Journal of ELECTRONIC MATERIALS, Vol. 47, No. 9, 2018
https://doi.org/10.1007/s11664-018-6402-7

Performance of Functionally Graded Thermoelectric Materials and Devices: A Review

CORSON L. CRAMER,[1,3] HSIN WANG,[1] and KAKA MA[2]

1.—Manufacturing Demonstration Facility, Oak Ridge National Laboratories, 1 Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831, USA. 2.—Colorado State University, Fort Collins, CO 80626, USA. 3.—e-mail: cramercl@ornl.gov

Direct energy conversion using thermoelectric generators (TEGs) is a research area of growing interest because of its potential for increasing energy efficiency. Bulk thermoelectric modules are used widely in industry as Peltier cooling devices. Currently, only bismuth telluride modules are commercially available for power generation. Significant efforts have been put into exploring promising materials and techniques to improve the figure of merit (zT) at laboratory scale (5–20 g). A variety of techniques have been investigated to improve the output and useful temperature range for common industrial TEGs made from bulk polycrystalline materials including segmentation, geometric pinning, and property gradients. However, the improvement in zT at device level (500–1000 g and up) is exceptionally limited. In addition, the thermal degradation of TEGs occurs when cracks form due to thermal stresses that arise from transient heat sources, which consequently lead to a decreased lifetime. Functionally graded material (FGM) thermoelectrics in bulk and polycrystalline form have been developed to mitigate some of these issues by improving the temperature bandwidth, current output range, and lifetime. The present work provides a review of functionally graded TEGs, including their manufacturing, usage and current techniques for improving their performance. This article also provides a pathway to additional research and approaches for improving the efficiency and temperature range, as well as reducing the property degradation of bulk polycrystalline TEGs.

Key words: Functionally Graded TEGs, thermal fatigue, polycrystalline TEGs, lifetime

INTRODUCTION: THERMOELECTRIC MATERIAL

Energy is released in the form of waste heat from many operating systems that use heat as their thermodynamic driving source, such as internal combustion chambers, power plants and industrial furnaces. Thermoelectric generators (TEGs) are solid-state devices that can turn the waste heat into electrical power. Most waste heat recovery systems are TEG modules that are placed at the waste heat source and are sometimes further cooled actively or passively. The energy conversion efficiency of current TEG modules with homogenous grain structure, without segmentation or cascading, is about 9–12%, while their service temperatures are most efficient in a small temperature range, approximately 200°C.[1,2] Bulk TE material have been improved with skutterudites and half-Heuslers, but the stability of skutterudites has been questionable at temperatures above 600°C.[3,4] Previous research of waste heat recovery systems has been limited to improvement of single materials in a short temperature span, while the improvement in lifetime has been overlooked. Improvement to the

(Received January 25, 2018; accepted May 18, 2018; published online May 31, 2018)

non-dimensional figure of merit for a thermoelectric material, zT, has been achieved; where $zT = \alpha^2 T/\rho k$; α is the Seebeck coefficient, which is a measure of the amount of voltage generated through the Seebeck effect per degree of temperature difference; T is the temperature; ρ is the electrical resistivity; and k is the thermal conductivity. zT is sometimes referred in the literature as the thermoelectric efficiency, because it is related to single element and device efficiency via the equation[1]:

$$\eta_{\text{opt}} = \frac{\Delta T}{T_{\text{h}}} \frac{\sqrt{1 + zT_{\text{ave}}} - 1}{\sqrt{1 + zT_{\text{ave}}} + T_{\text{c}}/T_{\text{h}}} \tag{1}$$

in which ΔT is the difference between the hot side temperature, T_{h}, and cold side temperature, T_{c}. The first term in (1) is the Carnot efficiency. At device level, the efficiency is simply the ratio of electric power output and the heat flux going through the module. Measured efficiency is generally lower than the η_{max} because of the additional thermal and electric interfaces. Thermoelectric generators are used successfully in space applications and have shown great potential for automotive applications,[5–7] so it is important to continue to make improvements to these systems and materials.

The lifetime of TEGs depends on the device degradation and failure, which can be abrupt or gradual. Although some performance data, such as DC power output, can be monitored, performance can be better characterized by parameters such as AC resistance. Regarding long-term degradation, device lifetime could be defined by the level (% change) of AC resistance.[8] Systems with heating rates of over $\sim$ 200°C/min and transient operation are examples of situations where the thermal stresses degrade TEGs with defects, crack initiation, and crack growth because of poor heat dissipation when the TEG is initially subjected to a heat source leading to increased thermal stresses.[9] In this case, thermal stress is initially very high and subsequently reaches a transient condition until the heat flow becomes steady. One critical challenge in developing TEGs is the degradation of original properties leading to a decrease in lifetime and efficiency, which is due to thermal fatigue caused by thermal expansion and thermal shock.[10–16] TEGs with prolonged lifetimes are in demand for applications with large temperature differences and for transient heat sources. Functionally graded materials (FGMs) can reduce the thermal stresses caused by large temperature differences and, thus, increase the TEG lifetime.[17] Previous studies have demonstrated that design of FGMs mitigated thermal cracking and improved the lifetime of the thermoelectric materials.[16,18,19]

