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Investigation of Thermoelectric Parameters of Bi_2Te_3: TEGs Assembled using Pressure-Assisted Silver Powder Sintering-Based Joining Technology

ANDREJ STRANZ,[1,2] ANDREAS WAAG,[1] and ERWIN PEINER[1]

1.—Institute of Semiconductor Technology and Laboratory for Emerging Nanometrology, TU Braunschweig, University of Technology, Braunschweig, Germany. 2.—e-mail: a.stranz@tu-bs.de

Operation of thermoelectric generator (TEG) modules based on bismuth telluride alloys at temperatures higher than 250°C is mostly limited by the melting point of the assembly solder. Although the thermoelectric parameters of bismuth telluride materials degrade for temperatures >130°C, the power output of the module can be enhanced with an increase in the temperature difference. For this, a temperature-stable joining technique, especially for the hot side of the modules, is required. Fabrication and process parameters of TEG modules consisting of bismuth telluride legs, alumina ceramics and copper interconnects using a joining technique based on pressure-assisted silver powder sintering are described. Measurements of the thermal force, electrical resistance, and output power are presented that were performed for hot side module temperatures up to 350°C and temperature differences higher than 300°C. Temperature cycling and results measured during extended high-temperature operation are addressed.

Key words: Pressure-assisted silver powder sintering, TEG module, joining technique for high temperatures

INTRODUCTION

Process-related waste heat in various energy-intensive processes, such as in steel and glass manufacturing, often remains unused and is lost to the environment. Using thermoelectric generators, heat can be converted directly into electrical energy. Thermoelectric waste heat recovery could reduce the primary energy consumption, and thus contribute to climate protection.

For Germany, the waste heat potential of the industrial production of 87.8×10^9 kWh annually was estimated at temperatures higher than 140°C and a further 44.4×10^9 kWh at temperatures between 60°C and 140°C.[1]

In practice, thermoelectric generators (TEGs) have been used for the operation of wrist watches and small wireless sensors, as well as for power generation for many space missions. This technique to convert heat to electricity is quiet, maintenance-free, compact and reliable. Therefore, TEGs are also attractive to exploit the waste heat produced in many industrial processes for electrical power generation. The advantages of TEGs are offset by relatively small module efficiency leading to an electricity price of about €5/W. The reason for this is the maximum efficiency of bismuth telluride-based TEGs, which is about 5% at a temperature gradient between 50°C and 230°C.[2] However, in spite of the deterioration of the thermoelectric material properties for average temperatures higher than 130°C, a further increase of the module output power can be expected in cases of enhanced temperature differences.

Therefore, it is required to extend the operating temperature range by improving the joining technology for TEG modules based on bismuth telluride.

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Conventional solder joints have a limited capability to withstand temperature cycle loading. Due to the high melting temperature of Ag (T_m = 962°C), sintered Ag joints have a much better resistance against cyclic loading (temperature, shock) even at higher temperature differences. Therefore, in this study, we employed a new pressure-assisted silver powder sintering technology to fabricate bismuth telluride-based TEGs with an extended operation temperature range.

The analysis of the temperature dependence of the parameters of bismuth telluride thermoelectric material (electrical conductivity and Seebeck coefficient) carried out in an international round robin study[3] shows that both the Seebeck coefficient and the electrical conductivity tend to fall with increasing temperature. The Seebeck coefficient $S(T)$ and the normalized electrical resistance $R(T)$ of bismuth telluride alloys were used to calculate the output power. Figure 1 shows the electrical output power, i.e. the ratio of the square of the output voltage and the resistance, of a TE couple of a bismuth telluride alloy as a function of the hot side temperature T_h for various cold side temperatures T_c. It can be seen that, with increasing T_h, the power output increases for all temperature differences.

