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Power generation of the touching Cu/Bi-Te/Cu composites under the periodically alternating temperature gradients

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Abstract The thermo-emf ΔV of the touching *p*- and *n*-type Cu/Bi-Te/Cu composites with different thicknesses of $t_{\text{Bi-Te}}$ and t_{Cu} was measured as a function of time by alternating the temperature difference ΔT at periods of $T = 20$, 60, 120, 240 and ∞ sec, where $t_{\text{Bi-Te}}$ was varied from 0.1 to 2.0 mm and t_{Cu} from 0 to 4.0 mm. As a result, ΔV changes significantly with $t_{\text{Bi-Te}}$, t_{Cu} and T. The effective thermo-emf ΔV_{eff} increases significantly with an increase of $1/T$ and exhibited a local maximum at $1/T = 1/240\ \text{s}^{-1}$. The resultant $|\alpha|$ and the effective temperature difference ΔT_{eff} were increased significantly by optimizing $t_{\text{Bi-Te}}$ and t_{Cu} at $1/T = 1/240\ \text{s}^{-1}$. The power generation ΔW_{eff} ($= \Delta V_{\text{eff}}^2/4R_{\text{calc}}$) estimated using the measured ΔV_{eff} and calculated R_{calc} also exhibited a local maximum at $1/240\ \text{s}^{-1}$ for an optimum combination of $t_{\text{Bi-Te}} = 0.1$ mm and $t_{\text{Cu}} = 2.0$ mm, so that the maxima ΔW_{eff} at $1/T = 1/240\ \text{s}^{-1}$ for the *p*- and *n*-type composites were 2.28 and 2.92 times higher than those obtained at $1/T = 0\ \text{s}^{-1}$. This significant increase in ΔW_{eff} is owing to both the increase in ΔT_{eff} and the increase in ZT due to the increase in $|\alpha|$. The power generation was thus found to be enhanced significantly by imposing the alternating temperature gradients on touching Cu/Bi-Te/Cu composites.

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Introduction

In recent years there has been renewed interest in finding new materials and structures for use in highly efficient cooling and energy conversion systems [1, 2]. This interest has been stimulated in considerable part by the opportunities that quantum well and quantum wire superlattices [3–5] might result in thermoelectric materials with high thermoelectric figure of merits $ZT = T\alpha^2/\rho\kappa$, where α is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity and T the absolute temperature. The increase in ZT leads directly to the improvement in the cooling efficiency of Peltier modules and in the electric generation efficiency of generators [6]. There have been some theoretical predictions [3–5, 7] that such superlattices will eventually have extremely high ZT as compared with those of the corresponding bulk materials. Indeed, the supperlattice structured thin film of Bi_2Te_3/Sb_2Te_3 reached an extremely high ZT of 2.4 [8], and it was owing to the significant reduction in κ.

Recently, it was reported by Bergman and Levy [9] that the resultant Z of a macroscopic composite device can never exceed the largest Z among the component materials, as long as the resultant α is not enhanced. When a semiconductor is kept in contact with a metal or a semiconductor with different types of conduction, a potential barrier generally occurs at their interfaces. Tauc [10] indicated theoretically about 50 years ago that when such a barrier was accompanied by a sufficiently great temperature drop, the additional barrier thermo-emf appears as a result of the separation of non-equilibrium carriers at the interface. The Seebeck coefficient corresponds to the ratio of the thermo-emf ΔV to ΔT, where ΔT is the temperature difference producing ΔV. Indeed, the barrier thermo-emf was observed directly in the *p*–*n* junctions [11] and appeared as an enhancement in the resultant Seebeck coefficient of the thermoelectric composites sandwiched between two metals [12–16]. For example, the resultant α of the *p*- and *n*-type Cu/Bi-Te/Cu composites welded with eutectic solder of Pb–Sn reached great values of 263 and –266 μV/K at 298 K, respectively, which are approximately 32 and 30% higher in absolute value than 202 and –205 μV/K of the intrinsic Bi-Te materials. As a result, the resultant *ZT* of the *p*- and *n*-type composites reached surprisingly great values of 1.53 and 1.66, respectively, which correspond to about twice as large as those of commercially utilized Bi-Te materials [15]. It was owing to the significant enhancement in the resultant $|\alpha|$.

The thermo-emf ΔV and Seebeck coefficient of thermoelectric materials have hitherto been observed and estimated under the steady temperature gradient. The thermoelectric modules have been utilized under only the steady temperature gradient. Unlike the conventional application of modules, now we take an interest in whether or not the thermo-emf of composites and thermoelectric materials is enhanced by imposing a periodically alternating temperature gradient on them, because such an examine has never been performed. The additional barrier thermo-emf ΔV of composites used in our experiment occurs in the forward-bias direction [12–16]. For this reason, it is expected that a sharper temperature drop occurs at the boundary of a composite under the alternating temperature gradients, resulting in the enhancement in the thermo-emf ΔV and the power generation ΔW. If so, it is possible to design the thermoelectric module system so that the alternating temperature gradients are imposed periodically on a thermoelectric generator, by alternating the hot and cold sides of a module at a period, even under the steady temperature difference. Such a thermoelectric system may thus be considered as useful means of further improvement in the energy conversion efficiency of a thermoelectric generator.

The purpose of this paper is to investigate whether the thermo-emf and power generation of touching Cu/Bi-Te/Cu composites are enhanced by imposing the alternating temperature gradients on composites and to what degree the power generation is increased by optimizing the period and the thickness of Bi-Te compound and copper, as compared to those obtained under the steady thermal gradient, and is to clarify the reason for the increase in the power generation.

Calculation and experiments

Calculation of the resultant ρ and κ of a composite material

Let us consider a composite device with a sandwich structure (M/T/M) in which a parallelepiped of the thermoelectric material T is sandwiched between two metallic parallelepipeds M, as shown in Fig. 1a and b. Here, we derive the resultant electric resistance *R* of a composite by treating it as an electric and thermal circuit [12–14]. The materials M and T have the same cross-sectional area *S* and two different thicknesses t_M and t_T, respectively. For simplicity, it was assumed here that the scattering of carriers and phonons never occurs at the interface between the materials M and T. When the electrical resistivities of the materials M and T are ρ_M and ρ_T, the resultant electrical resistivity ρ of a composite is expressed as

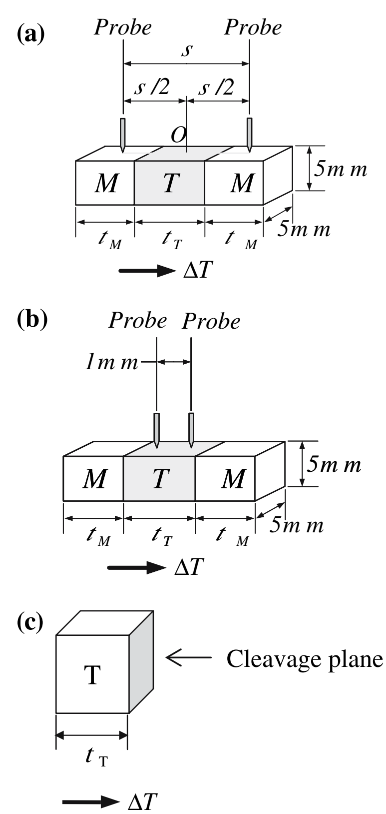

Fig. 1 Touching composite device with a sandwich structure (M/T/M) in which a parallelepiped of thermoelectric material T is touched tightly with two metallic parallelepipeds. The interval *s* between two probes is expressed by $s = t_T + 0.50$ mm, where t_T is the thickness of Bi-Te materials and t_M is the thickness of metal. In (**a**) the center of *s* is that of material T. In (**b**) two probes separated by a distance of 1 mm are placed on a thermoelectric material T. The relation between the direction of the temperature gradient and cleavage plane is shown in (**c**)

$$\rho = \frac{1}{s}(2\rho_M t_M + \rho_T t_T). \quad (1)$$

Here if we suppose $t_M = s(1-x)/2$ and $t_T = sx$ where s is the interval between two probes, Eq. 1 can be rewritten as

$$\rho = \rho_T\{x + b(1-x)\}, \quad (2)$$

where $b = \rho_M/\rho_T$. The resultant R of a composite is thus expressed as

$$R = \frac{s\rho}{S} = \frac{s\rho_T\{x + b(1-x)\}}{S}. \quad (3)$$

Similarly, the resultant thermal conductivity κ of a composite is expressed as

$$\kappa = \frac{\kappa_T c}{xc + (1-x)} \quad (4)$$

where $c = \kappa_M/\kappa_T$. In the present experiment, two probes are placed on a composite so that the interval s between them satisfies the relation $s = t_T + 0.50$ in a unit of millimeter. The resultant ZT was calculated from the relation $ZT = \alpha^2 T/\rho\kappa$ using the experimental α and the ρ and κ values obtained by substituting $x(= t_T/s)$, ρ_M, ρ_T, κ_M and κ_T into Eqs. 2 and 4.

