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Fabrication and characterization of thermoelectric power generators with segmented legs synthesized by one-step spark plasma sintering

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ABSTRACT

A thermoelectric (TE) power generator with eight pairs of segmented TE legs was fabricated and characterized. The segmented TE legs were synthesized by one-step spark plasma sintering (SPS), including n-type $Bi_2Te_3/PbSe_{0.5}Te_{0.5}$ and p-type $Bi_{0.3}Sb_{1.7}Te_3/Zn_4Sb_3$ legs. They were assembled on AlN substrates with patterned Cu electrodes by soldering to form a thermoelectric generator (TEG). Power generation of the TEG was measured using a desktop TEG testing instrument. A maximum output power of 48.6 mW was obtained at a temperature difference of 296 K. The Seebeck voltage of the segmented TE legs was 17.4% less than the theoretical value, which was satisfactory. The electrical resistance of the segmented legs was dramatically increased in comparison with that of the bulk materials, which was due to the large interfacial resistance between different segments in the TE legs; therefore, the interfacial resistance was found to be one of the key factors limiting the power generation of the segmented TEG. The output power of the segmented TEG without interfacial resistance was predicted to be 165.9 mW, and the corresponding efficiency was 1.53%. The experimental and simulation data demonstrate that it is feasible to fabricate a high-performance TEG with segmented legs synthesized by one-step SPS.

1. Introduction

Energy demand is surging with the rapid development of human society [1]. Recently, thermoelectric generators (TEGs) have attracted much interests among researchers, because TEGs have many advantages such as direct conversion from thermal energy to electricity, fast response, good reliability, and low noise [2–6]. For example, TEGs can be used to recapture the waste heat energy of automotive exhaust gas [7–11]; Portable TEGs can continuously supply power for wireless devices and sensors by collecting environmental energy [12–16].

The efficiency of TEG energy conversion depends on the intrinsic properties of thermoelectric (TE) materials and TEG fabrication processes. For the former, various high-quality TE materials were studied to improve the TEG efficiency, including Bi_2Te_3 [17–24], ZnSb [25–28], PbTe [29–32], $CoSb_3$ [33–34], half-Heusler [35–36], oxide [37–38] et al.. The TE material performance is evaluated using the dimensionless thermoelectric figure of merit ZT. This is defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity. The larger the ZT value, the better is the TE material. On the other side, different processes were adopted to fabricate TEGs. Welding was usually used to connect TE legs with electrodes in the assembly of TE modules [39–42]. Zhao et al. connected hot-side electrodes with $CoSb_3$-based materials by spark plasma sintering (SPS) and obtained a TE module with an efficiency of 6.4% [34]. Snyder et al. and Roth et al. fabricated cross-plane TE microgenerators using electrodeposition [39,43]. Goncalves et al. made a planar Peltier cooler on a flexible substrate [44]. Tan et al. used sputtering and mask technology to make a TE micro-device with columnar Cu film electrodes, which enhanced output power [45]. In addition, printing was used by Madan et al. to make TE devices [46].

Recently, segmented TE power generators have been extensively investigated. In segmented TE modules, two or three kinds of TE

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materials whose maximum *ZT* values appear at different temperature ranges are connected to form a single TE leg. Thus segmented TE legs possess a large average *ZT* value over a wide temperature range. Segmented TE modules with high efficiency or large output power were reported, including Mn_2Si-based, Bi_2Te_3-based, PbTe-based, and $CoSb_3$-based segments [40–42, 47–49]. In these segmented TE legs, different segments were usually connected together by welding; however, this process was complicated and the bonding alloys might have diffused into TE materials causing material degradation [50–53]. To eliminate welding processes, Yoon et al. used one-step SPS to fabricate an n-type segmented $Bi_2Te_3/PbSe_{0.5}Te_{0.5}$ leg whose output power was 15% and 73% higher, respectively, than those of individual Bi_2Te_3 and $PbSe_{0.5}Te_{0.5}$ legs with a temperature difference $\varDelta T$ of 400 K [49]. However, power generators with segmented TE legs synthesized using one-step SPS have not been reported in the literature, as far as we know.

In this paper, we synthesized n-type $Bi_2Te_3/PbSe_{0.5}Te_{0.5}$ and p-type $Bi_{0.3}Sb_{1.7}Te_3/Zn_4Sb_3$ segmented TE legs by one-step SPS and fabricated a π-shaped TEG with 8 pairs of segmented TE legs. The output power of the TEG was measured, the internal resistances of the module were fully analyzed, and the key factors to optimize the efficiency of the segmented TE module were found and discussed.

