Fabrication, characterization, and application-matched design of thermoelectric modules based on Half-Heusler FeNbSb and TiNiSn

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ABSTRACT

We describe the fabrication of thermoelectric modules based on Half-Heusler TiNiSn and FeNbSb and their performance assessment under different boundary conditions. Module design is guided by a multiphysics model implementing experimentally determined thermoelectric materials properties. We consider two types of boundary conditions: first, imposing fixed cold- and hot-side temperatures onto the module, and second, imposing fixed values for the heat transfer coefficients between module and heat sink and source, representative for a waste-heat-recovery system using the exhaust heat of an internal combustion engine. We compare the modeling results with experimental data obtained from Half-Heusler modules integrated into a heat exchanger mounted to the exhaust of a compact van.

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I. INTRODUCTION

Thermoelectric materials enable the conversion of heat into electric power and have the potential to improve the energy efficiency of vehicles with internal combustion engines through waste-heat recovery. Intensive research efforts have focused on understanding and optimizing thermoelectric material properties, thus improving the thermoelectric figure of merit zT ,^{1–13} but only a few attempts to build thermoelectric modules and assess their performance under conditions relevant to vehicle operation are reported in the literature.^{14–20}

In addition, thermoelectric modules are often tested on thermoelectric test benches imposing constant cold- and hot-side temperatures. These boundary conditions are only relevant in rare application cases and are not representative of a waste-heat-recovery system in a vehicle.

Here, we describe the fabrication of thermoelectric modules based on Half-Heusler TiNiSn and FeNbSb. Module geometry is guided by multiphysics modeling to maximize electrical power output by matching the thermal resistance of the module to the hot- and cold-side heat exchanger of a vehicle waste-heat-recovery system.

Experimental module output data, including data from a waste-heat-recovery system operated on a compact van under steady-state conditions, are compared to the modeling results.

II. EXPERIMENTAL SECTION

Arc melting in vacuum was used to prepare ingots of *p*-type $\text{FeTi}_{0.2}\text{Nb}_{0.8}\text{Sb}$ (abbreviated as FeNbSb) and *n*-type $\text{TiNi}_{1.06}\text{Sn}_{0.98}$ (abbreviated as TiNiSn) Half-Heusler alloys from the elements (for more details, see Ref. 7). Ingots were crushed and ground to powder with pestle and mortar, sieved to below 0.5 mm, and milled in a planetary ball mill in an argon atmosphere at 600 rpm for 15 cycles of 2 min with a break of 2 min in between each cycle [Fig. 1(a)]. 70 g of finely milled Half-Heusler powder was transferred in argon into a carbon die with an inner diameter of 50 mm and consolidated using spark plasma sintering between two 0.25 mm thick nickel discs with a diameter of 50 mm. To improve the mechanical and electrical contact between the *p*- and *n*-type Half-Heusler material and the nickel disc, 2 g of TiH_2 powder was mixed with 2 g of Half-Heusler powder and filled into the die between both sides of the bulk Half-Heusler powder and the neighboring nickel discs before sintering. This method reduces the average module contact resistance to below 1 m Ω . Spark plasma sintering was performed at a pressure of 50 MPa in the argon atmosphere by heating the *p*-type and *n*-type material up to 1000 °C and 900 °C, respectively, within 10 min, followed by a

FIG. 1. (a) Half-Heusler powder after milling, (b) Half-Heusler legs with nickel contacts, (c) Half-Heusler module consisting of 18 p-type and 18 n-type legs connected electrically in series between two ceramic aluminum nitride plates with copper contacts, and (d) current-voltage and power-voltage characteristics of Half-Heusler thermoelectric module measured at 30 °C cold-side temperature and 605 °C hot-side temperature.