Sample-preparation and measurements

The p-type $(Bi_{0.25}Sb_{0.75})_2Te_3$ doped with 6 wt% excess Te alone and n-type $Bi_2(Te_{0.94}Se_{0.06})_3$ codoped with 0.068 wt% I and 0.017 wt% Te were prepared by the Bridgman method, using pure Bi granule of 99.999% and pure Sb, Te, Se and I granules of 99.99% as starting materials [17, 18]. The materials were weighed out in appropriate atomic ratios, charged into a quartz tube and melted in an evacuated quartz tube by an induction heating to make a homogeneous melt without segregation. After melting, the compounds were unidirectionally solidified by the Bridgman method at a fast rate of 6 cm/h, to produce intentionally scattered second-phase precipitates in the ingot. It is the same growth rate as that employed in preparing the previous specimens [17, 18] and is close to one of various growth conditions reported by Yim and Rosi [19]. Naturally, the resulting ingots consisted of relatively coarse grains with the cleavage planes aligned partially parallel to the freezing direction.

In order to investigate the thermoelectric properties of the as-grown ingots, a parallelepiped of 5 × 5 × 15 mm^3 and a square plate of 10 × 10 × 2 mm^3 were cut from the central part of ingots, where the length of 15 mm and thickness of 3 mm were cut perpendicular to the freezing direction. The former specimens were subjected to Seebeck coefficient α and electrical resistivity ρ measurements (Sinku-Riko, Inc., Model ZEM-1), and the latter ones to thermal conductivity κ measurement (Sinku-Riko, Inc., Model TC-3000) after grinding into a disk of φ 10 × 3 mm. The Seebeck coefficient α was measured by the conventional technique, using two alumel–chromel thermocouples set at an interval of 8 mm, in the temperature range from 293 to 303 K with the temperature difference of about 10 K. The electrical resistivity ρ was measured concurrently by the four-probe method. Their results are listed in Table 1. The thermoelectric properties of α, ρ and κ were measured at 298 K within an accuracy of 2, 2 and 3%, respectively. The resultant accuracy was about 9% as a thermoelectric figure of merit ZT.

As shown in Fig. 1c, these as-grown p- and n-type Bi-Te ingots were cut into a parallelepiped of 5 × 5 × $t_{Bi\text{-}Te}$ mm^3, where the thickness $t_{Bi\text{-}Te}$ is perpendicular to the cleavage plane, i.e., parallel to the c axis of rhombohedral crystal structure and was varied from 0.1 to 2.0 mm, as listed in Table 2. The as-grown Bi-Te ingots were employed to prepare the touching p- and n-type Cu/Bi-Te/Cu composites in which both end coppers are pressed against Bi-Te compound at a constant force of about 10 N using a ratchet, as shown in Fig. 2. Both end coppers were prepared by cutting a long pillar with a square 5 mm on a side into five different thicknesses of t_{Cu} = 0.3, 1.0, 2.0, 3.0 and 4.0 mm, where the purity of copper was 99.99%. Their dimensions are listed in Table 2. Both end surfaces of Bi-Te compound and copper were polished mechanically by the lapping method to come in contact closely with each other. The degree of parallelism of so fabricated specimens was less than 3 μm.

The Seebeck coefficient of the composites pressed by a ratchet was measured using an apparatus fabricated by us. Figure 2 shows a schematic of the apparatus. It has two alumel–chromel thermocouples (0.25 mm in diameter) to detect temperatures and a voltage on the surface of a composite. The composite material is mounted on an X–Y stage and the temperature gradient was applied with two Peltier modules equipped to both ends of the specimen. Two Peltier modules are obtained from Komatsu Electronics Inc., the dimensions are 20 × 20 × 4 mm^3 and their ZT values measured by Harman's technique [21] are approximately 0.75 at 298 K. The measurement of the thermo-emf ΔV was made by alternating the temperature gradient between both ends of a composite at various periods of T = 20, 60, 120, 240 and ∞ sec, where a rectangular voltage with an amplitude of 1.7 V was imposed on two Peltier modules connected in series, as shown in Fig. 3. Two probes were then placed on both end coppers of a composite so that the interval s between them satisfies the relation $s = t_T + 0.50$ mm. The thermo-emf ΔV and the temperature difference ΔT of the touching composites with

Table 1 Thermoelectric properties measured at 298 K for pure Cu and along the direction perpendicular to the growth direction of the *p*- and *n*-type Bi-Te materials

	Cu	Bismuth-telluride	
		n-type	*p*-type
Electrical resistivity ρ ($\mu\Omega$ m)	0.0171	30.7	36.1
Seebeck coefficient α (μV/K)	+1.9	245.0	–208.7
Thermal conductivity κ (W/mK)	401[a]	0.559	0.788
Figure of merit *ZT*	1.57×10^{-4}	1.04	0.46
Specific heat *C* (J/cm^3 K)	3.44	0.153	0.185

[a] Ref. 20

Table 2 Thickness of copper and the *p*- and *n*-type Bi-Te materials which have a cross-sectional area of 5×5 mm^2

t_{Cu} (mm)	$t_{Bi\text{-}Te}$ (mm)	
	p-type	*n*-type
0.3	0.115	0.102
1.0	0.50	0.50
2.0	2.0	2.0
3.0	–	–
4.0	–	–

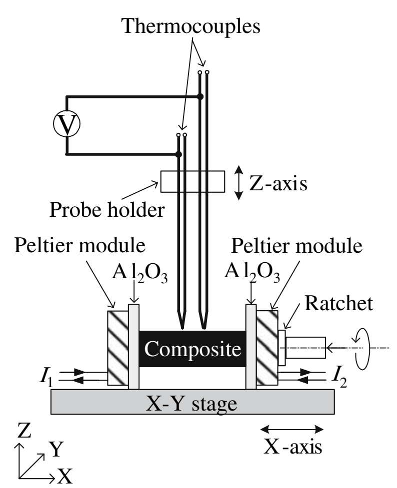

Fig. 2 Schematic configuration for the thermo-emf measurement of composite materials pressed at a constant force of 10 N by a ratchet

various combinations of $t_{Bi\text{-}Te}$ and t_{Cu} were measured as a function of time, up to $3T$ corresponding to three periods. The measurements of ΔV and ΔT under the steady temperature gradient (corresponding to $T = \infty$ sec) were made by reversing the direction of the steady temperature gradient before and after their measurements under the alternating temperature gradients. In the absence of the composite between two Peltier modules, the temperature difference ΔT_{blank} between the opposite alumina plates of two modules was measured by placing two probes on two alumina plates, to compare with ΔT in the presence of composite between them. Moreover, the electric current I flowing across two modules was measured as a function of time t at various periods, in order to investigate the dependence of the total electric resistance R_m of two Pelteir modules on T. The input energy W_{input} dissipated in two Peltier modules was then estimated as $R_m I_{eff}^2$, where I_{eff} is the effective electric current (will be described later) when a rectangular voltage with an amplitude of 1.7 V was imposed on two Peltier modules connected in series. The electric resistance R_{Cu} of copper leads was a constant value of 1.33 Ω, irrespective of T, so that R_m can be estimated from the relation $R_m = 1.7/I_{eff} - 1.33$ Ω using I_{eff} in a unit of A. The effective electric current I_{eff} flowing through them was approximately 0.7 A when a constant voltage of 1.7 V was imposed on two Peltier modules connected in series. The temperature difference ΔT was measured with an accuracy of 0.1 K and the voltage ΔV appeared on two probes was measured within an accuracy of 1%. However, the measurement of ρ was not made for the present composites, because the contact resistance is too large to obtain ρ with a high accuracy.

