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Studies on a Single Thermoelectric Couple Fabricated From Half-Heusler Alloy

E. Raj*, R. Gozdur, Ł. Bernacki and Ł. Ruta

Lodz University of Technology, Department of Semiconductor and Optoelectronic Devices, al. Politechniki 8, 93-590 Łódź, Poland

Doi: 10.12693/APhysPolA.147.209 *e-mail: ewa.raj@p.lodz.pl

The paper deals with thermoelectric materials typically applied in thermoelectric generators or solid-state heat pumps. The thermoelectric p–n couple under investigation is constructed from p-type and n-type half-Hausler alloys. The alloys are engineered not only to maximize efficiency, but also to be optimized for environmentally friendly manufacturing, abundant elements in compositions, and large-scale applications. The research work was focused on the thermoelectric response of half-Hausler p–n couple in the temperature range from 297 to 310 K. The temperature range was adjusted to a reference Bi_2Te_3-based material to validate the outcomes for the alloys investigated. Commercial software tools offer thermoelectric models, which are developed and fully proven for Bi_2Te_3-based thermoelectric materials.

topics: thermoelectric (TE) generator, half-Heusler (HH) alloys, energy conversion, energy harvesting

1. Introduction

The scientific interest in thermoelectric (TE) effects has been continuous for more than 200 years [1]. During this time, there has been no breakthrough in research and only a few specific applications can be noticed. However, thermoelectric effects themselves are distinguished as phenomena incorporating a rare dependence of electron current and heat. This fact provides motivation for work on the direct conversion of thermal energy into electrical energy using thermogenerators (TEG). The research trend in this field was initiated in 1885 by Rayleigh [1].

Advances in thermoelectric materials engineering are immediately implemented if they can somehow contribute to the increase in the efficiency of thermoelectric generators [2, 3]. An excellent example is the family of Hausler alloys with a general composition X_2YZ. Further reduction of symmetry creates 4 sublattices in the XYZ composition referred to as half-Hausler (HH) phases [4, 5]. Such alloys containing intermetallic elements can exhibit thermoelectric properties, creating narrowband p- or n-type semiconductor structures. Further modifications of these compositions by separate doping of each sublattice provide the potential for the development of new promising TE materials [3, 5].

Unfortunately, the development of technologies related to the production of thermoelectric devices does not follow the TE materials engineering. The experience gained so far in the development of Bi_2Te_3 thermoelectric devices is unique and crucial in the development of more efficient thermogenerators (TEG) [5, 6]. New TE materials are most often used in rapid prototyping as a direct replacement for Bi_2Te_3 alloy [7]. However, the results give a moderate increase in the efficiency of prototype TEGs. The paper presents simulation results of a Bi_2Te_3 thermocouple and a thermocouple made of commercial HH alloys [8]. For this purpose, the TE junction model available in the Ansys software was used. The basic thermoelectric characteristics of both prototype junctions were also measured to assess the convergence of the numerical simulation results. Moreover, the test results make it possible to assess the suitability of typical Bi_2Te_3 assembly methods for HH alloy applications. Furthermore, preliminary studies in HH alloy applications contribute to the sustainable development of TEG devices by using abundant elements and less environmentally burdensome manufacturing methods.

2. Material and sample

The thermoelectric couple tested consisted of two pellets with a square cross-section area of 1 mm^2 and an overall height of 1.9 mm. The top and bottom surfaces of the columns were covered with 2 μm copper layers to improve the soldering properties and assembly. The pellets were made of two

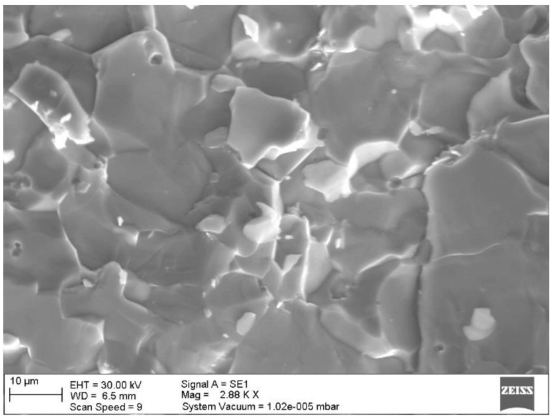

Fig. 1. SEM imaging of the n-type pellet microstructure.