temperature hold of 10 min and 5 min, respectively, and subsequent passive cooling down to room temperature. Using a diamond wire saw, the sintered pellets were cut into individual legs [Fig. 1(b)] with a base area of $1.75 \times 1.75 \text{ mm}^2$ and a height of 4.0 mm (controlled by the amount of powder filled into the die). Thermoelectric modules [Fig. 1(c)] were then assembled by brazing an array of Half-Heusler legs onto two 0.6 mm thick ceramic aluminum nitride plates with a base area of $25 \times 25 \text{ mm}^2$. Direct-bonded-copper contact layers with 0.3 mm thickness on the aluminum nitride plates connect *p*-type and *n*-type legs electrically in series and thermally in parallel. The brazing material is a standard nickel brazing material consisting of 74% nickel, 14% chromium, 4.5% iron, 3% boron, and 4.5% silicon. Brazing of the module assembly including the ceramic aluminum nitride plates with copper contacts was performed in a spark plasma sintering furnace at 4 kN in the argon atmosphere by heating to 900 °C within 30 min, followed by a temperature hold of 1 min, and passive cooling down to room temperature. During brazing, current flows through the resistive carbon die, heating the die. By thermal conduction, the module assembly is also heated. Two 1 mm thick copper wires were then soldered directly onto the copper plates to measure the current-voltage characteristics of the modules [Fig. 1(d)] in vacuum with a source meter. The test bench is equipped with a resistive heater consisting of tantalum wires embedded into an aluminum nitride ceramic and a heat sink consisting of a water-cooled copper block. Hot- and cold-side temperatures were measured with 0.75 mm type K thermocouples embedded at the contact pad of the module.

Phase purity of the *p*-type and *n*-type Half-Heusler materials was confirmed by X-ray diffraction. Seebeck coefficient (S) and electrical conductivity (σ) were measured under the argon atmosphere. Thermal conductivity (κ) of the thermoelectric material was calculated using $\kappa = \rho \alpha C_p$, with the thermal diffusivity (α) measured along the cross-plane direction by the laser flash method under argon flow without the contacting layers. The density ρ of the samples was determined also without the contacting layers by determining the volume geometrically. The specific heat capacity C_p was determined using the Dulong-Petit law $C_p = 3k_B$ per atom of the unit cell. See Ref. 7 for more details on the materials characterization.

Multiphysics modeling was performed within a COMSOL environment. The steady-state model incorporates the exact geometric details of the module and experimentally determined physical properties for the thermoelectric materials (Fig. 2) and the contact layer sequence in the contacts (as shown in Fig. S2 in the supplementary material). Solving the equation for heat and charge conservation yields the temperature and current for each computational node. For rapid screening through geometric and physical property spaces, the model is fully parametrized. The module is embedded into a virtual test bench, which can either impose constant cold- and hot-side temperature onto the module or constant heat transfer coefficients between the module and heat sink and source.

FIG. 2. Temperature dependence of (a) Seebeck coefficient, (b) electronic conductivity, (c) thermal conductivity, and (d) thermoelectric figure of merit of the *p*-type and *n*-type Half-Heusler materials used to build the thermoelectric modules and for the multiphysics modeling. Values for best-in-class *p*-type and *n*-type Half-Heusler materials from Refs. 13 and 21 are also shown for comparison.

III. RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the Seebeck coefficient S [plotted as $|S|$ in Fig. 2(a), $S < 0$ for n -type material, $S > 0$ for p -type material], electronic conductivity σ , thermal conductivity κ , and thermoelectric figure of merit zT of the p -type FeNbSb and n -type TiNiSn materials used to build the thermoelectric modules. Also shown in Fig. 2 are the corresponding values for p -type (FeNb_{0.88}Hf_{0.12}Sb) and n -type (Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn_{0.98}Sb_{0.002}) Half-Heuslers reported in Ref. 13 [Figs. 2(a) and 3(a)–3(c)] and Ref. 21 [Figs. 3 and 5] with some of the highest reported peak zT values for Half-Heusler materials in the literature. Based on the figure of merit zT , a theoretical upper limit for the module efficiency can be estimated.²² Generally, the efficiency of a thermoelectric module is defined by the ratio of the electrical power output divided by the thermal power supplied.²² In this work, we concentrate on maximizing the power output of the modules and not their efficiency. We note that our materials reported here are synthesized and processed in relatively large quantities to generate a baseline result and enable module development. There is still much room for improving the processing parameters to enhance the thermoelectric material properties. Also note that the nominal composition of our p -type FeNbSb material is comparable to the p -type material reported in Ref. 13, while our n -type TiNiSn material is free of expensive hafnium employed in Ref. 21. The low thermal

conductivity of the material in Ref. 21 is pivotal for its high zT value, which benefits largely from strong phonon scattering induced by the mass contrast between heavy hafnium and light titanium. Further optimization of material composition can be realized through doping and substitution to reach a compromise between cost and materials performance (e.g., see Ref. 7).