Results and discussion

Dependences of thermo-emf ΔV and temperature difference ΔT on T

The thermo-emf ΔV of the touching *p*- and *n*-type Cu/Bi-Te/Cu composites composed of the combinations of $t_{Bi\text{-}Te} = 0.1$, 0.5 and 2.0 mm and $t_{Cu} = 0$, 0.3, 2.0, 3.0 and 4.0 mm was measured as a function of time t by alternating the temperature difference ΔT at various periods of $T = 20$, 60, 120, 240 and ∞ sec. The amplitude of the thermo-emf ΔV remained little changed even when the direction of the temperature gradient was reversed. The dependences of ΔV and ΔT on t for the touching *p*-type composite composed of $t_{Bi\text{-}Te} = 0.1$ mm and $t_{Cu} = 2.0$ mm are shown in Fig. 4, as a representative example. It is seen from the figure that the amplitudes of ΔV and ΔT increase with an increase of T, while their waveforms vary significantly with a change in T but have a strong resemblance to each other. The waveform of ΔV is thus found to be dominated and determined predominantly by that of ΔT. It was also confirmed that the waveform and amplitude of ΔT vary not only with a change in T, but also with the combination of $t_{Bi\text{-}Te}$ and t_{Cu}.

Dependences of ΔV_{eff} and ΔT_{eff} on $1/T$

In order to estimate the effective value of the alternating thermo-emf ΔV, the effective thermo-emf ΔV_{eff} was calculated using the well-known relation

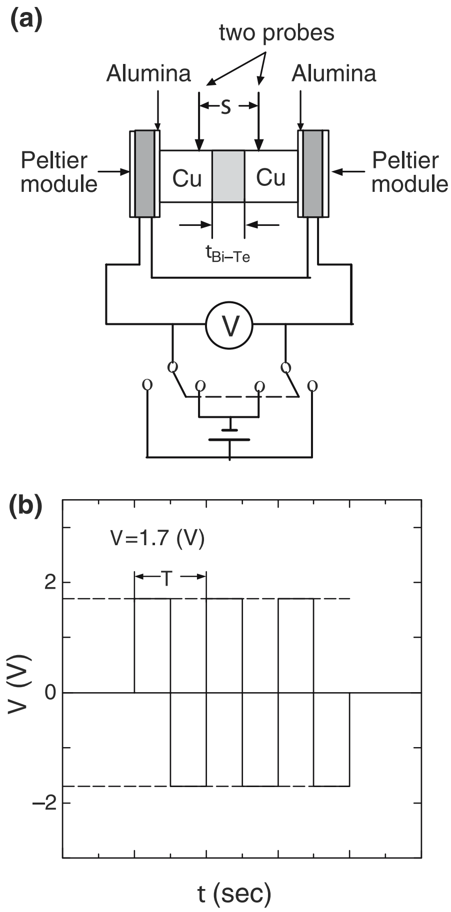

Fig. 3 (**a**) Schematic diagram of an electric circuit imposing the alternating temperature gradients on the touching Cu/Bi-Te/Cu composites. (**b**) Rectangular time variation of voltages of ±1.7 V imposed on two modules connected in series by switching the direction of electric current flowing through a circuit

$$\Delta V_{\text{eff}} = \sqrt{\frac{\sum (\Delta V_i)^2}{n}}, \qquad (5)$$

where ΔV_i is the i-th thermo-emf and n is the total number of data included in three periods. The effective temperature difference ΔT_{eff} and effective electrical current I_{eff} were also estimated in the same way. ΔV_{eff} and ΔT_{eff} were calculated for the p- and n-type composites composed of the combinations of $t_{Bi\text{-}Te} = 0.1$, 0.5 and 2 mm and $t_{Cu} = 0.3$ mm and ΔV_{eff} was plotted as a function of ΔT_{eff} in Fig. 5. As a result, ΔV_{eff} tends to increase monotonically with an increase of ΔT_{eff}, as already mentioned. For various combinations of $t_{Bi\text{-}Te}$ and t_{Cu}, ΔV_{eff} was plotted as a function of $1/T$ in Fig. 6. Consequently, ΔV_{eff} increases significantly with an increase of $1/T$, exhibits a local maximum at $1/T = 1/240\ s^{-1}$ except for a combination of $t_{Bi\text{-}Te} = 0.1$ mm and $t_{Cu} = 0.3$ mm and tends to decrease slowly with further increase of $1/T$. It indicates that the thermo-emf ΔV_{eff} is increased remarkably by imposing the temperature gradient alternating at an optimum period on composites. It is applicable to any combination of $t_{Bi\text{-}Te}$ and t_{Cu}. In addition, it indicates that the waveform of ΔV varies with a change in $1/T$, as mentioned earlier. As shown in Fig. 4, the serious modification of the waveform from a rectangular wave was indeed observed at $1/T = 1/20\ s^{-1}$ so that it resulted in the significant decrease in ΔV_{eff}, as shown in Fig. 6. Figure 7 shows the dependence of ΔT_{eff} on $1/T$ for various combinations of $t_{Bi\text{-}Te}$ and t_{Cu}. As in the case of ΔV_{eff}, ΔT_{eff} also has a local maximum at $1/T = 1/240\ s^{-1}$ (giving a local maximum of ΔV_{eff}) for any combination of $t_{Bi\text{-}Te}$ and t_{Cu}, although ΔT_{eff} varies greatly depending on the combination of $t_{Bi\text{-}Te}$ and t_{Cu}. The maximum ΔT_{eff} at $1/T = 1/240\ s^{-1}$ increases with an increase of $t_{Bi\text{-}Te}$, due to the low thermal conductance of Bi-Te material.

The reason why ΔT_{eff} has a local maximum at a period of $T = 240$ s is considered as follows. When the period T is shorter than 240 s, ΔT_{eff} is put down because the hot and cold sides are reversed before the temperatures of the hot and cold sides of a composite saturate. To the contrary, when T is longer than 240 s, the heat continues to transfer during a half-period ($T/2$) from the hot side to the cold of a composite, resulting in the decrease in ΔT_{eff}. Thus, the maximum ΔT_{eff} would appear at an optimum period of $T = 240$ s at which the temperatures of the hot and cold sides of a composite just begin to saturate.

