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Design of segmented thermoelectric generator based on cost-effective and light-weight thermoelectric alloys

Hee Seok Kim[a], Keiko Kikuchi[b], Takashi Itoh[c], Tsutomu Iida[d], Minoru Taya[a,*]

[a] Center for Intelligent Materials and Systems, Department of Mechanical Engineering, University of Washington, Box 352600, Seattle, WA 98195-2600, USA
[b] Department of Material Processing, Tohoku University, Sendai 980-8579, Japan
[c] EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[d] Department of Materials Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda-Shi, Chiba 278-8510, Japan

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ABSTRACT

A segmented thermoelectric (TE) generator was designed with higher temperature segments composed of n-type Mg_2Si and p-type higher manganese silicide (HMS) and lower temperature segments composed of n- and p-type Bi–Te based compounds. Since magnesium and silicon based TE alloys have low densities, they produce a TE module with a high specific power density that is suitable for airborne applications. A two-pair segmented π-shaped TE generator was assembled with low contact resistance materials across bonding interfaces. The peak specific power density of this generator was measured at 42.9 W/kg under a 498 °C temperature difference, which has a good agreement with analytical predictions.

1. Introduction

Thermoelectric (TE) module is effective in the direct conversion from thermal energy to electrical energy. Since TE energy conversion is based on all solid-state technology, it has unique advantages such as high reliability and quiet, environmentally friendly operation [1]. With these advantages, TE devices have been used in a wide range of applications from temperature measurement to waste heat recovery and refrigeration [2–4]. Recently, TE modules have been applied to automobiles [5,6] and unmanned aerial vehicles (UAV) for the purpose of thermal energy harvesting [7,8]. In automobile applications, the use of TE modules increases fuel efficiency by recapturing wasted exhaust heat and converting it to useable electricity [9].

The majority of research on thermoelectrics is aimed at increasing the figure-of-merit (ZT) value without considering other factors such as the interfacial bonding materials, weight, cost-effectiveness, environmental damage, and ease of mass production. For airborne and other weight-sensitive applications the specific figure of merit, defined as ZT divided by mass density, should be emphasized. Popular segmented TE generators working at a high temperature range use heavy alloys based on Lead Telluride compounds [10,11], $AgPb_mSbTe_{2+m}$ (LAST) [12], Te/Ag/Ge/Sb (TAGS) [10] and Co–Sb compounds [13,14]. Even though these popular TE materials provide higher ZT values, they have large densities of more than 8.0 g/cm^3. In addition, both lead (Pb) and tellurium (Te) are classified as toxic materials [15]. Oxide-based TE alloys, such as Co–O-based p-type and Zn–O-based n-type, are considered environmentally friendly but they have low electrical properties resulting in a generator with low output power [16]. Many thermoelectric generators use expensive materials such as the rare element Te, one of the key components in TE system, Ag in the LAST, and Ge in the TAGS systems, resulting in an increased cost of final device.

A segmented design of joined TE materials with different operating temperatures is widely utilized for maximizing output power [17]. This study focuses on bulk Mg_2Si of n-type [18] and higher manganese silicide (HMS, $MnSi_{2-x}$, $x = 0.250–0.273$) [19] of p-type integrated into the high temperature region of a segmented TE generator. Both of these materials have low densities compared with other TE material candidates and have operating temperatures up to 600 °C. This results in a lighter TE generator that has a higher specific output power, which is ideal for airborne engine applications. A choice of TE materials is an important factor to consider cost effectiveness assuming that the common metal electrodes and ceramic substrates are used for a module assembly. The Clarke index of Si, Mg and Mn have high ranks of 2nd, 8th and 9th respectively, indicating that these materials are more abundant compared with Ge,

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* Corresponding author. Tel.: +206 685 2850; fax: +206 685 8047.
E-mail addresses: tayam@u.washington.edu, tayam@uw.edu (M. Taya).

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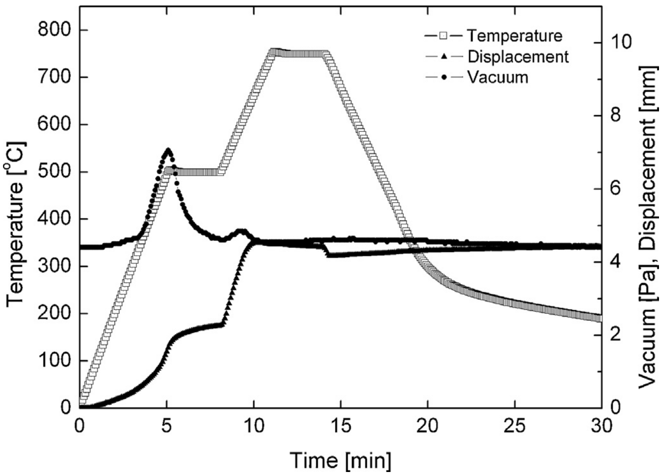

Fig. 1. Vacuum level and the displacement of the sample during the sintering with the temperature excursion of two-step SPS process.