One approach to increase the useful temperature range of a TEG is segmentation,[20] in which several different TEG materials with optimal properties for different temperature ranges are physically joined in descending order from high- to low-temperature materials. As an example, a TEG with segmentation consists of SiGe, PbTe, and Bi_2Te_3 with the following spatial arrangement: SiGe is on the hot side and connected to PbTe (middle section), which is connected to Bi_2Te_3 on the cold side. This three-part segmented TEG has not been implemented because of electrical current matching, but a PbTe and Bi_2Te_3 tandem has been made and had increased efficiency from the single materials alone.[21] One study shows how this configuration could be implemented with the proper design.[22]

Figure 1 displays the typical values of the figures of merit for several n-type thermoelectric materials as a function of operating temperature. Of the materials considered in Fig. 1, nano-structured PbTe exhibits the highest zT, 80% higher than that of bulk PbTe, which has been used since 1960.[2] Figure 1 shows that Bi_2Te_3 is the best candidate for applications below 250°C, and the optimal service temperature range for PbTe is 400–600°C. In contrast, semiconductors, such as $CoSb_3$ and La_3Te_4, are the best candidates to be used in high-temperature applications. SiGe has been reserved for the super-high temperature range when temperatures are over 1000°C. One large application for the super-high temperature regime is for hypersonic vehicles.[23] Researchers have attempted to improve thermoelectric temperature ranges by segmenting materials or tailoring the properties of a single material.[24–26]

Current Techniques for Improving Efficiency

Homogenous Property Manipulation

Doping can increase the electrical conductivity of a material and, in turn, its thermoelectric power output.[28,29] Also, thermal conductivity is a significant material property for thermoelectric materials and their functioning devices. For bulk material, the thermal conductivity is high compared to lower dimensional samples, such as thin films, due to

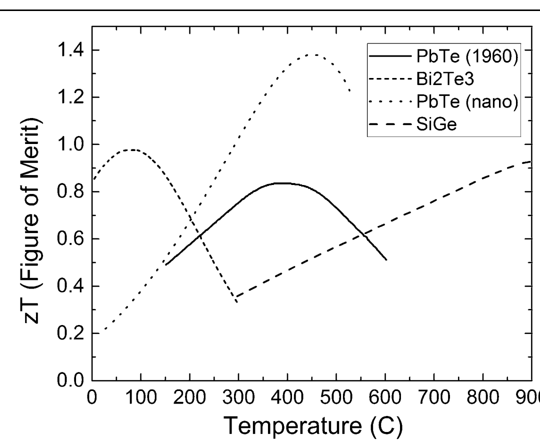

Fig. 1. The values of zT of common n-type thermoelectric materials as a function of temperature.[27] Reprinted with permission from Springer Nature: Nature Materials, G. J. Snyder and E. S. Toberer, Nat. Mater. 7, 105 (2008).

scattering.[30] Nano-structuring of thermoelectric material enhances the overall efficiency by significantly lowering the thermal conductivity.[31] Other strategies to increase disorder in the lattice to decrease lattice thermal conductivity in bulk material include the use of skutterudites and mixed-lattice atoms, such as half-Heusler alloys,[32,33] clathrates that scatter phonons but not electrons,[34] and complex intermetallic phases.[35] For these approaches, manipulating the crystal structure and band gap is vital for increasing the thermoelectric efficiency, and researchers continue to combine techniques to lower the thermal conductivity and enhance the thermoelectric output. The aforementioned improvements help to increase the zT when homogenous material is used with no additional improvements, but do not increase the temperature range. Techniques that involve non-homogeneous material with segmenting, cascading or staging, and grading improve efficiency as well as the useful temperature range of operation for a TE material and thus module.

Functionally Graded TEGs

In applications that require high power and high efficiency, large temperature differences are needed across the TEG. A critical limitation of using a material with homogenous microstructure in a large temperature difference is that a significant portion of the material, no matter if it is the hot side or cold side, does not operate in the temperature range where zT is greatest. As seen in Fig. 2, efficiency is improved by adding a material suitable for low service temperature in the lower temperature zone of the TEG. It allows the whole length of the TEG to operate with higher efficiency compared to the one using solely one material. This successfully allows for the segment of the legs that were subjected to a temperature range in which the original material was not contributing to the conversion process, to contribute to the overall power generation of the module. This also provides a material that could, in theory, operate in a wider temperature range because at any temperature within a reasonable operating temperature range, there is a section of the material that is working optimally. It is important to note that Fig. 2 only shows the TE materials, but proper metallization and brazing to the module housing is very important for efficiency and lifetime as will be discussed throughout this work. Segmentation is one way to combine materials with different optimal temperature ranges.[36] Cascading and staging are other methods that increase the efficiency of TEGs by placing material in the most efficient temperature range as well as a number of units at each stage.[37–39] Cascading has had considerable success with Peltier cooling devices, so there is promise with these techniques for increased efficiency in engineering applications.[40–42] In any case, much goes into the engineering and sizing of TEGs for application.

