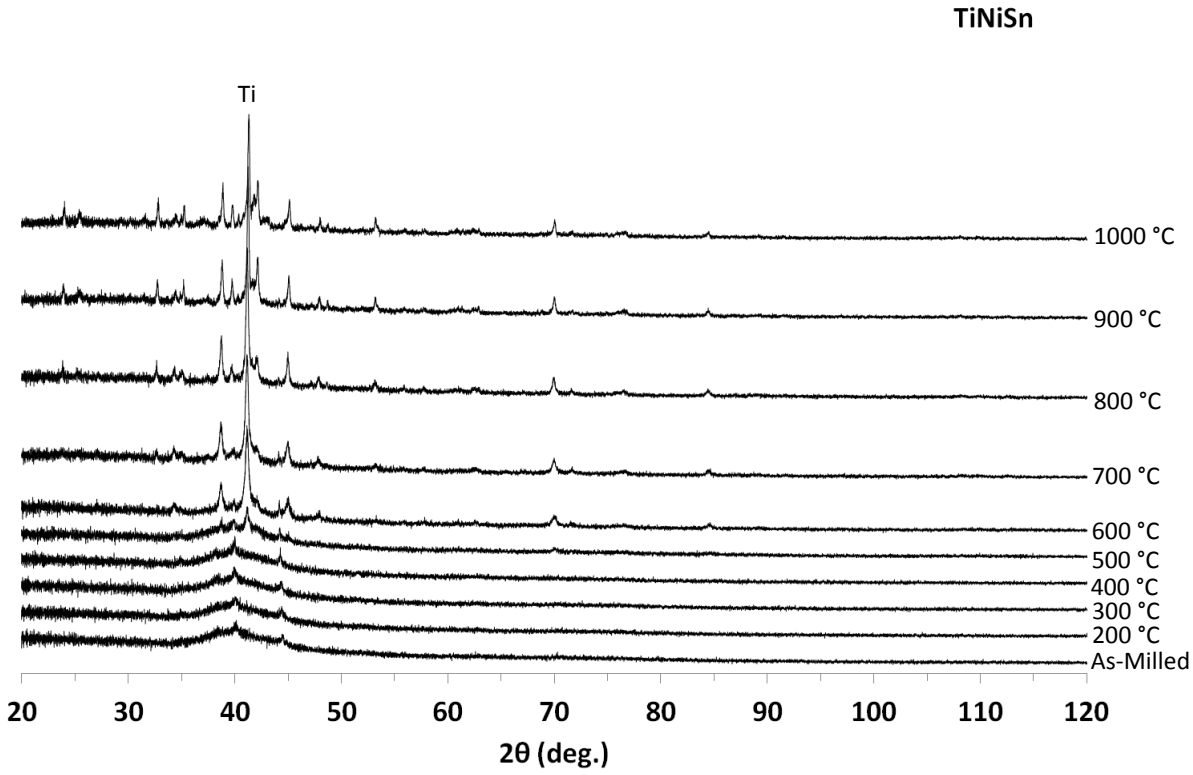

Fig. 6 X-ray 2θ profiles of the Ti–Ni–Sn TE material

3.2 Grain Size and Thermal Stability

An estimate of the grain size can be calculated from the FWHM values in the 2θ profiles (Figs. 5 and 6) using the Scherrer analysis. The evolution of the Scherrer-calculated grain size as a function of the annealing temperature for the 2 TE materials is plotted in Fig. 7. This plot indicates that the Scherrer grain size estimate increases after 400 °C for the Fe–Al–V TE material and after 500 °C for the Fe–Al–V TE material. Hence, it is anticipated that some grain growth occurs during ECAE consolidation and that this grain growth is more severe with increasing temperature. In the present analysis, the Scherrer grain size estimate is likely correlated to the

actual grain size of the TE microstructure, but further transmission electron microscopy is required to verify the mean grain size and the distribution of grain sizes within the sample. However, the trends observed in Fig. 7 suggest that the microstructure evolves at temperatures of 400–600 °C and above.