Ag and Te (rank 53, 66 and 70, respectively) [20]. The cost of Si, Mg and Mn has been stable and as low as 10 US dollar value in 1998 per kilogram for last 40 years while that of Te and Ge has been fluctuated and as much as 250 and 1000 US dollar value in 1998 per kilogram [21,22]. Thus, TE materials based on Si, Mg and Mn can be low-cost. In addition, Mg_2Si and HMS consist of non-toxic elements. Various processing routes of Mg_2Si have been reported such as direct melting [23], solid state reactions and hot press (HP) [24], the vertical Bridgman method [25,26], HP after melt-spinning [27], and microwave synthesis [28–30]. This study shows the processing route of TE legs using mechanical alloying followed by spark plasma sintering (SPS) since both mechanical alloying and SPS are rapid synthesis method to minimize grain growth, and can be carried out at relatively lower temperature compared to other synthesis methods such as direct melting, HP and vertical Bridgman method. The rapid and low temperature method is desired to reduce lattice thermal conductivity by increasing phonon scattering.

In this study, the synthesis of TE legs and the fabrication of TE module based on a typical π-shape design will be described. In the following, we will discuss the experimental work on the processing of TE materials, the characterization of TE properties and the measurements of as-assembled TE generator, followed by the comparison of the power output between the experiment and modeling.

2. Experimental

2.1. Preparation of TE legs

Mg (99.95%, Alfa Aeser), Si (99.9999%, Alfa Aeser) and Bi (99.999%, Alfa Aeser) were purchased as starting materials for the Bi doped Mg_2Si high temperature n-type segment. Polycrystalline Mg_2Si with Bi doping was synthesized with Mg:Si ratio of 67:33 (at%) including the Bi dopant (3 at%) using an electric furnace [18]. The obtained polycrystalline compound was crushed into powders via planetary ball milling with a tungsten carbide (WC) jar and balls. The powders were transferred to a glovebox with Ar atmosphere and set up in a graphite die for spark plasma sintering (SPS, Sumitomo Coal Mining Co., Ltd., Dr. Sinter 1020S). The assembled graphite mold of 15 mm in diameter was heated in a two-step procedure for SPS. The first step heats the specimen at 30 MPa from room temperature up to 500 °C with a rate of 100 °C/min and held the specimen at 500 °C for 3 min. This pre-heating step allowed one to maintain low vacuum level at the next sintering step. As shown in Fig. 1, the vacuum level in the SPS chamber started at 4.4 Pa, increased up to 7 Pa at 500 °C, dropped to 4.6 Pa after the 3 min holding step at 500 °C, and was held at 4.6 Pa for the rest of the process. For the second step, the powder in the graphite mold was pressurized up to 50 MPa while it was heated to 750 °C with a heating rate of 100 °C/min. After holding at 750 °C for 3 min, the specimen was cooled. This optimized two-step SPS process enabled one to keep the chamber vacuum level low, which minimized the chance of oxidation and contamination. The sintered Mg_2Si disk was cut into rectangular pillars of 4 mm × 4 mm × 5 mm by a diamond saw.

The fabrication of p-type higher manganese silicide (HMS) for the high temperature segment included improvements when compared with previous work [19] for enhancing fabrication stability. Powders of Mn (99.9%) and Si (99.9%) were individually put into an alumina milling jar with alumina balls, where the ball to powder volume ratio was 20:1. Mechanical grinding was carried out in vibration ball milling equipment for 10 h in Ar atmosphere and then the ground powders were mixed with a Mn:Si ratio (at%) of 35.5:64.5 in rotary blender at 100 rpm for 1 h in Ar atmosphere. The HMS compound was synthesized and consolidated simultaneously in the graphite mold of 20 mm in diameter at 900 °C and 30 MPa for 15 min in a vacuum by SPS method. This sintered HMS was then cut into 4 mm × 4 mm × 3.4 mm blocks by a diamond saw.

Both n-type and p-type Bi-Te based compounds working at low temperature range were purchased from Tellurex Inc. in the shape of 4 mm × 4 mm × 1 mm and 4 mm × 4 mm × 2.6 mm respectively.

2.2. Characterization and contact resistance

The Seebeck coefficient and electrical conductivity were measured by using a four-point probe measurement system (Ulvac, ZEM-3) on sintered 2 mm × 2 mm × 10 mm bars. For thermal conductivity measurements, a sample with 10 mm in diameter and 1 mm thickness was then prepared for the laser flash measurement system (Ulvac, TC-9000). This equipment was used to measure the thermal diffusivity and specific heat capacity of the specimen simultaneously from room temperature to 600 °C for the high temperature compounds and from room temperature to 300 °C for the lower temperature compounds of Bi–Te system.

Electrical contact resistance plays an important role in the segmented TE module generator. High contact resistance between TE segments or at the interface of the metal electrodes would decrease the generator's performance by reducing output power generation [31]. In addition, the electrical contact resistances at the intermediate bonding interfaces of TE segments are usually larger than those at the junctions of TE elements bonded with metal electrodes of hot and cold sides because it is hard to bond directly between semiconductor materials (TE legs) by soldering. Thus, before soldering processes, it is essential that Ti (50 nm) and Ag (1 μm) layers are coated by an electron-beam evaporator to increase the interface bonding. Ti is an active element and an ideal adhesion material between the semiconductor blocks and the metal coating layer. Ag has low wetting contact angle, which helps the surface stick to the bonding alloys. The contact resistance was measured using a four-point probe set up where two current probes were connected to both ends of a sample to generate current flow through the sample. One voltage probe was located at the end of the Cu electrode, while the other voltage probe was scanning along the sample length to detect voltage drop depending on distance between two voltage probes. The electric contact resistance was obtained from Ohm's law based on the measured currents and detected voltage drops across the bonding interfaces between the fixed and the scanning probe.