Dependence of ΔW_{eff} on $1/T$

The resultant electric resistance R_{calc} of the p- and n-type Cu/Bi-Te/Cu composites was calculated by substituting x, ρ_M and ρ_T into Eq. 3, where $x = t_T/s = t_T/(t_T + 0.50)$. So calculated R_{calc} increases linearly with an increase of $t_{Bi\text{-}Te}$. Generally, the effective power generation ΔW_{eff} should be calculated using the relation

$$\Delta W_{\text{eff}} = \frac{(\Delta V_{\text{eff}})^2}{R_{\text{calc}}} \cdot \frac{m}{(1+m)^2}, \qquad (6)$$

where $m = (1 + ZT)^{1/2}$ [13]. The value of $(1 + m)^2/m$ approaches to 4 as ZT comes close to 0. If $ZT \leqq 2.5$, one gets the inequality $(1 + m)^2/m \leqq 4.41$ so that the degree of contribution from ZT to $(1 + m)^2/m$ is estimated to be equal to or less than 9% at most. For this reason, the contribution from ZT to ΔW_{eff} was neglected so that the effective power generation ΔW_{eff} is calculated as $\Delta W_{eff} = (\Delta V_{eff})^2/4R_{calc}$ for all touching composites. As a matter of course, so estimated ΔW_{eff} should be somewhat larger than the practical ΔW_{eff}, because the value of $(1 + m)^2/m$ is approximated to 4 and the contact electric resistance is not taken into the calculation of R_{calc}. However, these approximations have little effect on the later discussion, because their approximations have almost the same effect on ΔW_{eff} of the

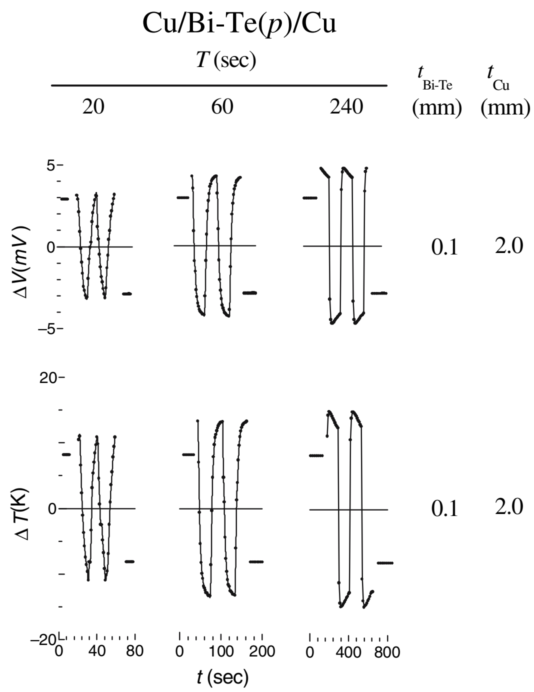

Fig. 4 Thermo-emf ΔV and temperature difference ΔT as a function of t for the p-type Cu/Bi-Te/Cu composites composed of $t_{\mathrm{Bi\text{-}Te}} = 0.1$ and $t_{Cu} = 2.0$ mm, where a voltage of 1.7 V was imposed alternatively at periods of $T = 20$, 60 and 240 s on two Peltier modules connected in series. The experimental data plotted on both sides of periodical signals correspond to $1/T = 0$ s^{-1}

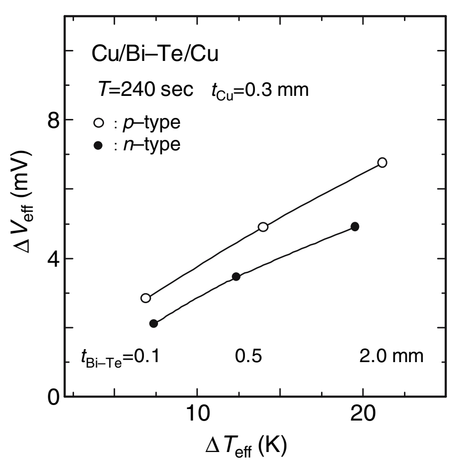

Fig. 5 ΔV_{eff} as a function of ΔT_{eff} for the p- and n-type Cu/Bi-Te/Cu composites composed of the combinations of $t_{\mathrm{Bi\text{-}Te}} = 0.1$, 0.5 and 2.0 mm and $t_{\mathrm{Cu}} = 0.3$ mm, where a voltage of 1.7 V was imposed alternatively at a period of $T = 240$ s on two Peltier modules connected in series

composites composed of various combinations of $t_{\mathrm{Bi\text{-}Te}}$ and t_{Cu}. In any case, so obtained ΔW_{eff} was plotted as a function of $1/T$ in Fig. 8. As a result, ΔW_{eff} increases significantly with an increase of $1/T$, has a local maximum at 1/240 s^{-1} for any combination of $t_{\mathrm{Bi\text{-}Te}}$ and t_{Cu} and wholly tends to decrease with further increase of $1/T$. The power generation of composites operating under the temperature gradient alternating at an optimum period was thus found to become much higher than those obtained under the steady temperature gradient (corresponding to $1/T = 0$). In addition, it is seen from the figure that the power generation ΔW_{eff} at $1/T = 1/240$ s^{-1} tends to increase as $t_{\mathrm{Bi\text{-}Te}}$ becomes thin. One reason for the increase in ΔW_{eff} at thin $t_{Bi\text{-}Te}$ is that the resultant electric resistance R_{calc} decreases with a decrease of $t_{\mathrm{Bi\text{-}Te}}$. In order to investigate another reason for the increase in ΔW_{eff} at thin $t_{\mathrm{Bi\text{-}Te}}$, the resultant $|\alpha|$ at $1/T = 0$ and 1/240 s^{-1} was calculated from the relation $|\alpha| = |\Delta V_{\mathrm{eff}}/\Delta T_{\mathrm{eff}}|$ and was plotted as a function of $t_{\mathrm{Bi\text{-}Te}}$ in Fig. 9a. As a result, the resultant $|\alpha|$ varies very little with a change in the period T but tends to decrease almost linearly with an increase of $t_{\mathrm{Bi\text{-}Te}}$, so that the resultants $|\alpha|$ of the p- and n-type composites composed of $t_{\mathrm{Bi\text{-}Te}} = 0.1$ mm and $t_{\mathrm{Cu}} = 0.3$ mm are 55 and 51% higher than those of the intrinsic Bi-Te compounds, respectively. Of course, the Seebeck coefficients α calculated from $\alpha = \Delta V_{\mathrm{eff}}/\Delta T_{\mathrm{eff}}$ at $1/T = 0$ s^{-1} for the p- and n-type intrinsic Bi-Te

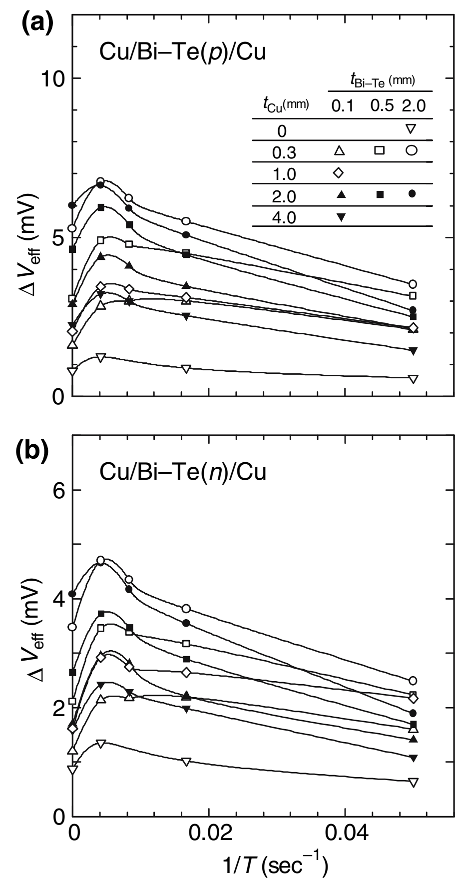

Fig. 6 Effective thermo-emf ΔV_{eff} as a function of $1/T$ for the p-type (**a**) and n-type (**b**) Cu/Bi-Te/Cu composites composed of the combinations of $t_{\mathrm{Bi\text{-}Te}} = 0.1$, 0.5 and 2.0 mm and $t_{\mathrm{Cu}} = 0$, 0.3, 1.0, 2.0 and 4.0 mm

