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Rapid processing and assembly of semiconductor thermoelectric materials for energy conversion devices

Ahmed El-Desouky, Michael Carter, Matthieu A. Andre, Philippe M. Bardet, Saniya LeBlanc*

Department of Mechanical & Aerospace Engineering, The George Washington University, USA

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ABSTRACT

Thermoelectric devices can convert heat to electricity. Recent advancements in the development of semiconductor thermoelectric materials have led to a significant increase in the thermoelectric figure of merit *ZT*. However, challenges in materials processing and assembly hinder the potential of thermoelectric power generation. An assessment of alternative advanced manufacturing methods for thermoelectric devices reveals the advantages of selective laser melting. While laser melting is a well-established additive manufacturing technique for metals, ceramics, and polymers, this study will provide the first investigations of semiconductor materials melt-processing using a laser. Preliminary experimental results demonstrate the effect of laser processing parameters on the microstructure and densification of the melt line.

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1. Introduction

Thermoelectric devices can convert thermal energy into usable electrical energy. When a temperature gradient exists across a semiconductor thermoelectric material, the more energetic electrons at the hot side will diffuse to the cold side until an electric field develops and prevents further diffusion; this phenomenon is the Seebeck effect. A thermoelectric module typically consists of n-type and p-type legs. These legs are connected electrically in series and thermally in parallel as shown in Fig. 1a. With the increasing interest in thermoelectric power generation for waste heat recovery, there has been continuous progress on the materials development front to increase materials' figures of merit, *ZT* [1–4]. However, significant increase in material *ZT* does not reflect the challenges of integrating materials into practical devices. Materials processing and integration challenges continue to be dominant factors behind the limited performance and high cost of thermoelectric generators [5–9].

In this work, we identify materials processing and assembly challenges for semiconductor materials in thermoelectric devices. We also provide insight into alternative materials processing and assembly solutions and deliver preliminary findings on the effect of selective laser melting on the densification of thermoelectric materials.

2. Thermoelectric device manufacturing

2.1. Material Considerations

The performance of thermoelectric materials is quantified by the dimensionless thermoelectric figure of merit $ZT = (S^2\sigma/k)T$ where S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity, and T is the temperature of the material. The main challenge in thermoelectric materials selection comes from the dependence of S, σ, and k on the band structure and charge carrier concentration. Normally, materials with a high Seebeck coefficient and good electrical conductance are also good conductors of heat. Thermoelectric materials are generally classified by their composition and structure (chalcogenide, clathrate, skutterudite, half-Heusler, silicide, and oxide) and/or by their dimension (bulk, film, nanowires, and quantum dot superlattices) [10]. In recent years, remarkable progress in increasing the peak *ZT* through tailoring microstructures and employing low dimensional materials such as nano-wires and quantum dots has been reported. However, these material advancements have been mostly confined to lab-scale practices and are yet to be demonstrated on the device level [8]. The progress in thermoelectric power generation is hindered by materials processing and device

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* Correspondence to: The George Washington University, Department of Mechanical & Aerospace Engineering, 800 22nd St. NW, Suite 3000, Washington, DC 20052, USA.

E-mail address: sleblanc@gwu.edu (S. LeBlanc).