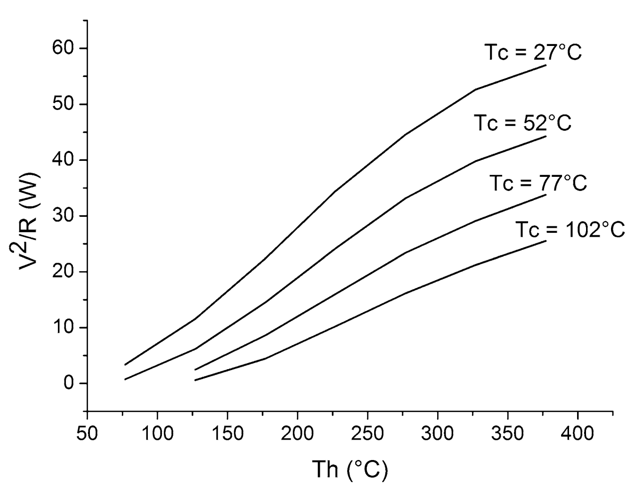

Fig. 1. Calculated output power of a Bi_2Te_3 couple versus the hot side temperature for various cold side temperatures.

FABRICATION AND MEASUREMENTS

In this work, a thermoelectric generator with Bi_2Te_3 legs as thermoelectric material was assembled using the pressure-assisted silver powder sintering technique. The high melting temperature of silver, 962°C and the adoption of the operating temperature of 350°C on the hot side of the module yielded a homologous temperature of 0.36, which is much lower than for solders. The comparatively low melting temperature of commercial solders such as SnCu (227°C) or SnSb (232°C) limits the use of bismuth telluride-based modules at high temperatures.[4] A further advantage of PASPS over soldering is that no liquid phase occurs in the joining process. Thus, the legs cannot slip and short circuits in the module are avoided. Additional advantages are the high electrical and thermal conductivity of the sintered silver layer, high adhesive strength of the interconnect, as well as good stability at thermal cycling load.[5,6] Another feature of PASPS is its high potential for automation in combination with a proprietary foil transfer method.[7] First, ceramics are metalized using electron beam physical vapor deposition (EBPVD). Then, the silver powder is transferred to the copper interconnects and Bi_2Te_3 legs. We used silver powder with micron-sized flakes (SF70A) purchased from Ferro, Hanau, Germany. In the next step, the interconnects are joined to the ceramics and, after arrangement of the legs on copper interconnects, the module is fabricated using the PASPS technique. The manufacturing process of the TEG using the PASPS technique is described in Table I. The complete joining process was conducted in air.

Figure 2 shows the exploded view drawing of the fabricated TEG module with 10 Bi_2Te_3 couples. The Ti/Au metalization on the top and bottom ceramics was deposited using e-beam evaporation (Table I). Using the PASPS process for joining the copper interconnects to ceramics, as well as for joining the bismuth telluride legs to copper interconnects, produces a good thermal coupling due to the high thermal conductivity of the sintered silver powder layer. Because of the proposed arrangement of the layers, thermal stresses caused by the different thermal expansion coefficients of the materials can be reduced. In Table II, the mechanical properties of the materials used in the module are summarized.

Table I. Manufacturing process of the TEG using the PASPS technique

Step	Process description	Process method/parameter
1	Metalization of alumina ceramics	EBPVD/50 nm Ti 500 nm Au
2	Coating of copper interconnects with silver powder by transfer method	5 MPa, 100°C, 1 min, ambient air
3	Joining of copper interconnects and ceramics	5 MPa, 270°C, 1 min, ambient air
4	Coating of Bi_2Te_3 legs with silver powder by transfer method	5 MPa, 100°C, 1 min, ambient air
5	Arrangement of legs and fabrication of module	5 MPa, 270°C, 1 min, ambient air

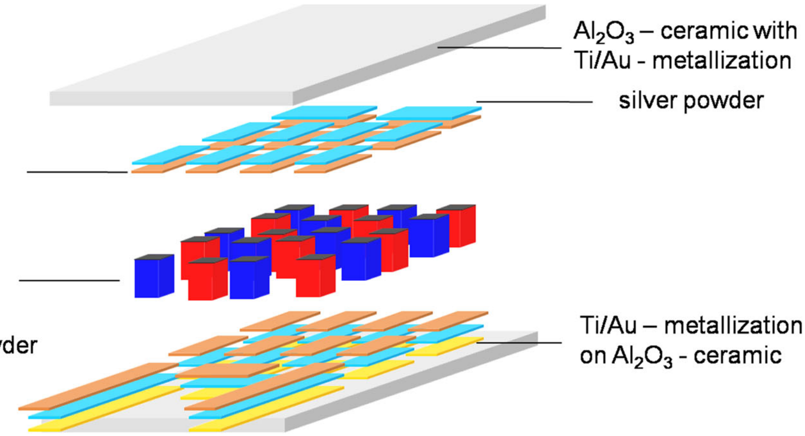

Fig. 2. Exploded view drawing of the TEG module with 10 couples fabricated using the PASPS technique.