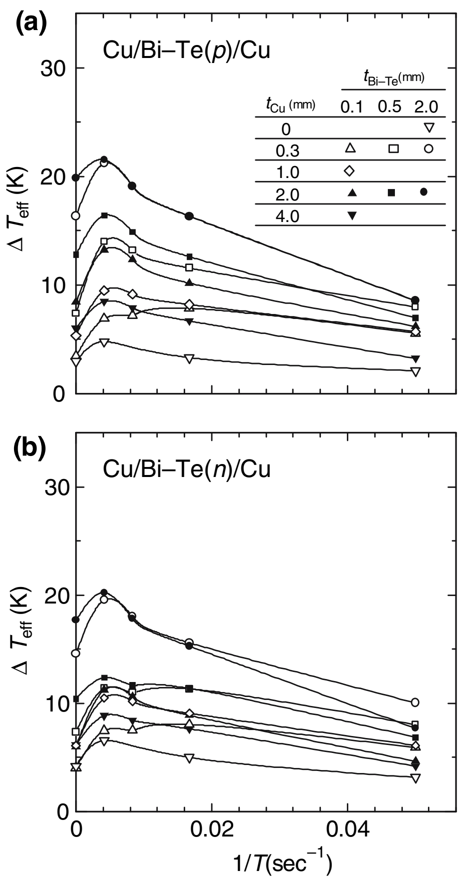

Fig. 7 ΔT_{eff} as a function of $1/T$ for the *p*-type (**a**) and *n*-type (**b**) Cu/Bi-Te/Cu composites composed of the combinations of $t_{\mathrm{Bi\text{-}Te}} = 0.1$, 0.5 and 2.0 mm and $t_{\mathrm{Cu}} = 0$, 0.3, 1.0, 2.0 and 4.0 mm

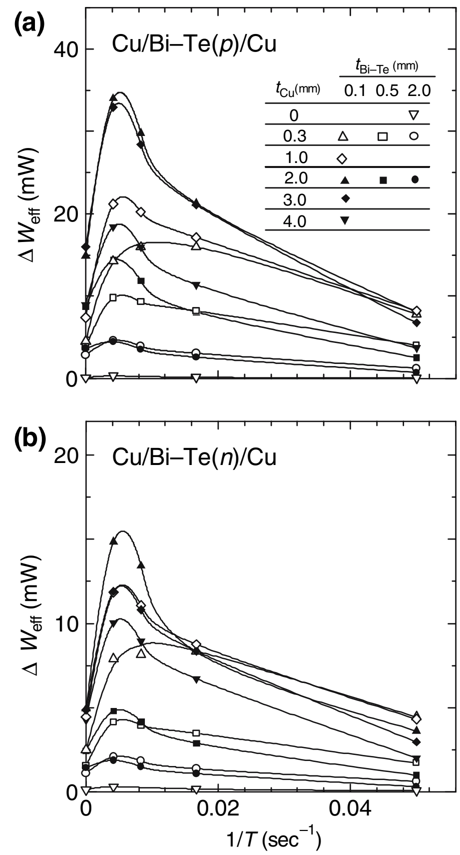

Fig. 8 ΔW_{eff} calculated as a function of $1/T$ using the relation $\Delta W_{\mathrm{eff}} = (\Delta V_{\mathrm{eff}})^2/4R_{\mathrm{calc}}$ for the *p*-type (**a**) and *n*-type (**b**) Cu/Bi-Te/Cu composites composed of the combinations of $t_{\mathrm{Bi\text{-}Te}} = 0.1$, 0.5 and 2.0 mm and $t_{\mathrm{Cu}} = 0$, 0.3, 1.0, 2.0, 3.0 and 4.0 mm, where R_{calc} was calculated from Eq. 3 using the experimental data listed in Table 1

materials agree with the experimental values listed in Table 1 within several percents. These degrees of increase in |α| of the present touching composites is much higher than 29% of the welded Cu/Bi-Sb/Cu [12], 21% of the welded Cu/Bi/Cu [12] and 32 and 30% of the welded *p*- and *n*-type Cu/Bi-Te/Cu composites [15]. In order to investigate whether this increase in |α| results from the contact electric resistance generated between Bi-Te material and copper, therefore, the resultants |α| of the touching composites composed of $t_{\mathrm{Bi\text{-}Te}} = 2.0$ mm and $t_{\mathrm{Cu}} = 0.3$ mm corresponding to $x = t_{\mathrm{Bi\text{-}Te}}/s = 0.80$ were compared with those of the welded Cu/Bi-Te/Cu composites of $t_{\mathrm{Bi\text{-}Te}} = 4.0$ mm and $t_{\mathrm{Cu}} = 5.0$ mm corresponding to $x = 0.69$, in which the observed and calculated ρ values coincide closely with each other [15]. The reason that the composites with x values close relatively to each other were employed here is that the degree of increase in |α| varies with x. Interestingly, the degrees of increase in |α| (at $x = 0.80$) of the touching *p*- and *n*-type composites are 20 and 16%, respectively, which were rather a little low compared to 25 and 19% (at $x = 0.69$) of the welded *p*- and *n*-type composites [15]. Clearly, it indicates that the degree of increase in |α| has nothing to do with the contact electric resistance. Therefore, the enhancement in |α| of the present composites are attributed to the appearance of the barrier thermo-emf generated at the boundary between Bi-Te compound with a low thermal conductivity and copper with a very high thermal conductivity [10].

The maximum ΔW_{eff} obtained at 1/240 s^{-1} were 34.0 and 14.9 mW for the *p*- and *n*-type composites composed of $t_{\mathrm{Bi\text{-}Te}} = 0.1$ mm and $t_{\mathrm{Cu}} = 2.0$ mm, respectively, which are 2.28 and 2.92 times as large as ΔW_{eff} obtained at $1/T = 0\ \mathrm{s}^{-1}$. The power generation of a composite under the alternating temperature gradients is thus enhanced significantly when it is composed of the combination of a thin thermoelectric material and two thick coppers, unlike a commercially utilized thermoelectric module composed of a thick thermoelectric material and two thin metal electrodes. The ratio of the maximum ΔW_{eff} for the *p*-type composite to that for the *n*-type one is 2.28 at $1/T = 1/240\ \mathrm{s}^{-1}$, whose value is just equal to 2.28 which is the ratio of *ZT* of the intrinsic *p*-type Bi-Te material to that of the intrinsic *n*-type one. It is thus sure that the power

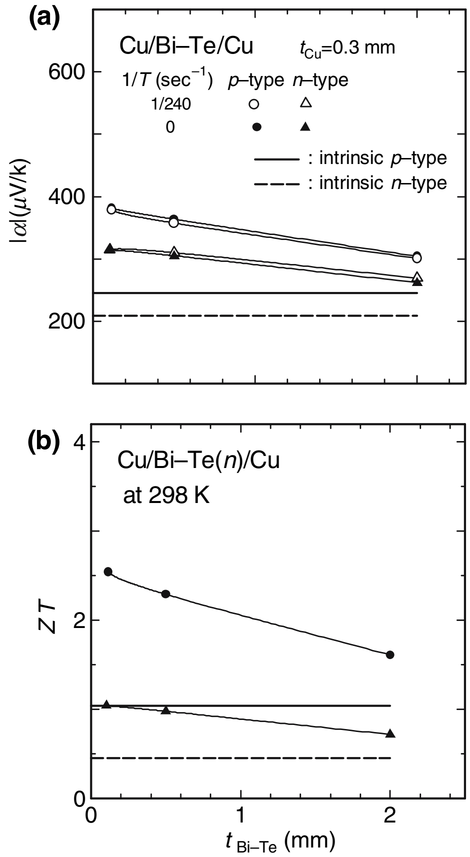

Fig. 9 (**a**) Resultant Seebeck coefficient |α| and (**b**) resultant ZT as a function of $t_{\text{Bi-Te}}$ for the p- and n-type Cu/Bi-Te/Cu composites composed of the combinations of $t_{\text{Bi-Te}} = 0.1$, 0.5 and 2.0 mm and $t_{\text{Cu}} = 0.3$ mm, where |α| was estimated from the relation $|\alpha| = \Delta V_{\text{eff}}/\Delta T_{\text{eff}}$ and ZT was calculated using the experimental α and the ρ and κ values obtained from Eqs. 2 and 4

generation of composites increases as ZT of Bi-Te material becomes high.