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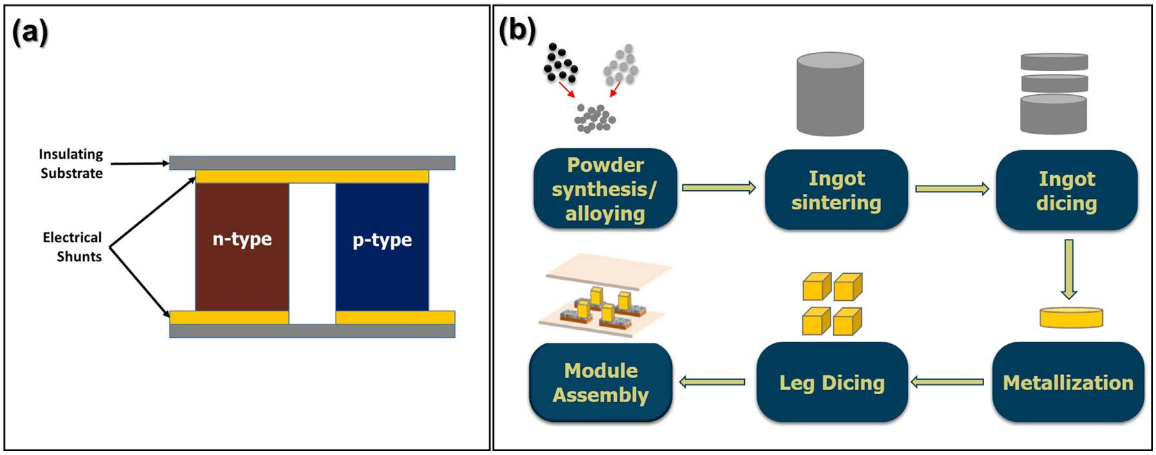

Fig. 1. Schematics of a thermoelectric unicouple (a) (a thermoelectric device consists of many couples between two electrically insulating substrates) and traditional thermoelectric device manufacturing steps (b).

engineering challenges. Continuing to improve the materials performance in isolation of materials processing considerations is insufficient to develop thermoelectric devices that can be used in practical applications.

2.2. *Thermoelectric materials processing*

Fig. 1b shows a schematic of a typical thermoelectric device manufacturing process. The constituents of a thermoelectric material are mechanically alloyed, and the resulting powder is consolidated into ingots through conventional sintering techniques such as hot pressing or spark plasma sintering. Dicing of the sintered ingot accounts for up to 50% of material losses due to chipping, cracking, and kerf losses [5,8]. The dicing step also poses geometric limitations on the thermoelectric leg shape and dimensions, so most thermoelectric legs in commercial devices are square or rectangular in shape. Finally, the legs are integrated into the final assembly, often through manual or automated pick-and-place operations which can be costly and time-consuming.

Multiple bulk thermoelectric materials (*e.g.*, chalcogenides, skutterudites, silicides, *etc.*) are promising for power generation; however, scalable production of these materials and integration into the devices are critical challenges. The use of thermoelectric generators in practical applications hinges on improving the device performance through employing more effective materials processing and assembly methods.

2.3. *Alternative manufacturing methods*

Advanced manufacturing methods, such as additive manufacturing, have the potential to address materials processing and assembly challenges in thermoelectric devices. Table 1 shows a comparison between traditional thermoelectric manufacturing and common additive manufacturing methods. The additive approach would eliminate lengthy assembly processes by enabling consolidation of thermoelectric legs directly onto substrates. The freeform nature of additively manufactured products allows designs that are not possible through traditional machining. Flexibility in the design of device geometries enables better device performance through optimization of leg size, shape, and pattern. In this section, we survey different additive manufacturing methods with the potential for thermoelectric materials processing. The methods surveyed included liquid-based methods, stereolithography and fused deposition modeling, powder-based methods, binder jetting and selective laser melting. More detail on these and other additive manufacturing methods can be found in many excellent reviews [11–17].

In stereolithography, a low power UV laser is used to solidify thin layers of a photosensitive polymer. Stereolithography can employ suspensions of materials, such as polymers and ceramics, up to 60% by volume, to produce consolidated, complex final parts, but it requires post-processing for binder-removal and sintering [13,18]. Binder jetting uses a print-head to dispense a binder

Table 1
Comparison of traditional thermoelectric manufacturing and additive manufacturing methods (stereolithography, fused deposition modeling, binder jetting and selective laser melting). Processing temperature ranges represent the consolidation temperature ranges associated with each manufacturing technique. While the traditional thermoelectric manufacturing process does not have a burnout post-processing step, there are joining steps like soldering/brazing.