Table II. Mechanical properties of the materials used in the module

	Al_2O_3 ceramic	Copper	Bi_2Te_3	Bulk Ag	Ag sinter layer 45% porosity
Coefficient of thermal linear expansion (10^{-6} K^{-1})	6–8	17	15–20	19	~20–21
Young's modulus (GPa)	200–350	120–130	50	83	~10
Thickness (mm)	0.6	0.25	1	–	~0.02

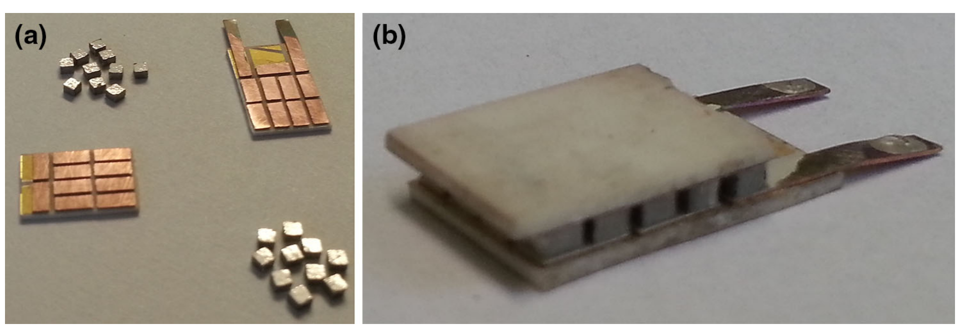

Fig. 3. Module components before joining (a); PASPS fabricated module (b).

This way to fabricate a TEG module represents an alternative to the use of expensive substrates like DCB (direct copper bonding) and also allows for larger choices in the selection of materials and dimensions.

Figure 3 a shows the module components before joining. The copper interconnects are already attached to the ceramics by PASPS. In Fig. 3 b, the fabricated module is shown. The dimensions of the module are $10 \times 8 \times 2.9$ mm^3 and of the Bi_2Te_3 legs, $1.5 \times 1.5 \times 1$ mm^3, respectively. The Bi_2Te_3 pellets, which were purchased from Peltron, Fürth, Germany, were delivered with a standard Ni metalization. Before assembling a module, selected single pellets were characterized. We measured resistivities, Seebeck coefficients, and thermal conductivities of the *n*- and *p*-type bismuth telluride alloys as summarized in Table III. Since PASPS requires a noble metal as the uppermost layer, the legs were covered by a few nanometers of gold using e-beam evaporation. The module was analyzed using the measurement setup shown in Fig. 4; it was placed between a ceramic heater and a copper cylinder serving as a large heat sink. The aluminum block between the heater and the module allows for mounting of a thermocouple directly on the warm side of the TEG and additionally smoothing of the temperature pulses from the heater.

Control of the heater and recording the measurement data were done using a LabVIEW program.

Table III. Thermoelectrical properties of assembled bismuth telluride alloys

	S (μV/K) @ 128°C	λ (W/mK) @ 128°C	σ (Ω cm) @ RT
n-Bi_2Te_3	−232.3 ± 1.4	1.86 ± 0.05	$(1.4 \pm 0.1) \times 10^{-3}$
p-Bi_2Te_3	214.6 ± 1.4	1.78 ± 0.08	$(1.3 \pm 0.3) \times 10^{-3}$