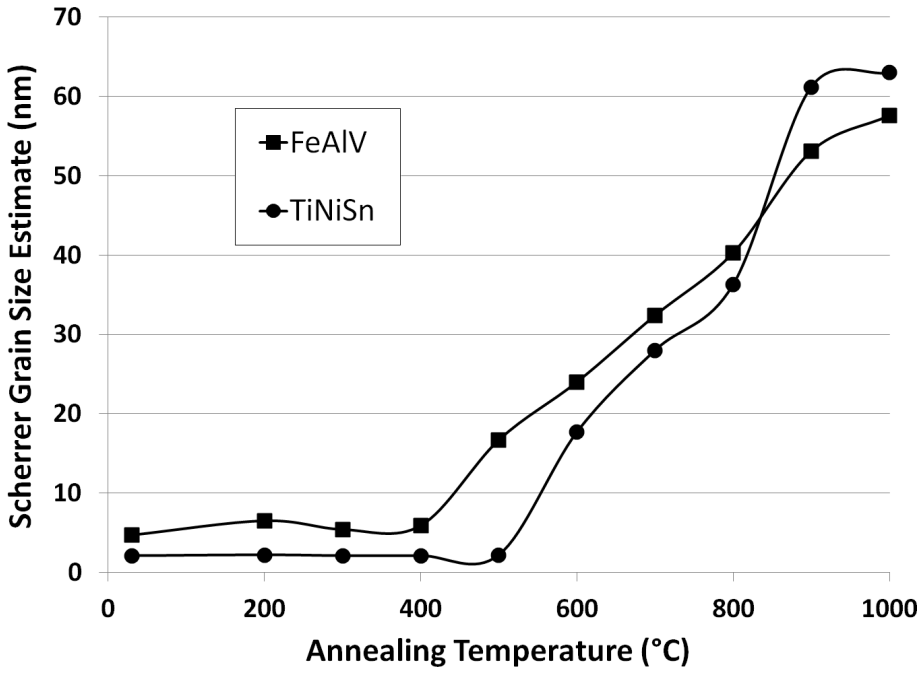

Fig. 7 Scherrer grain size estimate from X-ray 2θ profiles for the Fe–Al–V and Ti–Ni–Sn TE materials as a function of annealing temperature

The Vickers microhardness was also measured for the 2 TE materials as a function of the annealing temperature (Fig. 8). For each sample, multiple measurements were performed; the mean hardness value and the 1-standard deviation error bars are shown. While Fig. 7 shows that the microstructure is altered at higher annealing temperatures, the Vickers microhardness measurements indicate that the hardness is not as affected by annealing temperature. The large error bars for some samples at the higher annealing temperatures suggest that the microstructure is heterogeneous with multiple phases/regions of varying hardness/strength values.

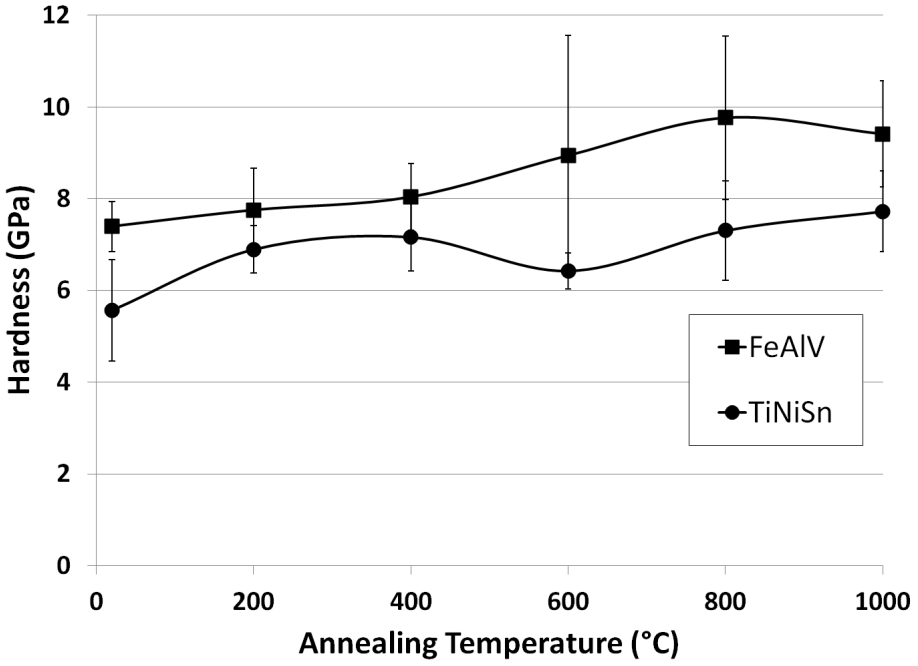

Fig. 8 Hardness from X-ray 2θ profiles for the Fe–Al–V and Ti–Ni–Sn TE materials as a function of annealing temperature

3.3 Consolidated Thermoelectric Powders

After the preliminary studies to assess the microstructure evolution at higher temperatures, the samples were then consolidated using the ECAE process for the various material/temperature/canning material combinations (Fig. 9). Figure 9 shows that there was difficulty consolidating the TE powder using ECAE (powder is the central material and the canning material surrounds it). This result was unforeseen based on extensive use of ECAE to consolidate nanocrystalline metal powders. In fact, the bottom image in Fig. 9 is the Ti–Ni–Sn material consolidated at 1,000 °C. The hollowed area is the result of the powder falling from the cavity upon machining open the canning material (i.e., no bonding between the powder particles). Visual inspection of the cross section of the canning material after a change in the canning material to copper at 600 °C showed that the type of canning material may have some influence on the degree of consolidation. However, this preliminary study into processing and consolidating low-cost TE materials raises a number of questions regarding potential reactions at high temperatures in these systems and how this impacts the microstructure. Subsequent microstructure analysis is needed to understand whether ECAE—as an example of consolidation via severe plastic deformation routes—is a viable option or if other consolidation methods need to be utilized in this case.