1. Multi-stage and segmented TEGs and thermoelectric compatibility.
   Thermoelectric efficiency and useful temperature range principally can be increased by manufacturing a segmented thermoelectric module utilizing different materials stacked together.[43,44] One popular design is the Bi-Te, PbTe, and Si-Ge stacked in order of rising temperature to achieve a TE material that can operate over broad temperature ranges.[2] Another segmented thermoelectric material showing promise for manufacture includes Bi-Te and $FeSi_2$, but the efficiency optimization is lacking in the literature.[24] A uni-couple of Bi-Te and Co-Sb showed that the thermoelectric efficiency is doubled compared to a simple Si-Ge TE material.[45] Work done on a Bi-Te and PbTe segmented couple shows that the useful temperature range increased compared to the individual material.[26] It is shown that cascading and geometric control can be used to improve the efficiency and sustain power output in a large temperature gradient.[46] Gradation improves the useful temperature range, but there are efficiency losses from the metal contacts joining the segments.[45,47–49]
   Cascading and multi-staging thermoelectrics are other functionally graded techniques for improving thermoelectric coolers.[50] These methods use many stages of different materials to get either a different number of legs at each stage or recycling output to maximize the total output of the TEG.[51] Segmentation, cascading, and multi-staging must be engineered with the correct materials. For this, the thermoelectric compatibility factor, s, where $s = (\sqrt{1+zT} - 1)/(\alpha T)$, is used as a tool for analyzing and sizing TEGs.[48,52,53] The compatibility factor comes from an optimization of the current output matching across two dissimilar TE materials that are being joined in the module. If the materials are not compatible within a certain current range, the materials should not be joined to make a segment, cascade, or stage. Some compatible materials have shown promise in these functionally graded modules.[54–56]
2. Property gradients in TEGs.
   Many thermoelectric designs are based on reducing electrical resistivity. Researchers have used dopants to change the carrier concentration of the material, thus increasing electrical conductivity.[28,29] An approach for enhanced thermoelectric efficiency in FGMs is tuning the peak zT by manipulating the amount of dopant at different spots in the material, making it nonhomogeneous. Initially, models were developed to verify the benefits of property gradations in thermoelectrics,[57] and a study

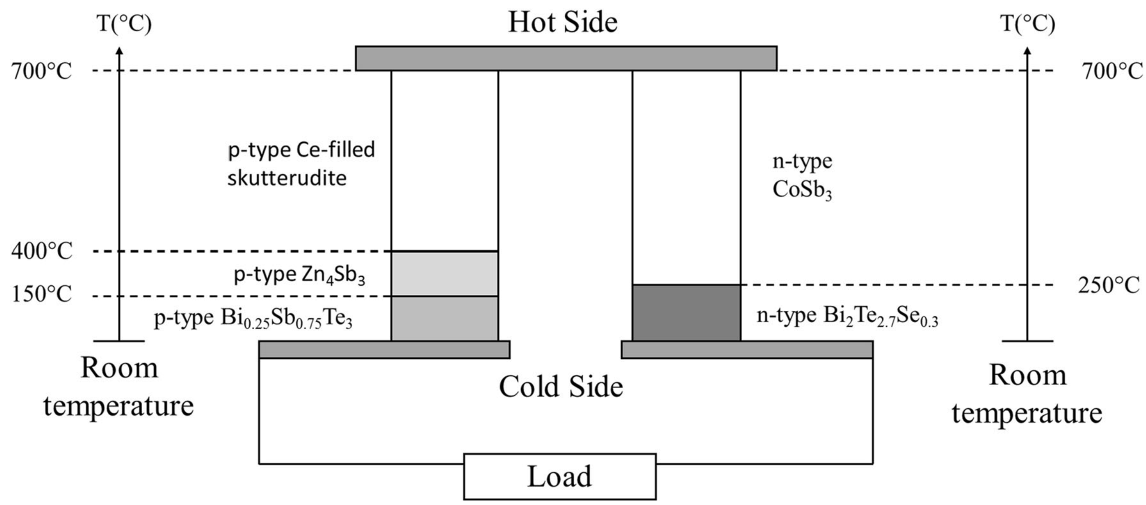

Fig. 2. Schematic of a high-performance multi-segmented thermoelectric generator.[2] Reprinted with permission from Taylor and Francis Group LLC Books, D. M. Rowe, Thermoelectrics Handbook: Macro to Nano, 1st edn. (CRC Press, Boca Raton, 2005), pp. 1–122.

showed that if all three TE properties (electrical resistivity, Seebeck coefficient, and thermal conductivity) improve spatially, the overall peak efficiency increases by 30%, but enhancing all properties in the direction of gradation in FGMs is usually arduous. Other models and simulations show that a carrier concentration gradient or compositional gradients will widen the useful temperature range of a thermoelectric material because the zT will peak at different temperatures.[17,58,59]

Carrier concentration gradients increased the zT in a study using the Bridgman method of melt material with Bi-Te.[60] The Bridgman method was used to make a carrier concentration gradient in a Pb-Te/Sn-Te system, and the output improved the temperature range of FGM versus compared to uniform homogeneous material.[61] A carrier concentration gradient was achieved in a *p*-type PbTe crystal by unidirectional solidification, but it is doubtful that the process could be controlled for applications.[62] A carrier concentration gradient of indium dopant in PbTe crystals was achieved by employing the Czochralski technique, showing that the optimal zT was shifted by about 50 degrees in temperature.[63] Functionally graded $Ge_{1-x}Si_x$ was developed with the Czochralski method in order to simultaneously achieve a concentration gradient and band gap gradient to optimize the zT for a wide temperature range.[64] One group shows a shifted zT with varying doping of PbI_2 in *n*-type PbTe.[65] Figure 3 shows that a carrier concentration gradient led to the shift of the peak of zT. FGM based on graded dopant will potentially produce a TEG with wider temperature bandwidth. The temperature bandwidth is shown to increase by using a grain size gradation.[66] Grain size gradation is done in two field assisted sintering technique/spark plasma sintering (FAST/SPS) forms and shows that the grain size helps with current output range and increases lifetime.[67] With the improvement of TE material, it is important to emphasize research efforts on implementation of the material into modules, which namely means that the contacts and contact resistance needs to be sufficient. The best contacts must be chosen for a given material, and different metals can be used on each side of a TEG. More about the contact resistance and engineering is discussed later.