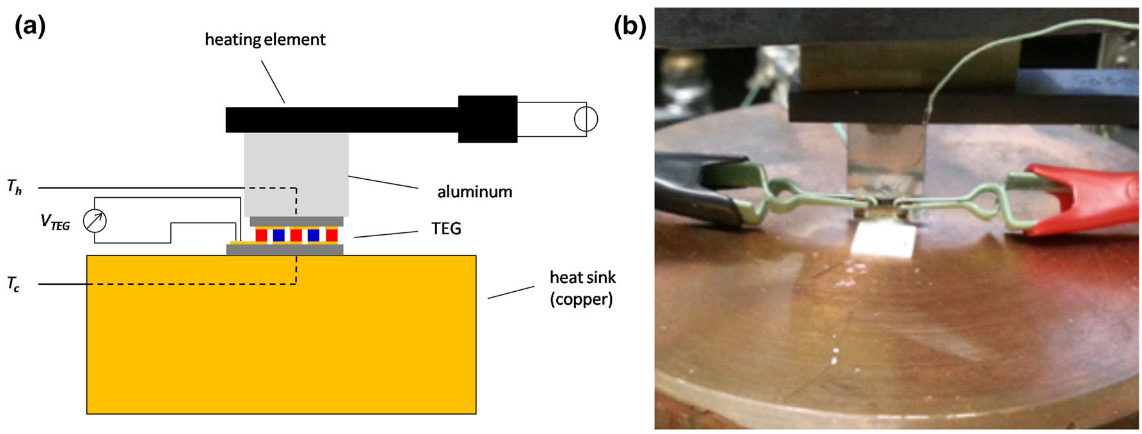

Fig. 4. Schematic (a) and image (b) of the measurement setup.

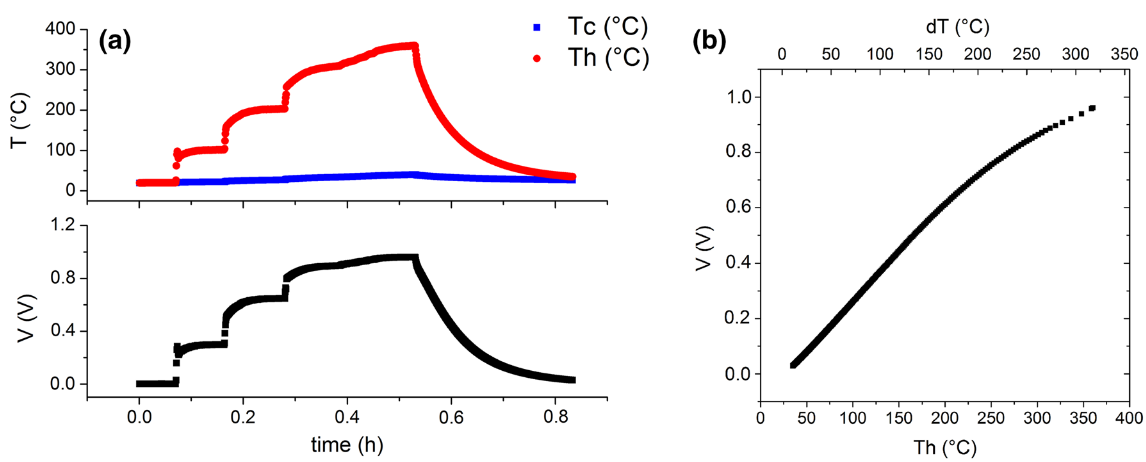

Fig. 5. Temperature and open-circuit voltage at the TEG module, depending on the measurement time (a) and the voltage as a function of the temperature difference $dT = T_h - T_c$ (b).

RESULTS AND DISCUSSION

Figure 5 a shows the temperature profiles at the TEG module during a measurement sequence, wherein the temperature on the hot side (T_h) was gradually increased to 350°C. The graph on the bottom left shows the corresponding open circuit voltage V generated by the Seebeck effect. In Fig. 5 b, the measured open-circuit voltage is shown as a function of the temperature difference ($dT = T_h - T_c$). It can be seen that the shape of the voltage curve is linear to about T_h = 200°C and has roughly a constant slope. The slope of the voltage curve describes the thermal power of the module. For the temperature range between room temperature and 200°C, the thermal power of the module is calculated using $S_{\text{module}} = \frac{V}{dT}$ to be 3.48 mV/K. The measurement shows that from about 200°C the slope of the voltage curve decreases. The reduction is attributed to the deterioration of the Seebeck coefficient of bismuth telluride towards higher temperatures. Despite the reduction in the thermal power of the module at high temperatures, the output voltage increases further with increase of the temperature difference.