	Materials		***Assembly***	***Geometry***	***Post-processing***	***Material losses***
	Common materials	***Processing temperature***				
Traditional thermoelectric manufacturing	Semiconductor thermoelectric materials	Low–High	Manual or automated	Limited to simple geometries (rectangular)	Dicing, soldering/ brazing	High
Stereolithography	Polymers, metals and ceramics	Low–High	Direct assembly	Free form	Required for binder burnout and sintering	Low
Fused deposition modeling	Polymers, composites and low-temperature alloys	Low	Direct assembly	Free form	Optional	Low
Binder jetting	Metals, polymers, ceramics and composites	Low–High	Direct assembly	Free form	Required for binder burnout and sintering	Low
Selective laser melting	Metals, ceramics, and composites	Low–High	Direct assembly	Free form	Optional	Low

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material which joins part of a thin layer of powder in the shape of the desired geometry. The complex part is built up layer-by-layer, and post-processing is required for binder burnout and sintering [15,19]. Both stereolithography and binder jetting offer routes for thermoelectric materials processing that would eliminate assembly and materials losses [20]. However, the need for polymer burnout and sintering through post-processing limits the potential of these technologies to reduce time and cost. Moreover, traditional pressure-less sintering used in post-processing can lead to porosity formation and poor adhesion to the underlying substrate, both of which increase electrical resistance and lower device performance. Fused deposition modeling is a melt-extrusion method where the print head melts a filament and directly deposits it onto a substrate. This method is typically used with polymers [13,19] or polymer-based composites [15,21]. While fused deposition modeling does not require post-processing, it has only been demonstrated on polymer based materials and low melting temperature solder alloys [22] and is not suitable for high temperature materials like those required for thermoelectric devices in exhaust waste-heat recovery applications.

Utilizing selective laser melting to process thermoelectric materials would enable rapid production and assembly of thermoelectric legs onto substrates without the need to post-process [23]. In selective laser melting, a laser beam locally melts a thin layer of powder in a desired pattern. The process is repeated for subsequent layers of powder to form a three-dimensional structure. Selective laser melting can produce near full-density final parts of metals and ceramics without the need for post-processing [11,12,24–26]. Fig. 2 shows a typical off-the-shelf thermoelectric module and a schematic of selective laser melting of thermoelectric legs on a ceramic substrate. Depositing and melting the thermoelectric material onto the substrate could improve mechanical adhesion and minimize contact resistance. Furthermore, material losses can be minimized since excess loose powder can be used in future runs.

3. Experiments

This experiment investigates the consolidation behavior of a traditional thermoelectric semiconductor material, bismuth telluride (Bi_2Te_3), in response to laser processing. Selective laser melting of Bi_2Te_3 and other thermoelectric materials hinges on the ability to deposit powders in a layer-by-layer fashion. Metal powders used in layer-by-layer manufacturing are typically produced with atomization methods that make spherical-shaped particles with good flow characteristics [26–28]. While atomization of spherical shape thermoelectric powder has been demonstrated in literature [29,30], most commercial thermoelectric powders have irregularly shaped particles prepared using mechanical comminution methods, so uniform layer-by-layer deposition is not possible with off-the-shelf thermoelectric material powders. In this proof of concept experiment, commercial Bi_2Te_3 powder (-325 mesh, 99.99% trace metals basis, Sigma Aldrich) was compacted under a uniaxial pressure of $\sim$295 MPa into disks 6 mm in diameter and $\sim$0.5 mm thick.

Single melt lines were formed on the surface of the powder compacts using a Photonics Industries DM Series Dual Head High Pulse Energy (0–10 kHz) Nd: YLF laser (527 nm wavelength). The laser beam had an approximately Gaussian profile ($M^2 = 13.6$) and was focused to a spot size of $\sim$300 μm diameter with a 500 ns pulse length. The powder compacts were mounted on an Optics Focus linear motorized translation stage (MOX-0-200) using a sample holder that was built in-house, and the translation speed was set to 40 mm/s using an Optics Focus Motion Controller (MOC-01-1-110). The laser repetition rate was set at 5 kHz and the average power was set to 3 W and 5 W (0.6 and 1 mJ/pulse corresponding to $\sim$0.8 J/cm^2 and 1.2 J/cm^2 at the present scan speed, respectively) to investigate the effect of laser power variation on the melting behavior of Bi_2Te_3 powder compacts. Processed samples were cleaved across the melt lines, and scanning electron micrographs of the cross-section and the top surface were taken using a field emission scanning electron microscope (Zeiss Sigma VP).