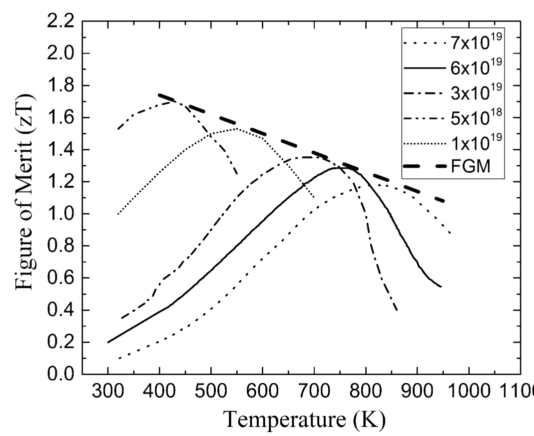

Fig. 3. Dimensional Z for carrier concentration FGMs.[17] Reprinted with permission from Elsevier, M. Koizumi, Compos. Part B Eng. 28, 1 (1997).

Mechanical Performance: Thermal Fatigue

Few studies on thermal stress effects on thermoelectric material and TEG lifetime exist in the literature.[10–14,16] However, the influence of thermal cycling and its effects on degradation have been characterized by several groups.[10,11,18,68–72] Cracking induced by thermal stress degrades the electrical properties and, thus, the lifetime, or ability to retain initial properties and efficiency of the TEGs. Cracking mitigation in ceramics has been achieved by designing materials with a thermal conductivity gradient, but this concept has not been applied to TEGs.[73] Thermal stress cracking leads to the failure of the material by the stress that builds up due to thermal expansion during transient heating. The thermal stress is expressed in (2), where E is the modulus of elasticity, α_{CTE} is the coefficient of thermal expansion, and T is the temperature. Assuming there are no geometric constraints, the side that is in tension is the colder side of the TEG device or TE leg.

$$\sigma_{\mathrm{thermal}} = E\alpha_{\mathrm{CTE}}\Delta T \tag{2}$$

When a ceramic specimen is subjected to sufficiently severe thermal shocks, micro-cracks could nucleate at pre-existing defects and grow to large cracks. Crack propagation in thermally shocked ceramics may be halted depending on the severity of thermal shock, thermal stress field characteristics and material properties. Thermal shock resistance (TSR) is characterized by (3), where σ_S is the strength of the material at room temperature and k is the thermal conductivity.

$$\mathrm{TSR} = \frac{k\sigma_S}{E\alpha_{\mathrm{CTE}}} \tag{3}$$

If one measures the strength of a thermally shocked ceramic specimen, the material generally exhibits the behavior as shown in Fig. 4; the strength remains unchanged when the thermal shock ΔT (difference between the initial temperature of the material and applied temperature at the surface) is less than a critical value, ΔT_c, called the critical thermal shock. At $\Delta T = \Delta T_c$, the strength suffers a precipitous drop and then decreases gradually with increasing severity of thermal shock as shown in Fig. 4. Both specimen size and material properties influence the residual strength of the ceramics exposed to a thermal shock.

A functionally graded microstructural cutting tool was proposed in,[75,76] and it was hypothesized that the thermal conductivity gradient and mechanical property gradient would effectively mitigate heat and reduce the wear of the material. A schematic diagram of a graded microstructure is shown in Fig. 5, which was the first published study that proposed grain size gradation for a thermal conductivity gradient using an FGM.[17] The graded cutting tool would expose the small grain side to the cutting surface because of increased hardness and strength that small grains provide through the Hall–Petch relationship.[77–79] The cutting tool with small grains on the working side also provides higher strength for thermal shock resistance. The graded microstructure in the FGM led to a gradual change of the material properties with respect to position; namely, the grain size gradient resulted in a thermal conductivity gradient for transferring heat more quickly during transient heat up to lessen thermal stresses in TEG devices and TE materials.

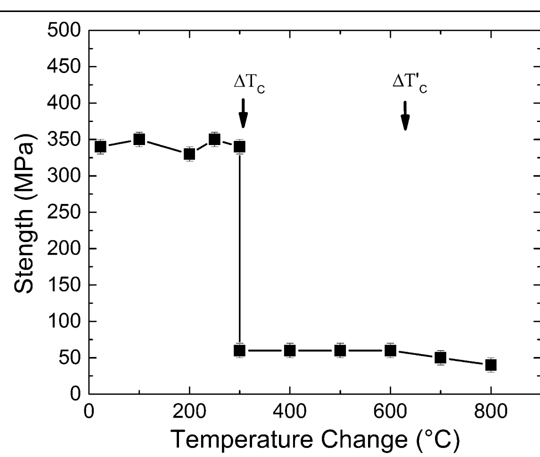

Fig. 4. Critical thermal shock and thermal shock residual strength of ceramics.[74] Reprinted with permission from John Wiley and Sons, D. P. H. Hasselman, J. Am. Ceram. Soc. 52, 600 (1969).