Next, the resultant ZT at 298 K was estimated at $1/T = 0$ s^{-1} for the touching p- and n-type composites composed of $t_{\text{Bi-Te}} = 0.1$, 0.5 and 2.0 mm and $t_{\text{Cu}} = 0.3$ mm, as shown in Fig. 9b, on the assumption that both the contact electric resistance and contact thermal resistance are zero. As a whole, the resultant ZT of touching composites tends to decrease with an increase of $t_{\text{Bi-Te}}$, but the degree of increase in ZT is found to be related closely with the magnitude of ZT of the intrinsic Bi-Te materials. The resultant ZT at $t_{\text{Bi-Te}} = 0.1$ mm were 2.54 and 1.05 at 298 K, respectively, which are 2.44 and 2.30 times as large as those of the corresponding intrinsic Bi-Te materials. Of course, these ZT of touching composites should be overestimated because the contact electric resistance is neglected in the estimation of ZT. Judging from the fact that the resultant ZT was enhanced significantly in the welded Cu/Bi-Te/Cu composites [15], however, the resultant ZT should be somewhat increased, even in the present touching composites. Therefore, the significant increase in ΔW_{eff} at $1/T = 1/240$ s^{-1} for the touching composites composed of $t_{\text{Bi-Te}} = 0.1$ mm and $t_{\text{Cu}} = 2.0$ mm is found to result from both the increase in ZT due to the increase in |α| and increase in ΔT_{eff} due to the optimization of the period T.

Dependence of ΔW_{eff} on t_{Cu}

The effective electric current I_{eff} flowing across two Peltier modules and the total electric resistance R_{m} of their modules were plotted as a function of $1/T$ in Fig. 10a for the touching p- and n-type composites composed of $t_{\text{Bi-Te}} = 0.1$ mm and $t_{\text{Cu}} = 2.0$ mm which exhibit the highest ΔW_{eff}. As a result, I_{eff} tends to increase with an increase of $1/T$, due to the lowering of R_{m} with $1/T$. The input energy W_{input} estimated from the relation $W_{\text{input}} = R_{\text{m}} I_{\text{eff}}^2$ for the p- and n-type composites decreases monotonically with an increase of $1/T$, as shown in Fig. 10b. The increase in I_{eff} and the decease in R_{m} with $1/T$ are explained by the following reason. That is, when the voltage V was applied across the electrodes joined to both ends of a thermoelectric element in Peltier modules, the charged electrodes at both ends of a thermoelectric element attract the charge carriers of opposite sign and repulse the charge carriers of the same sign, so that a thermoelectric material is

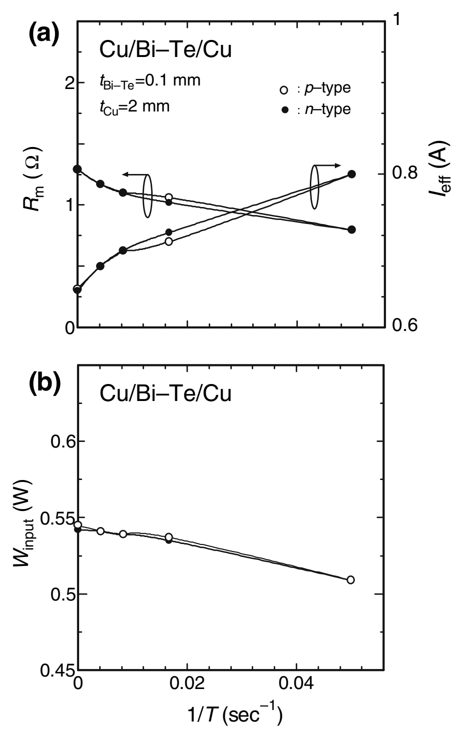

Fig. 10 (**a**) R_{m}, (**b**) I_{eff} and (**c**) W_{input} as a function of $1/T$ for the p- and n-type Cu/Bi-Te/Cu composites composed of a combination of $t_{\text{Bi-Te}} = 0.1$ mm and $t_{\text{Cu}} = 0.3$ mm

somewhat polarized electrically and at the same time some temperature difference is produced between both ends of a thermoelectric material. However, so produced temperature difference acts to disperse carriers condensed at its both ends, resulting in some reduction of the temperature difference. When the direction of voltage was switched suddenly, however, charge carriers condensed at an end of a thermoelectric material are moved to the opposite end by both attractive and repulsive interactions between the newly charged electrodes and carriers. Then the initial temperature gradient in a thermoelectric element acts to help carriers to move to the opposite end, leading to the increase in I_{eff}, so that R_m decreases with an increase of $1/T$. This is the reason that I_{eff} increases with an increase of $1/T$. When the period of the alternating voltage V became shorter, carriers go and return easily and frequently between the opposite ends of a thermoelectric material, due to the attractive and repulsive forces generated repeatedly between the charged electrodes and carriers, resulting in the reduction in the total electric resistance of two modules. Therefore, the shorter the period of the alternating voltage, the lower the total electric resistance R_m of two modules.

The power generation ΔW_{eff}, the effective temperature difference ΔT_{eff} and input energy W_{input} at $1/T = 0$ and $1/240$ s^{-1} for the composites composed of the combinations of $t_{Bi\text{-}Te} = 0.1$ mm and $t_{Cu} = 0.3$, 1.0, 2.0, 3.0 and 4.0 mm were plotted as a function of t_{Cu} in Fig. 11. As a result, both ΔW_{eff} and ΔT_{eff} at $1/T = 1/240$ s^{-1} have a local maximum at $t_{Cu} = 2.0$ mm. The t_{Cu}-dependence of ΔW_{eff} has a strong resemblance to that of ΔT_{eff}. The power generation ΔW_{eff} at $1/T = 1/240$ s^{-1} is much larger than that at $1/T = 0$ s^{-1}. In the absence of the composite between two Peltier modules, ΔT_{blank} was also measured and plotted as a function of t_{Cu} in Fig. 11b and c, where ΔT_{blank} is the effective temperature difference between the opposite alumina plates of two Peltier modules and then the interval between two modules corresponds to the length of composites. ΔT_{blank} values at $1/T = 0$ and $1/240$ s^{-1} increase significnalty with an increase of t_{Cu} and tend to saturate above $t_{Cu} = 3.0$ mm, while ΔT_{eff} values at $1/T = 0$ and $1/240$ s^{-1} decrease with an increase of t_{Cu} above $t_{Cu} = 2.0$ mm. Comparing the t_{Cu}-dependence of ΔT_{eff} with that of ΔT_{blank}, it is thus found that the thermal radiation and convection are dominant in the short interval (below $t_{Cu} = 2$ mm) between two Peltier modules, while in the long interval (above $t_{Cu} = 2$ mm), the heat transfer through a composite contributes predominantly to the decrease in ΔT_{eff}. The maximum ΔT_{eff} might thus appear at $t_{Cu} = 2.0$ mm where the heat transfer through a composite starts to become dominant. When a composite is sandwiched between two Peltier modules, the input energy W_{input} at $1/240$ s^{-1} was almost the same as that at $1/T = 0$ s^{-1} and both of them varied very little with a change in t_{Cu}, as shown in Fig. 11c. It is thus found that W_{input} is unaffected by the period T of the alternating temperature gradients and the length of composites, at least in the combinations of $t_{Bi\text{-}Te} = 0.1$ mm and $t_{Cu} = 0.3$, 1.0, 2.0, 3.0 and 4.0 mm.