4. Results and discussion

Single melt lines were observed on the top surface of the Bi_2Te_3 compacts in the wake of the laser beam at 3 W and 5 W average power (Fig. 3a, c). For both power settings, complete melting was evident at the center of the scan line while the edges showed partial consolidation due to the Gaussian distribution of the laser beam. The increase in average power resulted in an increase in the width of the fully consolidated line (420 μm at 5 W compared to 290 μm at 3 W). Randomly oriented microcracks were observed on the top surfaces for both power settings. Surface cracking is a common selective laser melting defect that takes place in brittle materials due to thermally induced stresses during material expansion and shrinkage [31].

The depth of the melt line is shown in (Fig. 3b, d). At 3 W average power, consolidation under the melt line was not evident; melting likely only occurred at a small depth of less than 10 μm. The disk irradiated at 5 W average power had a clear arc-shaped consolidated region beneath the melt line. The depth of the consolidated region was highest ($\sim$50 μm) at the center and

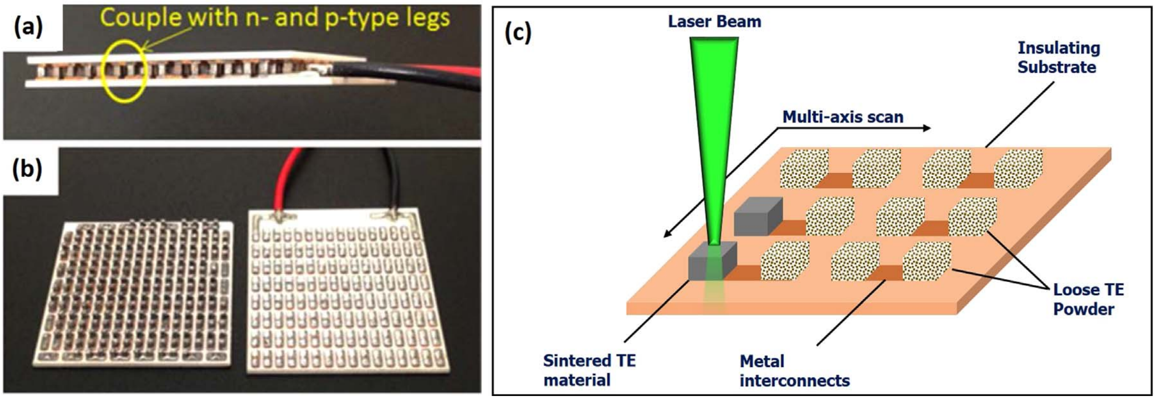

Fig. 2. A typical off-the-shelf thermoelectric module showing multiple thermoelectric couples (a) and the interior of the module (b) [8]. Schematic of laser melting of multiple thermoelectric legs on a substrate (c).