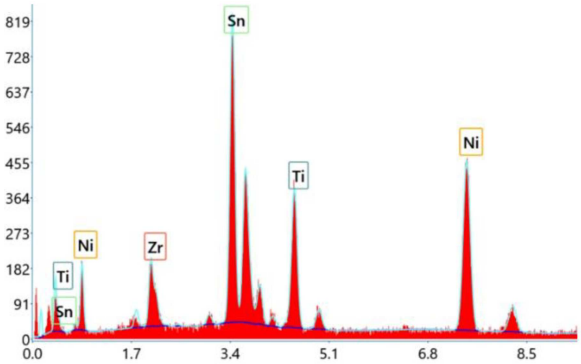

Fig. 2. Intensity spectrum observed in EDS analysis of the n-type sample.

TABLE I

Bulk material properties of thermoelectric alloys determined at room temperature [8].

Parameter	n-type alloy	p-type alloy
Seebeck coefficient S [μV/K]	-145	110
electric conductivity s [S/cm]	1350	3500
thermal conductivity k [W/(m K)]	5.5	7.2
density r [g/cm^3]	7.4	8.2
heat capacity C_p [J/(g K)]	0.31	0.29
linear expansion coefficient ΔL [1/K]	9.1×10^{-6}	8.1×10^{-6}

HH alloys (commercial name Vacotherm), which exhibit p-type and n-type semiconductor properties. They were connected into the TE couple by means of cooper bars and a soldering technique. The physical parameters of the alloys are collected in Table I.

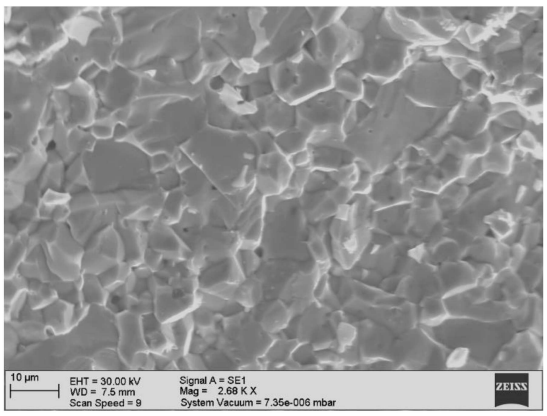

Fig. 3. SEM imaging of the p-type pellet microstructure.

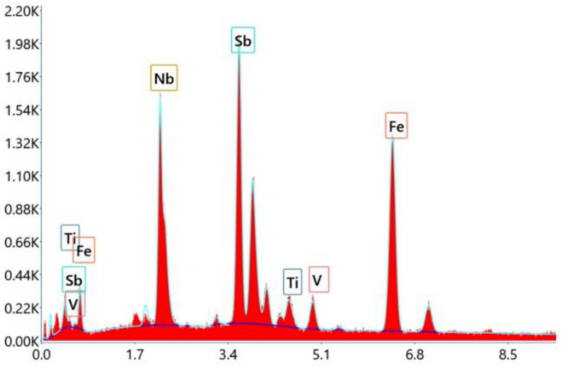

Fig. 4. Intensity spectrum observed in EDS analysis of the p-type sample.

Microstructures of the TE alloys were studied using scanning electron microscopy (SEM) (Zeiss EVO, Germany). Energy-dispersive X-ray spectroscopy (EDS) composition analysis was conducted using the Octane Elect EDS probe and EDAX software tools. Studies were carried out on cross-sections of the pellets used to form the single p–n couple. The obtained SEM images and EDS spectra are presented in Figs. 1–4. A quantitative analysis of compositions is presented in Table II.

SEM images reveal grain-patterned structures without uncorrelated shapes and sizes. However, the p-type microstructure consists of smaller and slightly more regular grains with an average size below 10 μm. The cause of the reduced grain size of the p-type composition may be a higher Ti dopant content [9, 10].