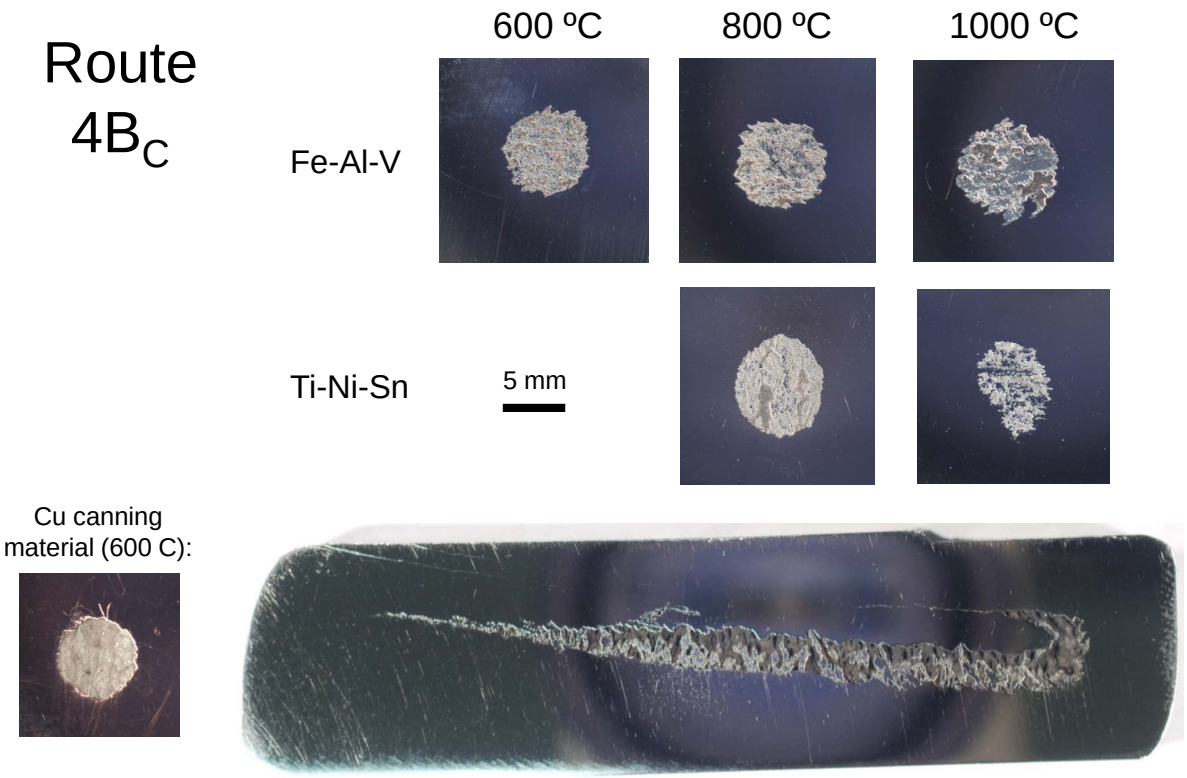

Fig. 9 Optical images of cross sections of consolidated TE powders using route B_c

4. Conclusions

The research objective of this seedling effort is to examine the feasibility of experimentally processing HH TE materials using existing powder processing capability at ARL. Two candidate low-cost HH TE materials were examined herein: Fe–Al–V and Ti–Ni–Sn. These materials were processed using conventional powder metallurgy techniques with ECAE processing used for consolidation. Two studies were pursued. An initial study on the effect of annealing temperature for the 2 HH alloys was used to evaluate the influence of ECAE temperature on the microstructure. This study showed that at temperatures of 400–600 °C and above, the microstructure of the TE material changes. The hardness was comparable for all annealing temperatures, but there was a larger amount of variability in some of the higher annealing temperature samples that indicates a heterogeneous microstructure. A second study utilized the ECAE process at various temperatures to consolidate the 2 TE material powders. The powder consolidation was poor for many of the material/temperature combinations with the nickel

canning material. The copper canning material visually showed a better degree of consolidation of the TE powder. Future work is required to understand the microstructure conditions that led to the poor consolidation in these alloys using ECAE consolidation.

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List of Symbols, Abbreviations, and Acronyms

ARL	US Army Research Laboratory
ECAE	equal channel angular extrusion
FWHM	full width half maximum
HH	half-Heusler
IUPAC	International Union of Pure and Applied Chemistry
TE	thermoelectric
ZT	thermoelectric efficiency

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