Figure 3(a) shows the experimentally measured current-voltage and power-voltage characteristics of a thermoelectric module with 18 p -type FeNbSb and 18 n -type TiNiSn legs measured on the test bench imposing a constant hot-side temperature of 605 °C and a cold-side temperature of 30 °C. Under these conditions, the module generates an open-circuit voltage of 1.9 V and a short-circuit current of 6.6 A (corresponding to a high current density in the legs of 215 A/cm²). Matching the external load resistance to the internal resistance of the module, a maximum output power of 3.1 W is measured experimentally (red line).

The blue line represents simulated values from the steady-state multiphysics model based on heat conservation [Eq. (1) in Ref. 23] and charge conservation [Eq. (2) in Ref. 23] taking the materials data in Fig. 2 and the exact module geometry in Fig. S2 in the [supplementary material](#) into account,

$$-\nabla \cdot (\kappa \nabla T) = \frac{j^2}{\sigma} - \nabla \cdot (ST\sigma(\nabla V + S\nabla T)), \quad (1)$$

$$\nabla \cdot j = 0. \quad (2)$$

Here, T (K) is the local temperature, j (A/m²) is the local current density, ρ (kg/m³) is the gravimetric density of the material at a specific location, C_p (J/kg K) is the specific heat capacity, κ (W/m K) is the thermal conductivity, σ (S/m) is the electronic conductivity, and S (V/K) is the Seebeck coefficient. The model neglecting the radiative heat losses causes a slight deviation between experimental and simulated data. Figure 3(b) shows the results of an extended model based on Eq. (3) in which radiative heat losses are taken into account following the Stefan-Boltzmann law, where the Stefan-Boltzmann constant σ_{SB} (not to be confused with electronic conductivity σ) is scaled by an empirical emissivity factor ϵ , taking into account heat emitted by one leg and absorbed by a neighboring leg including reflection and reemission phenomena,

$$-\nabla \cdot (\kappa \nabla T) = \frac{j^2}{\sigma} - \nabla \cdot (ST\sigma(\nabla V + S\nabla T) + \epsilon\sigma_{SB}T^4). \quad (3)$$

The emissivity factor ϵ is fixed here at a value of 0.3, which provides the best match between experiments and model and will be kept constant for all further modeling results, despite the fact that the value may slightly change when the material composition and module geometry are changed.

The model corrected for radiative heat losses can now also be applied to estimate the output performance of a thermoelectric module with best-in-class materials. A comparison of simulated module output data is shown in Fig. 3(c). A hypothetical module with best-in-class Half-Heusler materials would thus generate an open-circuit voltage of 3.4 V, a short-circuit current of 6.4 A, and a maximum output power of 5.4 W. The higher open-circuit voltage

FIG. 3. Comparison of measured and simulated module output data (a) without and (b) with taking into account radiative heat losses in the model, (c) comparison of simulated module output data for the Half-Heusler material used to fabricate the modules and best-in-class Half-Heusler materials reported in Refs. 13 and 21, (d) module output power as a function of leg width (w) and leg height (h) at fixed cold- and hot-side temperatures with lines of constant h/w^2 ratio (given in units of 1/mm).

and consequently higher output power is mainly attributed to the large Seebeck coefficient of the n -type material of Ref. 21.

The model can also be employed to determine the optimum leg dimensions, which maximize module output power under a set of given conditions. In Fig. 3(d), the module area and the number of legs per module were kept fixed at $25 \times 25 \text{ mm}^2$ and 36, respectively, while the impact of leg width w (maintaining a quadratic leg base and constant distance between leg centers) and leg height h on module output power was explored. Inspection of Fig. 3(d) reveals that at fixed cold- and hot-side temperatures (30°C and 605°C), a leg height to leg base area ratio h/w^2 near $0.5/\text{mm}$ maximizes output power, with the output power increasing for increasing leg width w . If leg height is fixed to 4.0 mm , the optimum leg width is 3.25 mm , resulting in the optimum compromise between minimizing electrical resistance of the module, while maintaining a sufficiently high-temperature gradient across the thermoelectric legs.

While fixed temperature can easily be imposed on a thermoelectric module test bench, leaving it to the heater and cooler to maintain actively constant temperature, the cold- and hot-side heat transfer coefficients HTC_c and HTC_h between the thermoelectric module and the heat sink and source are fixed in realistic applications [schematically depicted in Fig. 4(a)]. Under these conditions, cold- and hot-side temperatures depend on module geometry, module material properties, and the temperature of the heat sink and source.