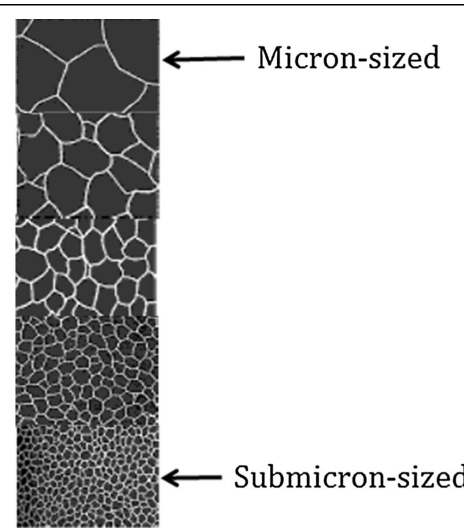

Fig. 5. Schematic of functionally graded cutting tool, where material composition gradient was first proposed and a continuous thermal conductivity gradient was suggested. The side exposed to the cutting surface is the small grains, while the large grain side is exposed to a heat source in a TEG setup.[75] Reprinted with permission from Springer Nature, R. M. Mahamood and E. T. Akinlabi, in Functionally Graded Materials, (Springer, Cham, 2017), p. 9.

Current Methods for Improving TEG Lifetime

Little effort has gone into lifetime characterization of TEGs. Thermal fatigue results from cycling of temperature and can cause crack initiation. Thermal shock and thermal stresses from transient heating of TEGs cause cracks and other forms of defects, leading to poor lifetime of thermoelectric devices.[15,16] Thermo-mechanical stresses in TEGs were previously investigated.[80] One group tested the efficiency and TE properties as a function of the thermal cycles to obtain lifetime in terms of the property degradation, and they found that the resistance increased with the number of thermal cycles.[18] Another study monitored the thermal cracking and lifetime of the Bi-Te system and found that thermal stresses are higher during transient heating, that the thermal shock resistance can be calculated, and that an empirical formula can be used to ensure no failure occurs with given temperatures.[11] Failure from thermal expansion and thermal shock were tested in some high-temperature thermoelectrics, and it was found that TE material can fail, but the metal contact interface and CTE mismatch is more important for TEG design.[10,13]

Geometric pinning is an approach to spread heat more effectively in TEGs and has been modeled extensively to mitigate transient thermal stresses that degrade lifetime.[19,81,82] The tapered geometry has also been known to improve the efficiency and act as a current diverter.[83–85] Using a tapered TEG leg geometry, the area decreases continuously along the TEG. Compared to a TEG of the same material with constant area, or no pinning, and the same heat flux, q, the TEG with geometric pinning has smaller temperature differences, which lessen thermal stresses as shown in (3), where k is the thermal conductivity, A is the cross-sectional area, and T is the temperature.

$$q = -kA(T_2 - T_1) \quad (4)$$

Pinning of the geometry was also explored to mitigate the thermal stress in thermoelectrics; the setup for pinning the geometry is shown in Fig. 6.[19] Al-Merbati et al.[19] and Erturun et al.[86] also applied the approach of geometric pinning to alleviate high stresses in TEGs. Other groups have successfully mitigated thermal stresses by layering, segmentation, and composite fabrication.[11,72,87] Hatzikraniotis et al. characterized the efficiency and lifetime of a thermoelectric in terms of durability when they correlated the crack formation and growth to consequent electrical resistance changes.[18] It is evident, of course, that crack initiation with full crack growth is completely unwanted in TE materials.

In addition, multilayered composites exhibited better resistance to thermal stress cracking compared to individual layers of material.[72] Microstructure greatly affects the thermal stress behavior primarily due to the thermal conductivity differences.[88] A microstructural FGM has shown to mitigate transient thermal stresses leading to longer lifetime in the thermoelectric material.[67] FGMs can provide methods to increase the lifetime of thermoelectric materials, but there has been little development and research in this area. It is possible to design a TE material with longer lifetime and a wider efficiency range based, so it is important to understand the two independent effects on a TE material and TEG device.

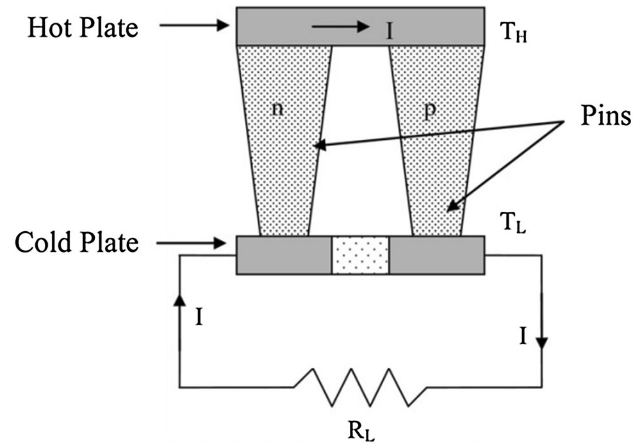

Fig. 6. Schematic of a thermoelectric generator and pin configuration.[19] Reprinted with permission from Elsevier, A. S. Al-Merbati, B. S. Yilbas, and A. Z. Sahin, Appl. Therm. Eng. 50, 683 (2013).

