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Effect of the thickness of Bi–Te compound and Cu electrode on the resultant Seebeck coefficient in touching Cu/Bi–Te/Cu composites

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Abstract The resultant Seebeck coefficient α of the touching p- and n-type Cu/Bi–Te/Cu composites with different thicknesses of $t_{\mathrm{Bi-Te}}$ and t_{Cu} was measured as a function of t, where $t_{\mathrm{Bi-Te}}$ was varied from 0.1 to 2.0 mm, t_{Cu} from 0.3 to 4.0 mm and t is the lapse time after imposing the voltage. The temperature difference ΔT is produced by imposing a constant voltage of 1.70 V on two Peltier modules connected in series. The resultant α of composites was calculated from the relation $\alpha = \Delta V/\Delta T$, where ΔV and ΔT were measured with two probes placed on both end coppers. ΔV decreases abruptly with an increase of t below t = 5 min, while above t = 7 min, it tends to saturate to a constant value. The resultant α and saturated ΔV vary significantly with changes in t_{Cu} and $t_{\mathrm{Bi-Te}}$. When a composite has a combination of t_{Cu} = 1.0 mm and $t_{\mathrm{Bi-Te}}$=0.1 mm, the generating powers ΔW $(=(\Delta V)^2/4R)$ estimated using the saturated ΔV and calculated electrical resistance R for the p- and n-type composites have great local maximum values which are 4–5 times as large as those obtained for the conventional combination of $t_{\mathrm{Bi-Te}}$ = 2.0 mm and t_{Cu} = 0.3 mm. It is surprising that the generating power ΔW is enhanced significantly by sandwiching a very thin Bi–Te material between two thick coppers, unlike the conventional composition of thermoelectric modules. On the other hand, when a composite has a combination of $t_{\mathrm{Bi-Te}}$ = 0.1 mm and t_{Cu} = 0.3 mm, the resultant α of the p- and n-type composites exhibited great values of 711 and –755 μV/K, respectively, so that the maximum resultant ZT of the p- and n-type composites reached extremely large values of 8.81 and 5.99 at 298 K. However, the resultant ZT decreases rapidly with an increase of t_{Cu} or $t_{\mathrm{Bi-Te}}$. The resultant ZT is thus found to be enhanced significantly not only in superlattice systems but also in macroscopic composites. The present enhancement in ZT is attributed to the large barrier thermo-emf generated in the Bi–Te region shallower than 50 μm from the boundary.

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 due to the

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effects of the quantum confinement of carriers. Indeed, the superlattice 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, unlike the superlattice systems, 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 the thermo-emf. The appearance of the barrier thermo-emf was indeed observed in the p-n junctions by illuminating them with infrared light pulse from a laser [11]. Most recently, it was also observed as an enhancement in the resultant α even in macroscopic thermoelectric composites [12–14] corresponding to the metal–semiconductor junction, in which a thermoelectric semiconductor is sandwiched between two metals. For example, the significant increase in the resultant α was observed by us in macroscopic n-type M/T/M (M = Cu or Ni and T = $Bi_{0.88}Sb_{0.12}$) composites welded with Bi–Sb alloy [12]. The maximum α of these composites was –110 μV/K, which is 29% higher in absolute value than –85 μV/K of Bi–Sb alloy. The maximum ZT of these M/T/M composites was only a small value of 0.44 at 298 K, but the degree of increase in ZT reached a large value of 69% [13]. Such a dramatic increase in ZT of macroscopic composites was attributed to a significant enhancement in α. Similar phenomenon was also observed even in the n-type Cu/Bi/Cu composite welded with pure Bi in which the maximum α is 21% higher in absolute value than –70 μV/K of Bi [12]. In addition, the maximum 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, at a relative thickness of 0.98 for a thermoelectric material, which are approximately 32% and 30% higher in absolute value than 202 and –205 μV/K of the intrinsic Bi–Te compounds [15]. As a result, surprisingly great ZT values of 1.53 and 1.66 were achieved for the p- and n-type Cu/Bi–Te/Cu composites, respectively, and they correspond to about twice as large as those of commercially utilized Bi–Te compounds [15]. It has been clarified by us that the phenomenon of increase in α occurs not only in the p-n junctions, but also in the composites in which a thermoelectric semiconductor is sandwiched between two metals. Such phenomena of an enhancement in α were observed in both the welded and touching composites [15, 16]. The composite materials with a sandwich structure may thus be considered as useful means of further improvement in ZT of bulk thermoelectrics.

Generally, the barrier thermo-emf occurs in the forward-bias direction (with a plus sign in the p-type region and a minus sign in the n-type region) or in the reverse-bias direction, depending on the position of the temperature gradient and the physical properties of the interface [11]. The barrier thermo-emf occurs in the forward-bias direction, at least in macroscopic composites mentioned above. However, it has hardly been investigated how the thermo-emf ΔV of composites changes with the combination of $t_{Bi–Te}$ and t_{Cu}. In addition, the region where the barrier thermo-emf is generated has not yet been clarified. For this reason, the resultant α was measured as a function of $t_{Bi–Te}$ or t_{Cu} and of distance r from the boundary for touching Cu/Bi-Te/Cu composites.