3. Numerical simulations

Numerical simulations were carried out to evaluate the usefulness of the studied HH alloys for low-temperature-grade thermoelectric generation

TABLE II

Compositions of the p-type and n-type samples observed in EDS analysis.

Element	Nominal composition [wt%]	Normalized level [wt%]	Atomic level [at.%]
p-type sample			
Ti	3	2.5	4.4
V	3	2.5	4.1
Fe	22	25.0	37.7
Nb	25	24.7	22.4
Sb	47	45.3	31.4
n-type sample			
Ti	14	13.6	21.9
Ni	25	30.3	39.8
Zr	12	8.9	7.5
Sn	49	47.2	30.7

TABLE III

Bulk material properties of thermoelectric alloys determined at room temperature.

Material	Thermal conductivity k [W/(m K)]	Resistivity ρ [Ω m]	Seeback coeff. S [μV/K]
n-type Bi_2Te_3	1.44	1.01×10^{-5}	−208
p-type Bi_2Te_3	1.42	1.01×10^{-5}	205
n-type HH alloy	5.55	7.70×10^{-6}	−148
p-type HH alloy	7.18	2.91×10^{-6}	124
copper	401	1.69×10^{-8}	
solder	34.0	1.42×10^{-7}	
ALSub	2.00		

purposes. A numerical model of the single semiconductor thermocouple has been created. The outline of the analyzed structure is presented in Fig. 5.

ANSYS software was used to create the numerical model. The generated grid covers about 60 000 elements (being a combination of structured and unstructured mesh) and is the result of the performed mesh sensitivity tests. The set of simulations was run for the following assumptions and boundary conditions:

- The temperature on the cold side equals 293 K.
- The temperature on the hot side changes in the range 294–298 K (for experimental verification up to 312 K).

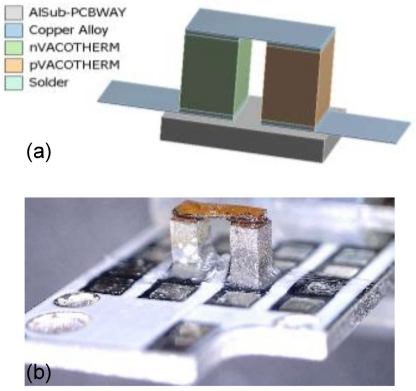

Fig. 5. Single thermocouple geometry outline (a), layout of thermocouple pellets on an aluminum PCB (b).

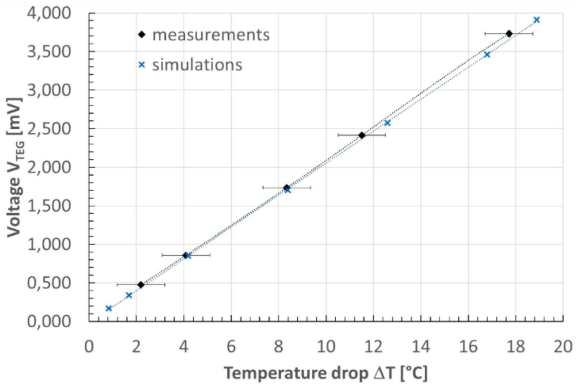

Fig. 6. Results of measurements vs simulations for a single thermocouple fabricated from HH alloys.

- A voltage of 0 V is defined on the right bottom copper track.
- The current flows from the p-type side to the n-type side and changes in the range from 0 to $2I_{\max}$ ($I_{\max}$ depends on the type of material and the temperature drop across the thermocouple).
- Adiabatic boundary conditions are assumed on all other external surfaces.

The properties of the materials taken for simulations are gathered in Table III.

The AlSub is a printed circuit board (PCB) laminate with an aluminum core, which forms an insulated substrate of the TEG.

The comparison of numerical and experimental results is shown in Fig. 6. The measured and calculated voltage generated across the thermocouple V_{TEG} is presented as a function of the temperature drop ΔT. The numerical results have been obtained from a set of simulations that had been run for a current of 0 mA and an enforced temperature difference ΔT of 1–19 K. The obtained simulation and measurement results are consistent.