The work on ZnO with layering and continuous grain size gradations shows how grain size is another tool for designing thermoelectrics and can lead to enhanced lifetime, as suggested by the resistance increase in Fig. 7.

Modeling of TEG FGMs

Modeling efficiency as a function of current or current density is important for thermoelectric output, because the output is affected by property transitions and gradients.[49,57] Jin's model for power output of FGM TEG systems is a valuable tool concerning property gradients.[89] Many others have modeled TEGs in order to understand the effects of gradations, but none have been as successful as Jin's model.[51,90–92] In Jin et al., modeling of a composite thermoelectric material graded from 100% Bi_2Te_3 to 100% SiGe shows that the efficiency is higher for a large range of current density compared to the uniform SiGe sample.[89] In this model, the output is shown in Fig. 8. The gradation is partitioned into discrete layers of material. The enhancement is from the properties at different temperatures based on Bi_2Te_3 having higher efficiency at lower temperature. However, SiGe has higher efficiency at higher temperature. In this study, the data for the enhancement of the efficiency versus current density is presented without zT values. The equation for conversion efficiency in

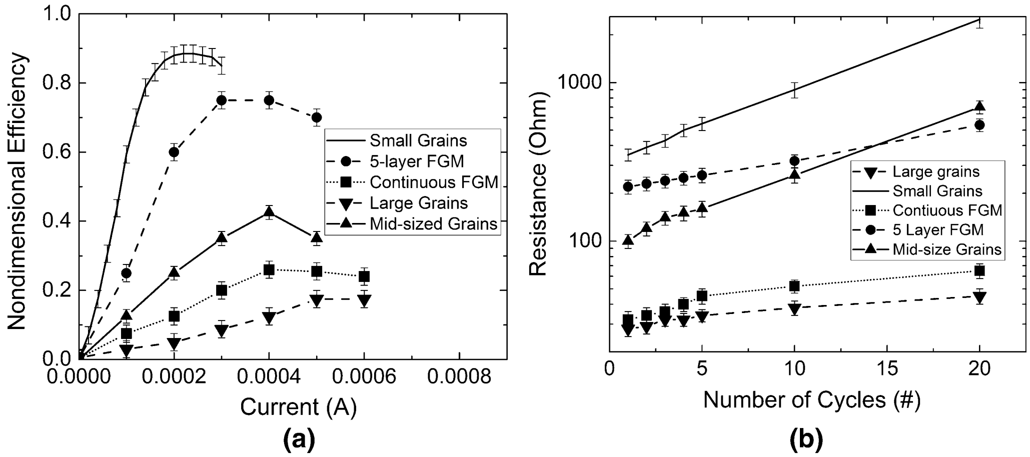

Fig. 7. Data of grain size gradation showing two FGMs have wider current ranges than homogenous grain size samples and both have less degradation in properties.[67] Reprinted with permission from Springer Nature, C. L. Cramer, W. Li, Z.-H. Jin, J. Wang, K. Ma, and T. B. Holland, J. Electron. Mater. 47, 866 (2018).

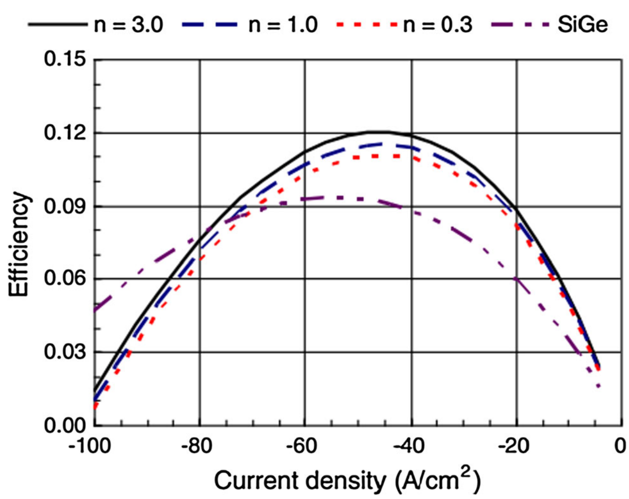

Fig. 8. Energy conversion efficiency versus electrical current density for a PbTb–SiGe graded nanocomposite of varying gradations, n, which is the degree of sigmoidal property difference across the thickness.[89] Reprinted with permission from Springer Nature, Z.-H. Jin and T. T. Wallace, J. Electron. Mater. 44, 1444 (2015).

terms of the thermoelectric properties is given below in (5),

$$\eta = \frac{J\sum_{n=0}^{N}\alpha_n(T_{n+1}-T_n) + J^2\sum_{n=0}^{N}\rho_n h_n}{-k_N\frac{T_h - T_N}{h_N} + \frac{1}{2}\rho_N J^2 h_N + J\alpha_N T_h}, \quad (5)$$

where the efficiency, η, is calculated using a multi-layered material model as follows, where J is the current density, T_n (n = 1, 2, …, N) are the temperatures at the interfaces between the layers, $T_0 = T_c$, $T_{N+1} = T_h$, k_n, S_n, and ρ_n are the thermal conductivity, Seebeck coefficient and electrical resistivity of the nth layer, respectively, and h_n is the thickness of the nth layer. Jin's work is shown below in Fig. 8, which indicates that a 3–4% increase in efficiency is predicted in a large current density range with property gradients that are very small from the hot side to the cold side. Namely, the thermal conductivity transitions from 1.2 W/mK on the cold side to 2.5 W/mK on the hot side, the Seebeck coefficient transitions from 230 μV/K on the cold side to 200 μV/K on the hot side, and the resistivity transitions from 3.1×10^{-5} Ω-m on the cold side to 2×10^{-5} Ω-m on the hot side. Jin's model was applied and validated using a layered ZnO thermoelectric material with graded grain size showing how grain size affects the current output.[67]