For the determination of the internal resistance R_{TEG} of the module, the open circuit voltage and the

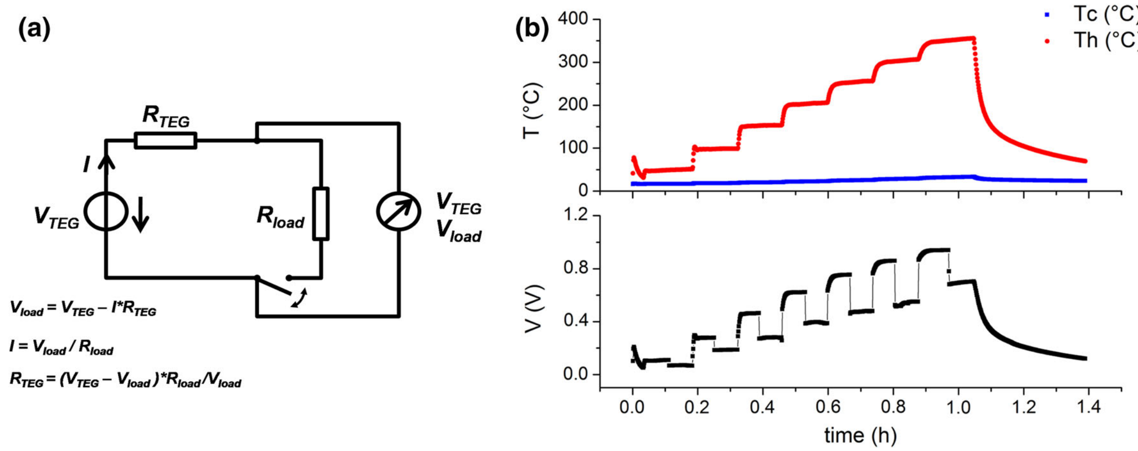

Fig. 6. Equivalent circuit diagram to determine the internal resistance of the module R_{TEG} (a), temperature and voltage of the TEG module depending on the measurement time (b). Within each temperature step, the switch was turned from open to closed, i.e. open-circuit voltage V_{TEG} and voltage over a constant load V_{load} were successively measured.

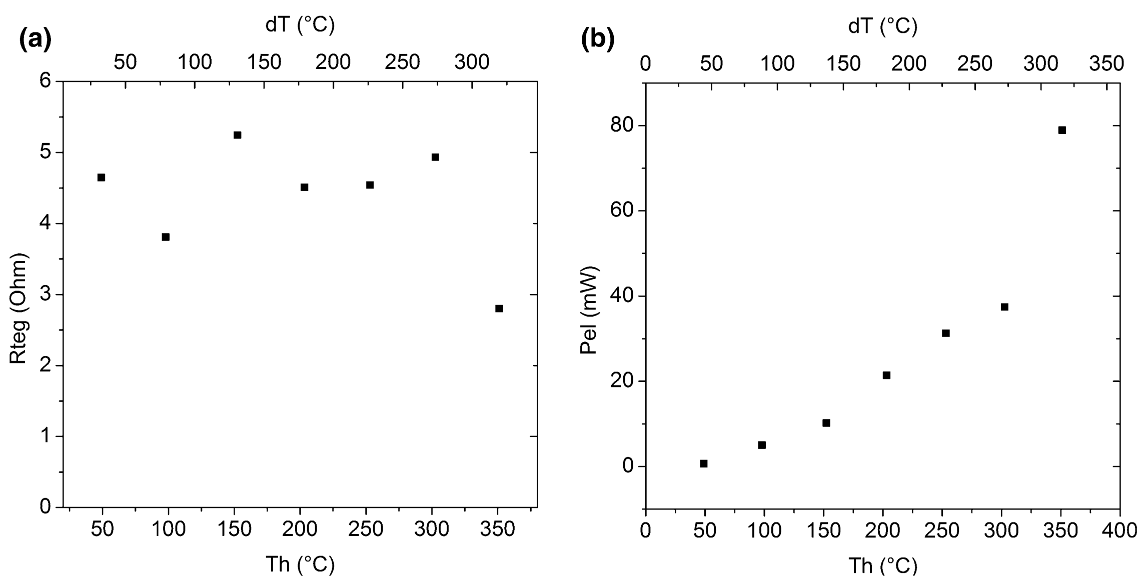

Fig. 7. Calculated internal resistance of the module (a) and output power (b).

voltage at a fixed load resistance at various steps of constant temperature difference were alternately measured (Fig. 6). The measurements were repeated six times with the total time of 8.3 h for all repetitions. The result of the last measurement sequence is shown in Fig. 6 b.