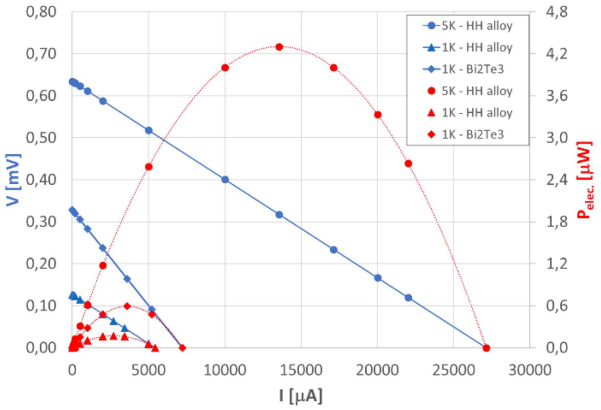

Fig. 7. Voltage response and power generation for temperature difference of 1 K and 5 K.

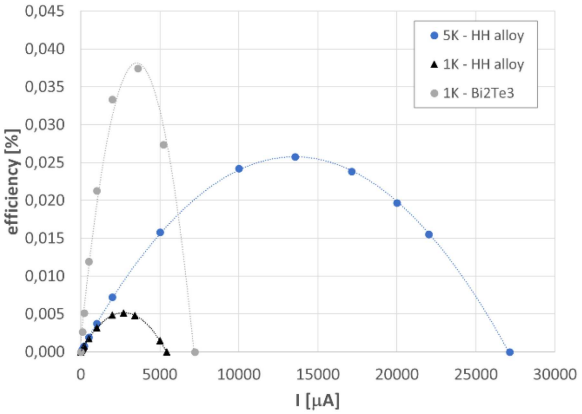

Fig. 8. Efficiency as a function of current obtained for two different materials.

Further simulations have been conducted to evaluate the performance of the thermocouple operating in the TEG mode. The voltage response and electric power generated in a single thermocouple are presented in Fig. 7. The curves are plotted for temperature differences of 5 K and 1 K and compared to the Bi_2Te_3 response at 1 K. Furthermore, Fig. 8 depicts the efficiency of the electric power generation for the modelled structures. The characteristic parameters calculated based on the performed simulations are gathered in Table IV.

The single thermocouple made of HH alloys is characterized by 2.5 times smaller open circuit voltage for the temperature difference of 1 K compared to the commonly used Bi_2Te_3 thermocouples. Even though the maximum current value is only 30% smaller, the generated power is still 3 times smaller. The obtained efficiency of energy conversion for the studied material is comparable to bismuth telluride solution for 5 times bigger temperature difference across the thermocouple. ZT factor for the HH alloys is 4 times smaller ($ZT = 0.25$) than of reference Bi_2Te_3 material ($ZT = 1.0$).

TABLE IV

Comparison of simulation results for thermocouples operating in TEG mode.

Parameter	Bi_2Te_3	Vacotherm	Vacotherm
temperature difference ΔT [K]	1.0	1.0	5.0
open circuit voltage V_{OC} [mV]	0.328	0.127	0.634
short circuit current I_{SC} [mA]	7.2	5.4	27.1
maximum current $I_{\max}$ [mA]	3.6	2.7	13.6
maximum power $P_{\max}$ [μW]	0.59	0.20	4.30
efficiency $\eta_{\max}$ [%]	0.037	0.005	0.026

It is worth emphasizing that the investigated HH alloys are designed for significantly higher operation temperatures. Nevertheless, the results demonstrate the feasibility of HH alloy-based TEGs as power sources for ultra-low power electronics or battery expanders.

4. Conclusions

The simulation studies for a single thermocouple justify further research on the full TEG model with the aid of Ansys software. The obtained experimental results validate the calculated parameters of TEGs based on HH alloys and Bi_2Te_3 materials. Although the superior thermal behaviour of bismuth telluride is visible, the research outcomes and benefits connected with the environmentally friendly manufacturing process and the abundant elements in the compositions argue in favour of using HH alloys in high-temperature TEGs.

Acknowledgments

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