Processing of TEG FGMs

Typical TE materials are pressed and free sintered, but that limits the ability to control gradation, unless the powder is graded. More work has gone into sintering thermoelectrics with SPS because the processing is much faster, and studies show that SPS is a highly viable method for manufacturing TEGs because of fast processing, high relative densities, and improved directional properties, but the mass production of SPS materials is still lacking.[93] Using some of the advance techniques with SPS and modified tooling, FGMs can be achieved with SPS. Simulations of controlled TE material processed with SPS were done because of the property tailoring.[94] In general, SPS is a good method for consolidating TE material to be used in small-batch sized modules.

Modification in SPS tooling has helped to fabricate parts that were not thought achievable, but throughput is very low with processing of one specimen at a time.[95] A conical die arrangement was used to induce an in situ thermal gradient during sintering to axially densify different phases of material at different spots in the die.[96] One group created an axial microstructural gradient from fully dense to open porosity in a single step by using an offset die arrangement, which is an arrangement that creates a thermal gradient across the sintering specimen from increased current density through the offset plunger where there is less contact surface area. The concept of an offset die was used in another study to stabilize phases creating the first grain size gradient in an axial sample even though the grain size gradation was not the goal.[97] The first SPS processing of FGM TEGs was designed with modified tooling using a conical die approach intended for microstructural variation control.[98] A layered powder system of $Pb_{1-x}Sn_xTe$ was fabricated with different dopant concentrations using a free sintering method.[99] While there was little comparison in properties to a sample with homogeneous microstructure, enhancement in temperature ranges was achieved.

Contact Issues and Degradation of Interfaces

To integrate a TE material into a module or working device, the TE must be metallized and joined to a superstrate or housing. Contacts help to keep the efficiency high,[100] but it is well-known that failures of TEGs are not limited to TE materials. In fact, failures at the interfaces due to thermomechanical stresses and diffusion/contamination because of interconnect and interface materials could be equally damaging to the device performance and lifetime. To fabricate thermoelectric modules, the thermoelectric material must be joined to metal contacts. For a full module and working device, the metallization material must be compatible in terms of adherence and thermal expansion with both the *n*- and *p*-type materials.[101,102] Surfactant layers and mixed alloys are one way to help make intimate contact with TE material, but the lifetime of those contacts is still in question. One intricate study showed how *n*-type skutterudite TE material can be processed into a module by using a Mo diffusion barrier, high-temperature braze, and aluminum interconnect to the alumina housing,[103] but the diffusion barrier had some porosity and the process involves many steps (Fig. 9). One other set of materials could be a nickel diffusion barrier with a silver interconnect.

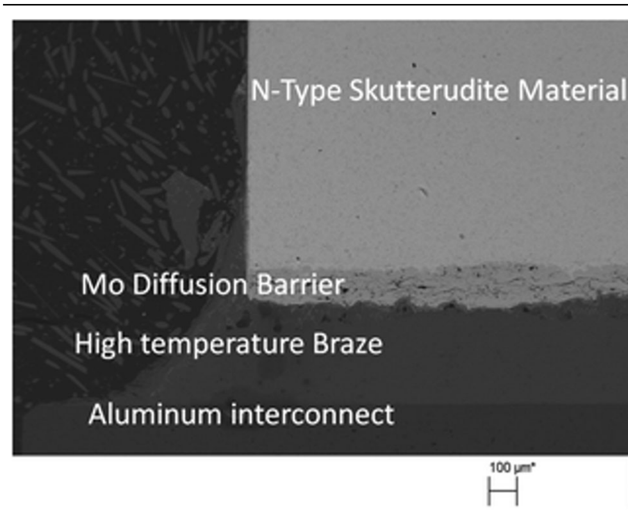

Fig. 9. SEM image of a sectioned TE element showing the TE material, the Mo diffusion barrier, the braze, and the aluminum interconnect. The porosity observed in the Mo diffusion barrier is likely one cause of the higher than expected module resistance.[103] Reproduced by permission of PCCP Owner Societies, J. R. Salvador, J. Y. Cho, Z. Ye, J. E. Moczygemba, A. J. Thompson, J. W. Sharp, J. D. Koenig, R. Maloney, T. Thompson, J. Sakamoto, and H. Wang, Phys. Chem. Chem. Phys. 16, 12510 (2014).