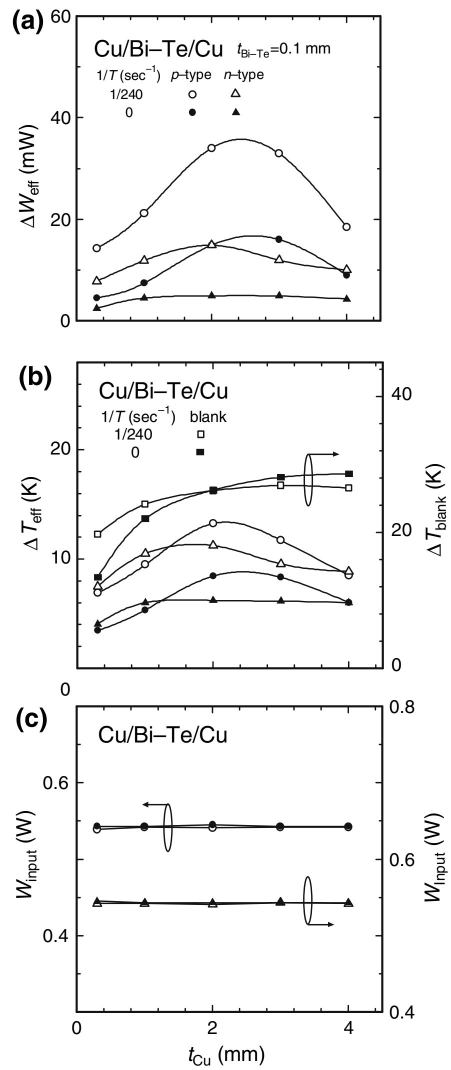

Fig. 11 (**a**) ΔV_{eff}, (**b**) ΔT_{eff} and ΔT_{blank} and (**c**) W_{input} as a function of t_{Cu} for the *p*- and *n*-type Cu/Bi-Te/Cu composed of the combinations of $t_{Bi\text{-}Te} = 0.1$ mm and $t_{Cu} = 0.3$, 1.0, 2.0, 3.0 and 4.0 mm, where ΔT_{blank} is the temperature difference between the opposite alumina plates of two Peltier modules in the absence of the composites between them

The energy conversion efficiency $\Delta W_{eff}/W_{input}$ at $1/T = 0$ and $1/240$ s^{-1} was estimated for the *p*- and *n*-type Cu/Bi-Te/Cu composites composed of $t_{Bi\text{-}Te} = 0.1$ mm and $t_{Cu} = 2.0$ mm which has the highest ΔW_{eff}. As a result, $\Delta W_{eff}/W_{input}$ for the *p*- and *n*-type composites were 6.29 and 2.75% at $1/T = 1/240$ s^{-1}, respectively, which are 2.30 and 3.02 times as large as those obtained at $1/T = 0$ s^{-1}. The later low energy conversion efficiency results from the low ZT of the intrinsic n-type Bi-Te material. However, the energy conversion efficiency of the p-type composite exceeded the Carnot's efficiency ($\Delta T_{eff}/T_h = 4.2\%$, T_h: the temperature of the hot side), although there is much heat transfer to or from the surroundings. The reason for the overestimation of the energy conversion efficiency is that the contact electric resistance was neglected in calculating ΔW_{eff}. However, the t_{Cu}-dependence of ΔW_{eff} would remain almost unchanged, even if it was taken into the calculation of ρ, because the degree to which the contact electric resistance effects the resultant ρ is almost the same for the composites with the same $t_{Bi\text{-}Te}$.

Next, ΔW_{eff} at $1/T = 0$ and $1/240\ s^{-1}$ was plotted as a function of ΔT_{eff} in Fig. 12 for the p- and n-type Cu/Bi-Te/Cu composites composed of $t_{Bi\text{-}Te}$=0.1 mm and t_{Cu} = 0.3, 1.0, 2.0, 3.0 and 4.0 mm. Although ΔT_{eff} values at $1/T = 1/240\ s^{-1}$ are higher than those at $1/T = 0\ s^{-1}$, ΔW_{eff} of the p- and n-type composites fall roughly on a parabolic curve, so that the relation between ΔW_{eff} and ΔT_{eff} is expressed by $\Delta W_{eff} = 0.230(\Delta T_{eff})^2$ for the p-type composite and $\Delta W_{eff} = 0.127(\Delta T_{eff})^2$ for the n-type one. The reason why the dependence of ΔW_{eff} on ΔT_{eff} is expressed by a simple quadratic function is that ΔV_{eff} is in proportion to ΔT_{eff}, as shown in Fig. 5. Then, the maximum ΔT_{eff} values at $1/T = 1/240\ s^{-1}$ for the p- and n-type composites were about 60 and 80% larger than those at $1/T = 0\ s^{-1}$, respectively. The significant increase in ΔW_{eff} is thus owing to both the increase in ΔT_{eff} and the increase in ZT due to the increase in $|\alpha|$. In addition, ΔW_{eff} at $1/T = 0$ and $1/240\ s^{-1}$ for the p- and n-type Cu/Bi-Te/Cu composites composed of $t_{Bi\text{-}Te}$ = 0.1, 0.5 and 2.0 mm and t_{Cu} = 2.0 mm was plotted as a function of $t_{Bi\text{-}Te}$ in Fig. 13. As a result, ΔW_{eff} for the p- and n-type composites decreases significantly and hyperbolically with an increase of $t_{Bi\text{-}Te}$. It is thus found that ΔW_{eff} is highly sensitive to the thickness of Bi-Te material rather than that of copper electrode. When $t_{Bi\text{-}Te}$ is less than 0.1 mm, therefore, ΔW_{eff} for the touching composites is expected to be enhanced more significantly. In designing a high-performance generator, however, it may be required to

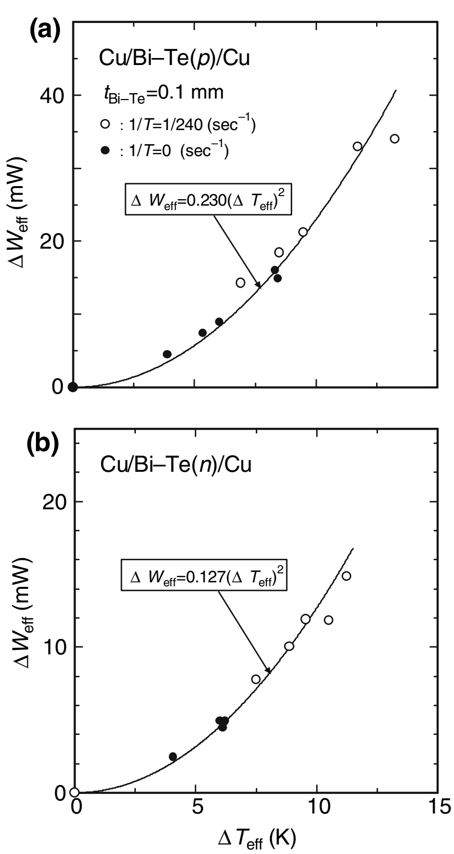

Fig. 12 ΔW_{eff} as a function of ΔT_{eff} for the p-type (**a**) and n-type (**b**) Cu/Bi-Te/Cu composites composed of the combinations of $t_{Bi\text{-}Te}$ = 0.1 mm and t_{Cu} = 0.3, 1.0, 2.0, 3.0 and 4.0 mm, where a voltage of 1.7 V was imposed alternatively at periods of $1/T = 0$ and $1/240\ s^{-1}$ on two Peltier modules connected in series