FIG. 4. (a) Schematics showing a thermoelectric module sandwiches between a water-cooled cold-side heat exchanger and a hot-side exhaust gas heat exchanger with lamellar fins, (b) module output power as a function of leg width and leg height for fixed heat transfer coefficient values of the cold and hot-side heat exchanger for a FeNbSb and TiNiSn Half-Heusler module, (c) module output power for best-in-class Half-Heusler materials from Refs. 13 and 21, and (d) comparison of current-voltage and power-voltage characteristics of the module geometries matched (to hot-side) heat exchanger.

For the calculations, we assume a cold-side heat transfer coefficient HTC_c of $4 \text{ kW/m}^2 \text{ K}$ corresponding to a flat water-cooled copper plate. Hot-side heat transfer coefficient HTC_h is set to $1.5 \text{ kW/m}^2 \text{ K}$, which corresponds to a realistic value for a copper-based exhaust gas heat exchanger with optimized lamellar fins (five fins per module, with length 30 mm , height 18 mm) extracting heat from, e.g., an internal combustion engine's exhaust gas without generating significant backpressure for the charge exchange of the internal combustion engine (while the module test bench provides heat at $140 \text{ kW/m}^2 \text{ K}$ to maintain a hot-side temperature of 605°C in the previous case). Figure 4(b) shows that under these boundary conditions, a leg height to leg base area ratio h/w^2 near $1/\text{mm}$ provides maximum output power for modules with our Half-Heusler materials. If leg height is fixed to 4.0 mm , the optimum leg width is 1.75 mm (resulting in a temperature difference of 345°C), which differs from the previous fixed-temperature boundary conditions. For the best-in-class materials combination, the maximum shifts to lower h/w^2 ratios as can be seen in Fig. 4(c), so if keeping a leg height of 4.0 mm , the leg width can be increased to 2.5 mm to maximize output power. This smaller h/w^2 ratio results from the different thermoelectric material properties of the materials in Refs. 13 and 21. The significantly lower thermal conductivity and the higher Seebeck coefficient of the best-in-class materials overcompensate the lower electrical conductivity. The ultimate design of a waste-heat-recovery system will also consider the cost of the various components.²⁴ For cases in which material costs dominate, it is beneficial to choose a design with lower areal leg coverage and shorter legs. However, for low cost materials, the cost associated with the heat exchanger typically dominates.

Figure 4(d) shows the output power expected from the simulation for an optimized module design with a fixed leg height of 4.0 mm resulting in an optimum leg width of 1.75 mm for our materials reaching a maximum output power of 1.6 W . For the same module geometry, the module with the best-in-class materials reaches 2.8 W . These values are lower than 3.1 W and 5.4 W obtained at fixed temperatures.

Finally, we integrated the module with our material into a heat exchanger with above specifications mounted to the exhaust of a

FIG. 5. Comparison of experimental and simulated module output data for a module integrated into a heat exchanger mounted on the exhaust gas conduct of a compact van driving at 100 km/h .

compact van with a natural-gas-powered internal combustion engine. Current-voltage and power-voltage characteristics were measured during steady-state operation at 100 km/h on a dynamometer. The experimental results show excellent agreement with the simulated results under fixed HTC boundary conditions (Fig. 5).

IV. CONCLUSION

In summary, we described the fabrication and characterization of thermoelectric modules based on Half-Heusler FeNbSb and TiNiSn. While much of the thermoelectric literature characterizes thermoelectric modules at fixed cold- and hot-side temperatures, our results show that it is essential to consider fixed HTC boundary conditions instead for a given heat exchanger configuration. Multiphysics modeling serves as an important guide for optimizing the module geometry. Future work should be expanded to transient operating conditions, e.g., during a complete standardized driving cycle, the worldwide harmonized light vehicles test procedure (WLTP),²⁵ or the federal test procedure (FTP-75).²⁶ However, the duration of these cycles is only about 30 min with a cold engine start and demands only low loads from the internal combustion engine. These conditions are highly disadvantageous to demonstrate the potential of thermoelectric waste-heat recovery due to the thermal inertia and low exhaust gas temperatures. Steady-state cycles starting with warmed-up engines and higher loads such as the world harmonized stationary cycle²⁷ (WHSC) for heavy-duty vehicles would provide a more advantageous scenario for waste-heat recovery in automobile applications.

SUPPLEMENTARY MATERIAL

A description of the test bench for the characterization of thermoelectric modules as well as a schematic of the thermoelectric modules including contacting layers is provided as [supplementary material](#).

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