With the measured voltages and the known value of the load resistance R_{load}, the internal resistance R_{TEG} of the module can be calculated:

$$R_{TEG} = \frac{(V_{TEG} - V_{load}) \cdot R_{load}}{V_{load}} \quad (1)$$

Figure 7 a shows the calculated internal resistance of the module as a function of the hot side temperature. The relatively high values of the internal resistance of $\sim$4–5 Ω, as well as no increase in resistance with increasing temperature which are expected for bismuth telluride, is an indication that the internal resistance is dominated by the contact resistance between the copper interconnects and the bismuth telluride legs. Assuming an average specific electrical resistance of a Bi_2Te_3 couple of 2.4 mΩ cm,[3] the resistance of 20 Bi_2Te_3 pellets of $1.5 \times 1.5 \times 1\ mm^3$ in series amounts to 0.21 Ω and the average specific contact resistance of the 40 sinter contacts is calculated to $(2.1–2.7) \times 10^{-3}\ \Omega\ cm^2$. This value is more than three orders of magnitude higher than for soldered contacts. The maximum output power P_{el} is then calculated using the values of the internal resistance R_{TEG} for the case of load matching. The maximum power of the module for temperature differences up to dT = 320°C and a hot side temperature up to T_h = 350°C is calculated to be P_{el} = 79 mW. We

Table IV. Module fabricated in this work in comparison with commercially available modules

	Provider 1	Provider 2	This work
Max. temperature difference (°C)	(50–230)	(30–300)	(30–350)
Max. output power (mW/mm^2) at load match	4.9	6.1	1 (~10)[a]
Size of module (mm^3)	40.1 × 44.7 × 3.6	40 × 40 × 4.5	10 × 8 × 2.9

The data of provider 1 and provider 2 are taken from the corresponding datasheets.[a]At R_{TEG} = 0.36 Ω.

observed an increase of P_{el} with T_h and dT. Surprisingly, the value of P_{el} = 79 mW is higher by more than a factor of two than P_{el} = 38 mW at dT = 270°C and T_h = 300°C, which is caused by the strong decrease of the module internal resistance (cf. Fig. 7a). We attribute this effect to an improvement of the contact resistance probably related with beneficial additional sintering of the Ag layer at temperatures above 300°C. By variation of the powder composition, reduction of the surface roughness of the legs, and chemical treatment of the copper interconnects, the contact resistance can be significantly reduced.[8] Thereby, a significantly increased output power can be expected. Meanwhile, we have already obtained in first experiments with single leg couples a reduction of the contact resistance to $8.5 \times 10^{-5}\ \Omega\ cm^2$, which would result in a much lower R_{TEG} = 0.36 Ω. Fabrication of a complete TEG to validate this approach is in progress and further reduction of contact resistance will be included in future work.

CONCLUSIONS

In this work, we have investigated pressure-assisted silver powder sintering as a joining technique for a TEG module, instead of soldering, in order to increase the operational temperature range of bismuth telluride-based modules. A TEG module with dimensions of 10 × 8 × 2.9 mm^3 was fabricated and analyzed. The sintering technique has been used both for joining between the bismuth telluride legs and copper interconnects, as well as for joining the copper interconnects and alumina ceramics. We measured the output voltage of the module for hot side temperatures up to 350°C and temperature differences up to 320°C. It was found that the output voltage is stable in this temperature range. For the internal resistance of the module, we see higher values compared to soldered modules. The reason for such high resistance is the electrical contact between the bismuth telluride legs and the copper interconnects. Reduction of the internal resistance will significantly increase the output power, so that the bismuth telluride-based TEG modules can be used effectively at higher temperatures.

Table IV shows the maximum output power per square millimeter of the module compared to commercially available TEGs.

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