2. Experimental

2.1. Material synthesis and characterization

High-purity powders (≥99.99%) were used as raw materials to compose n-type $Bi_2Te_3/PbSe_{0.5}Te_{0.5}$ and p-type $Bi_{0.3}Sb_{1.7}Te_3/Zn_4Sb_3$ TE legs. These powders were charged into stainless-steel vials according to corresponding stoichiometric compositions and subjected to a mechanical alloying (MA) process with Ar protection by ball milling. To make an n-type segmented leg, 5 g $PbSe_{0.5}Te_{0.5}$ milled powder was charged into a carbon die and tightly pressed. Then, 5 g Bi_2Te_3 milled powder was placed on top of the $PbSe_{0.5}Te_{0.5}$ powder and pressed again [49]. Subsequently, the carbon die charged with $PbSe_{0.5}Te_{0.5}$ and Bi_2Te_3 powders was spark plasma sintered (SPSed) at 400 °C with an axial compressive stress of 50 MPa. P-type segmented legs were similarly prepared. Table 1 lists the experimental conditions in the MA and SPS processes. The sintered segmented specimens were cut into cube-shaped pieces of $3 \times 3 \times 3.7$ mm^3 by wire-electrode cutting and polished with sand papers. The length of Bi_2Te_3, $PbSe_{0.5}Te_{0.5}$, $Bi_{0.3}Sb_{1.7}Te_3$ and Zn_4Sb_3 segments is 2.0, 1.7, 1.7, and 2.0 mm, respectively.

Non-segmented specimens were prepared using the same sintering processes. Phase identification of $PbSe_{0.5}Te_{0.5}$ and Zn_4Sb_3 specimens was carried out with X-ray diffractometry (XRD, D/max-RB RIGAKU, Japan) using Cu K_α radiation. The Seebeck coefficient S and electrical conductivity σ were measured using a Seebeck Coefficient/Electrical Resistance Measuring System (LSR-3, LINSEIS, Germany) in He gas. The thermal diffusivity α was measured using a laser flash apparatus (LFA457, NETZSCH, Germany). The heat capacity C_p was obtained using differential scanning calorimetry (Q2000, TA, USA). The density ρ was obtained using the Archimedes method (XS105, METTLER TOLEDO, Switzerland). The thermal conductivity κ was calculated according to $\kappa = \alpha \times \rho \times C_p$.

2.2. Module fabrication

Fig. 1 shows the fabrication processes of a segmented TE module with eight pairs of legs. Aluminum nitride (AlN) plates with patterned 30 μm-thickness Cu electrodes were used as top and bottom plates in TE modules. The size of AlN plates was 25×25 mm^2. AlN was chosen because of its large thermal conductivity and good electrical insulation. At first, Sn-95 Pb solder paste was placed on Cu electrodes by hard-mask printing. Then, segmented TE legs were sequentially soldered with the bottom plate and top plate on a heater at 360 °C. At the end, lead wires were connected to the Cu pads on the bottom plate with Sn solder. The top- and side-view photos of a π-shaped TE module are shown in Fig. 1. A 3D model of the TE module with eight pairs of segmented legs is shown in Fig. 2(a). To clearly illustrate the segmented legs, the top AlN plate and Cu electrodes are not presented. Additionally, a schematic of a pair of segmented legs is shown in Fig. 2(b).

In this work, the pair of TE legs n was determined to be eight for the following reasons. First, the output power and voltage of the TEG are proportional to n due to the serial connection. The larger the n, the larger are the output power and voltage. A large output power or voltage is needed for testing and actual applications. Second, the purpose of this work is to demonstrate the feasibility of a TEG with segmented legs synthesized by one-step SPS. If n is too small, the structure of the module is too simple to exhibit potential fabrication issues, which is not good for the optimization and expansion of the module. Third, it is difficult for a prototype device made in a laboratory to fabricate a module with a large number of n, because the preparation of TE legs is time-consuming and the module assembly is not easy. Therefore, we chose $n =$ eight with a tradeoff among the module properties, fabrication easiness, and device scalability.

2.3. Module test

The power generation of assembled TE modules was tested on a desktop TEG testing instrumentation whose schematic is shown in Fig. 3 [54]. TE modules were clamped between the heater and heat sink. A clamping pressure was applied manually with a torque wrench to guarantee an effective thermal contact [54]. The temperatures of the heater and heat sink were controlled using a programmable logic controller (MK1000, INSTECTM, USA). The actual temperatures at the hot and cold ends of the TE modules were measured simultaneously using thermocouple thermometers. The temperature difference $\varDelta T$ was raised by elevating the temperature at the hot end.

The open-circuit voltage V_o and short-circuit current I_s of the TE modules were measured using a high power system SourceMeter® (2651A, KEITHLEY INSTRUMENTS INC., USA). The maximum output power of the TE modules P_m at certain $\varDelta T$ was calculated using Eq. (1):

$$P_m = I_s V_o / 4. \tag{1}$$

No external resistance or load was used in the setup for the measurement (Fig. 3).

Table 1
Experimental conditions in MA and SPS processes.

Material		MA rotation speed	MA ball mill time	SPS temperature	SPS axial pressure	SPS sintering time
n-type	$PbSe_{0.5}Te_{0.5}$	450 rpm	3 h	400 °C	50 MPa	10 min
	Bi_2Te_3	450 rpm	3 h	400 °C	50 MPa	10 min
p-type	Zn_4Sb_3	200 rpm	2 h	400 °C	50 MPa	10 min
	$Bi_{0.3}Sb_{1.7}Te_3$	450 rpm	3 h	400 °C	50 MPa	10 min