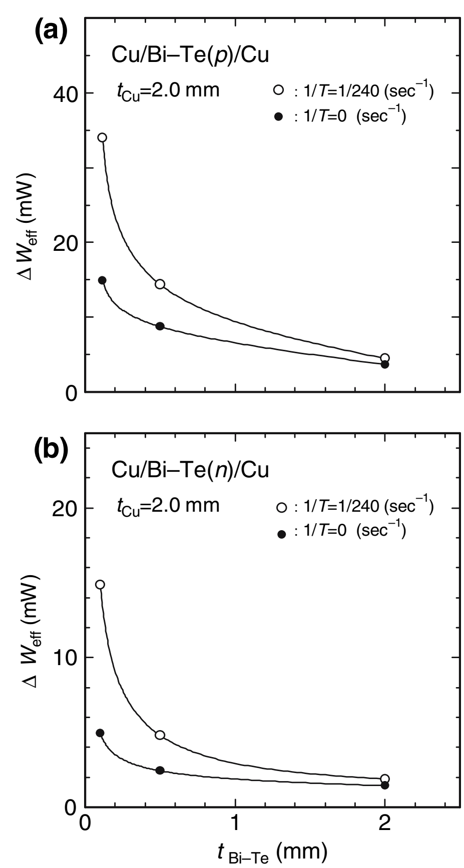

Fig. 13 ΔW_{eff} as a function of $t_{Bi\text{-}Te}$ for the p-type (**a**) and n-type (**b**) Cu/Bi-Te/Cu composites composed of the combinations of $t_{Bi\text{-}Te}$ = 0.1, 0.5 and 2.0 mm and t_{Cu} = 2.0 mm, where a voltage of 1.7 V was imposed alternatively at periods of $1/T = 0$ and $1/240\ s^{-1}$ on a composite

determine an optimum combination of $t_{Bi\text{-}Te}$ and t_{Cu}, according to the heat capacity of the hot and cold sources.

When a composite composed of an optimum combination of $t_{Bi\text{-}Te}$ and t_{Cu} was operated under the temperature gradient alternating at an optimum period, therefore, the energy conversion efficiency may be increased more significantly. In such a composite, non-equilibrium system carriers in the interior of the bismuth-telluride compound near the boundary would be separated strongly by a sharper temperature drop produced by the alternating temperature gradients, resulting in the enhancement of the barrier thermo-emf [11]. In any case, it is thus necessary to optimize the thickness and cross-sectional area of copper and bismuth-telluride, in designing a high-performance generator. Of course, it would be fully possible to design the thermoelectric module system so that the alternating temperature gradients are imposed periodically on a thermoelectric generator, by alternating the hot and cold sides of a generator at a period, even under the steady temperature difference. The application of an alternating temperature gradient to a newly designed thermoelectric module is thus considered to lead to further improvement in the energy conversion efficiency of a thermoelectric generator.

Summary and conclusion

The thermo-emf ΔV and temperature difference ΔT of the touching *p*-and *n*-type Cu/Bi-Te/Cu composites composed of the combinations of $t_{Bi\text{-}Te} = 0.1$, 0.5 and 2.0 mm and $t_{Cu} = 0$, 0.3, 2.0, 3.0 and 4.0 mm were measured as a function of time *t* by imposing the temperature gradients alternating at various periods of $T = 20$, 60, 120, 240 and ∞ sec on composites. Two probes were placed on both end coppers of a composite so that the interval *s* between them satisfies the relation $s = t_T + 0.50$ mm. The waveform of the ΔV of composites changes greatly with *T*. The effective thermo-emf ΔV_{eff} measured for the *p*- and *n*-type composites increases with an increase of $t_{Bi\text{-}Te}$, but surprisingly it also depends strongly on t_{Cu}. However, this increase in ΔV_{eff} was found to be closely related with the increase in ΔT_{eff}.

Most of the effective thermo-emf ΔV_{eff} for the *p*- and *n*-type composites increase abruptly with an increase of $1/T$ and exhibited a local maximum at $1/T$=1/240 s^{-1}. The maximum ΔV_{eff} of the *p*- and *n*-type composites appeared in a composite composed of $t_{Bi\text{-}Te} = 2.0$ mm and $t_{Cu} = 0.3$ mm. It was owing to the increase in ΔT_{eff} at $1/T = 1/240\ s^{-1}$. However, the power generation ΔW_{eff} estimated using the measured ΔV_{eff} and calculated R_{calc} exhibited the maximum value at $1/T = 1/240\ s^{-1}$ for a combination of $t_{Bi\text{-}Te} = 0.1$ mm and $t_{Cu} = 2.0$ mm, unlike a combination of $t_{Bi\text{-}Te} = 2.0$ mm and $t_{Cu} = 0.3$ mm giving the maximum ΔV_{eff}. It is attributed to both the decrease in R_{calc} and increase in the resultant $|\alpha|$ which are due to the reduction in $t_{Bi\text{-}Te}$. The increase in $|\alpha|$ is considered to result from the increase in the barrier thermo-emf, which is caused by a sharp temperature drop produced at the boundary between Bi-Te compound and copper. The maximum power generation ΔW_{eff} obtained at $1/T = 1/240\ s^{-1}$ for the *p*- and *n*-type composites were 2.28 and 3.01 times as large as those at $1/T = 0\ s^{-1}$. It is owing to the fact that ΔT_{eff} is increased more significantly at $1/T = 1/240\ s^{-1}$ than at $1/T = 0\ s^{-1}$; for example, the degree of increase in ΔT_{eff} is about 60% for the *p*-type composite and about 80% for the *n*-type one. In brief, the resultant $|\alpha|$ and the effective temperature difference ΔT_{eff} are increased significantly by optimizing $t_{Bi\text{-}Te}$, t_{Cu} and the period *T*, so that ΔW_{eff} was increased remarkably. Therefore, the significant increase in ΔW_{eff} is owing to both the increase in ΔT_{eff} and the increase in *ZT* due to the increase in $|\alpha|$. In conclusion, the application of an alternating temperature gradient to a thermoelectric generator is thus considered to result in further improvement in the energy conversion efficiency of a thermoelectric generator.

References

1. Wood C (1988) Prog Phys 51:459
2. Mahan G, Sales B, Sharp J (1997) Phys Today 50:42
3. Hicks LD, Dresselhaus MS (1993) Phys Rev B 47:12727
4. Hicks LD, Harman TC, Dresselhaus MS (1993) Appl Phys Lett 63:3230
5. Broido DA, Reinecke TL (1995) Appl Phys Lett 67:1170
6. Goldsmid HJ (1964) Thermoelectric refrigeration. Plenum, New York
7. Koga T, Rabin O, Dresselhaus MS (2000) Phys Rev B 62:16703
8. Venkatasubramanian R, Siivola E, Colpitts T, O'Quinn B (2001) Nature 413:597
9. Bergman DJ, Levy O (1991) J Appl Phys 70:6821
10. Tauc J (1953) Czechosl J Phys 3:282
11. Balmush II, Dashevsky ZM, Kasiyan AI (1995) Semiconductors 29:937
12. Yamashita O, Odahara H, Satou K (2005) J Mater Sci 40:1071. DOI: 10.1007/s10853-005-6919-z
13. Yamashita O, Satou K, Odahara H, Tomiyoshi S (2005) J Appl Phys 98:073707
14. Odahara H, Yamashita O, Satou K, Tomiyoshi S, Tani J, Kido H (2005) J Appl Phys 97:103722
15. Yamashita O, Odahara H (2006) J Mater Sci 41:2795. DOI: 10.1007/s10853-006-6133-7
16. Yamashita O, Odahara H (2005) J Mater Sci (accepted)
17. Yamashita O, Tomiyoshi S (2004) J Appl Phys 95:6277
18. Yamashita O, Tomiyoshi S (2004) J Appl Phys 95:161
19. Yim WM, Rosi FD (1972) Solid State Electron 15:1121
20. Kittel C (1996) Introduction to solid state physics. John Wiley & Sons, New York
21. Harman TC (1958) J Appl Phys 29:1373