For metal contacts to be efficient, they must make ohmic contact with the thermoelectric material; be of low contact resistance or lower electrical resistance than the thermoelectric element; match the thermal expansion of the thermoelectric legs; and be chemically compatible with their surrounding materials.[104,105] Ohmic contacts have no voltage dependence on resistance, so they do not limit the current output. Research on the compatibility of contacts has been conducted on more industrial thermoelectric material.[106,107] Once a good metallization material and process is selected, the metal and thermoelectric material interface will be subject to degradation form thermal cycling.[108] Electrical property degradation from crack initiation and growth from thermal fatigue, thermal shock, and thermal expansion mismatch is one mode of degradation in TE material and TEGs. Diffusion of one material into the other is another mode of degradation for FGM TE materials and electrical contact interfaces. For the thermoelectric material, the diffusion of metal at the contact interface will change the properties and degrade the performance over time.[109]

Information on electrical contacts for efficient and long-lasting thermoelectric module devices is lacking in the literature. There needs to be more focus on finding proper contacts for the promising materials including diffusion barriers, brazes, and interconnects. Furthermore, for systems that have efficient contacts, the lifetime and degradation of the interfaces must be studied. Difficulties with thermal cracking and diffusion at the interfaces are unwanted and can be mitigated with the proper materials and techniques. With more research on contacts and interfaces, thermoelectrics will be more efficient and have extended service life, and they can be engineered for the more complex FGM thermoelectrics.

Future Direction

Time and intricate engineering are required to fabricate the best thermoelectric for a given application, and there are techniques for mitigating transient thermal stresses, as well as widening the temperature bandwidth, but they have not been used on common bulk modules of existing industrial TE material. The direction moving forward with these common materials is to optimize them as much as possible before moving on to more complex materials or thin-film materials. Because bulk, polycrystalline TEGs are used widely in industry, it is important to increase the performance of the materials. Typically, it is difficult to improve the zT of these materials, so the focus on FGMs for extended lifetime, as well as temperature or current density bandwidth, is important. With prolonged lifetime, the annual costs of operating thermoelectrics will decrease. In improving the temperature bandwidth, one material can be used instead of many bonded together. Using one material will cut down on costs, make for ease of manufacturing, and cut out metal contact issues in the middle of a device. Expanding the temperature or current density range can provide a TEG that works over a larger temperature range so that small, thin modules can still be used efficiently in a larger range of temperatures. This can also be applied to high-power, thick modules where maximum temperature difference is achieved. Another area in need of further study is the adequate pairing of n-type and p-type materials. In most thermoelectric materials, the performance of n-type material and p-type material of similar crystal structure and chemical composition is not balanced. In bulk materials such as skutterudite and half-Heusler, the zT of n-type materials is significantly higher than the p-type counterpart. In some cases, such as $MgSi_2$ (n-type) and tetrahedrite (p-type), the two legs must be different materials and require different bonding and interface materials. Developing FGMs that can improve and balance the performance of both legs is also important.

FGMs allow for one material to be used instead of multiple materials because the properties shift along the thickness, either allowing for a TEG with larger temperature bandwidth or one to be used in a large temperature gradient grain size, which can be used as a variable for improving thermoelectric output, temperature range, and lifetime. This is preceded by what kind of powder is used, or what method of fabrication is chosen for the TE material. An even larger zT range could be achieved with varying dopant concentration. This can be done with layering powder in SPS, but little has been studied with this enhancement. Early work on some FGMs for these types of developments has proven to be advantageous. Improving the bulk, polycrystalline material is a good place to start. Then, some of the more advanced techniques can and should be applied to the more complex materials.

With current, promising materials, the contact metal degradation should be studied because it is critical for the overall lifetime of a module. Contacts can have their own complications, such as cracking and poor adhesion to the housing material or the thermoelectric material. The thermoelectric material and metal contact interface could also experience cracking from thermal expansion mismatches, as well as unwanted diffusion of the two.

Another method of fabricating FGM TE materials is through 3-D printing in powder beds, where different powders can be used with multiple hoppers. Some 3-D printing of TE has been conducted, but it is far from optimized. In the case of 3-D printing, it could be possible to print contacts with thermoelectric material and achieve consolidation of the whole module except housing materials. A situation calling for both quantum well and bulk submicron-sized thermoelectric might arise, and in that case, the optimal module becomes highly complex in design. The engineering and design of bulk thermoelectric can still benefit from further research and it is worthwhile to use all the tools available. This review makes it known that there are more methods for improvements of bulk, polycrystalline thermoelectric material and modules.

CONCLUSION

Much work has been devoted into improving zT with new materials and techniques. From skutterudites to complex oxides, the developments in zT for bulk nanostructured TEGs are still progressing with more of the significant findings in thin-film materials or metastable semimetals. There are many common bulk, polycrystalline thermoelectrics used in industry that could benefit from more improvements with FGM for extended lifetime and extended useful temperature range. Some of these enhancements are based on temperature range widening, current output range, and lifetime. There has been some work in these areas, but not enough to start making an industry impact. Thermoelectrics with higher efficiency, temperature range, and lifetime can be developed with further engineering in bulk, polycrystalline material. Some of these methods have been shown in simple oxides, but they will likely translate to the more complex thermoelectrics, as well. Once research of bulk, polycrystalline materials has been completely exhausted for performance enhancements, it would be beneficial to include them in module research for industrial use. By using FGM methods, controlling properties, controlling thermal stresses, and designing proper electrical contacts for less crack initiation and diffusion, thermoelectric research will help industry thrive with efficient and long-lasting TEGs using current materials.

ACKNOWLEDGEMENTS

Corson L. Cramer would like to thank Olivia Shafer for help formatting and editing. This material is based upon work supported by the US Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Advanced Manufacturing and Propulsion Materials program under the Vehicle Technology Office, under Contract No. DE-AC05-00OR22725.

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