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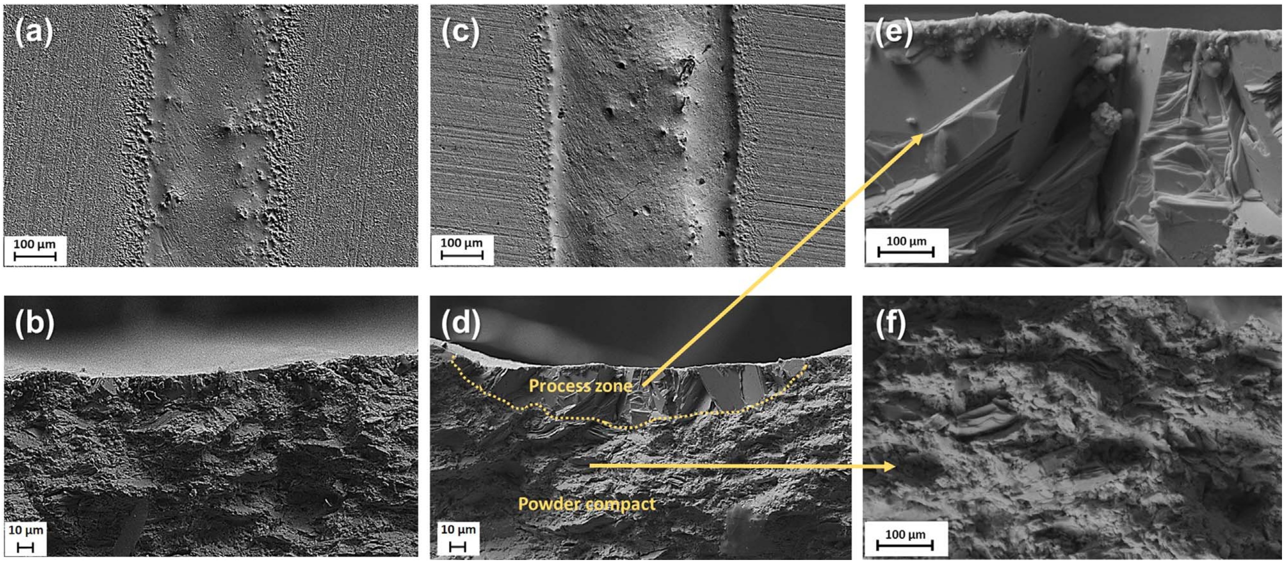

Fig. 3. Scanning electron micrographs of a melt line on a bismuth telluride powder compact surface processed with a 3 W and 5 W laser average power (a, c), cross-section (fracture surface) under the incidence of laser (b, d), and higher magnification images of the fracture surface showing the melt zone *versus* unconsolidated powder compact regions (e, f).

decreased near the edge of the melt line. The partial melting on the surface and the decrease in the depth towards the boundaries is a result of the Gaussian distribution of the beam.

The results provide evidence that Bi_2Te_3 can be processed using selective laser melting. The processing parameters of a nano-second pulsed laser source were adjusted to achieve a melt depth (~50 μm) that is greater than the size of the largest particle (~45 μm). Optimization of the process is needed to achieve larger melt depths and attain a sufficient overlap between deposited layers of powders [26]. In our previous work, excessive material ejection and splatter was observed at a higher fluence of 1.8 J/cm^2 [32]. High intensity laser-matter interactions can lead to significant evaporation and the development of high recoil pressures on the work surface as well as supersonic flow conditions in the vapor above the work surface [33]. These effects are not completely undesirable since recoil pressures can have the advantageous effect of flattening the molten pool or even driving deeper consolidation [34,35]. Evaporation and recoil pressures must be controlled in order to reduce undesirable effects such as splatter and material ejection. Intense plasma recoil pressure can be avoided by using a continuous wave laser similar to most commercial selective laser melting systems or by using a pulsed laser with a higher repetition rate and longer pulse width. The average powers used on compacted powder will need to be adapted to process loose powder beds where successive reflections increase the optical penetration depths and give rise to volumetric heating [35].

5. Conclusion

Materials processing and assembly challenges continue to hinder progress in thermoelectric power generator development. Advanced manufacturing methods such as selective laser melting provide alternative materials processing routes that could improve the thermoelectric device performance and lower costs. A traditional thermoelectric semiconductor material (Bi_2Te_3) was successfully processed using selective laser melting. The depth of melting achieved on Bi_2Te_3 powder compacts was greater than the starting powder's largest particle size, indicating at least one complete layer of powder was consolidated. Optimization of the thermoelectric powder and laser parameters is crucial for advancing additive manufacturing of thermoelectric devices.

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