The purpose of this paper is to investigate whether the resultant α of touching Cu/Bi–Te/Cu composites is changed significantly with the combination of $t_{Bi–Te}$ and t_{Cu} and to specify the region where the barrier thermo-emf is enhanced significantly. If so, we take an interest in to what degree the resultant α, the resultant ZT and the generating power ΔW of touching composites are enhanced by optimizing the combination of $t_{Bi\text{-}Te}$ and t_{Cu}.

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. Here, we derive the resultant electrical resistivity ρ and thermal conductivity κ of a composite by treating it as an electrical 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 and there is no barrier thermo-emf leading to an enhancement in the resultant

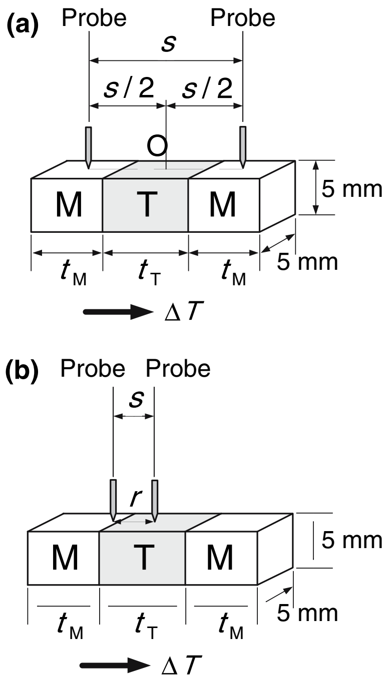

Fig. 1 Touching composite device with a sandwich structure (M/T/M) in which a parallelepiped of thermoelectric material T is sandwiched between two metallic parallelepipeds M, where s is the interval between two probes and t_T and t_M are the thicknesses of Bi–Te compounds and metals, respectively. (**a**) The center of the interval between two probes corresponds to that of material T. (**b**) One probe located on metal is adjacent to the boundary while another is placed on material T at the distance r from the boundary

α. 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

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

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

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

where $b = \rho_M/\rho_T$. If the thermal conductivities of the materials M and T are κ_M and κ_T, the resultant thermal conductivity κ of CTD is expressed as

$$\kappa = \frac{\kappa_M}{(1+x)+xc}, \qquad (3)$$

where $c = \kappa_M/\kappa_T$. In the present experiment, two probes are placed on both end coppers of a composite so that the interval s between them satisfies the relation $s = t_T + 0.35$ in a unit of millimeter.

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], where these materials were obtained from Kojundo Chemical Laboratory Co., Ltd. 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. The as-grown p-type ingot is a two-phase material consisting of an alloy matrix and a Te-rich phase, where the grain present in the matrix has an average size of about 1 mm in length and 0.2 mm in width and the length direction of lamellar grains is almost parallel to the cleavage planes [20]. On the other hand, the as-grown n-type ingot also consists of a lamellar structure, where the Se-rich layers and the Te-rich ones appear alternately. Both layers have an average length of about 1 mm, while the Se-rich layers have an average width of about 0.1 mm but the Te-rich ones about 0.3 mm [20]. The length direction of these thin layers is almost parallel to the cleavage planes, like the as-grown p-type ingot. The Se-rich regions just correspond to the Te-poor regions and vice versa.

In order to investigate the thermoelectric properties of the as-grown ingots, a parallelepiped of $5 \times 5 \times 15$ mm^3 and a square plate of $10 \times 10 \times 2$ 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 specimen was subjected to Seebeck coefficient α and electrical resistivity ρ measurements (Sinku-Riko, Inc., Model ZEM-1), and the latter one to thermal conductivity κ measurement (Sinku-Riko, Inc., Model TC-3000) after grinding into a disk of $\phi 10 \times 3$ 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*.

These as-grown p- and n-type Bi–Te ingots were employed to prepare the touching p- and n-type Cu/Bi–Te/Cu composites. The as-grown Bi–Te ingots were cut into a parallelepiped of $5 \times 5 \times t_{\mathrm{Bi\text{–}Te}}$ mm^3, where the thickness $t_{\mathrm{Bi\text{–}Te}}$ is perpendicular to the freezing direction, i.e., perpendicular to the cleavage plane and was varied from 0.1 up to 2.0 mm, as listed in Table 2. Copper plates and parallelepipeds were fabricated by cutting a long pillar with a square 5 mm on a side into five different thicknesses of t_{Cu} = 0.3, 0.5, 1.0, 2.0 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 touching p- and n-type Cu/Bi-Te/Cu composites are constructed by sandwiching a Bi–Te plate between two copper plates or parallelepipeds, as shown in Fig. 1. The Seebeck coefficient of the composites 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 is mounted on an *X–Y* stage and the temperature gradient was applied with two Peltier modules equipped to both ends of the composite. Two Peltier modules are pressed on a composite at a constant force of about 10 N by a ratchet. The measurement of the thermo-emf Δ*V* was made by producing the temperature difference between both ends of a composite, along the direction perpendicular to the freezing direction of Bi–Te ingot. The thermo-emf Δ*V* and temperature difference Δ*T* of the touching composites with various thicknesses of $t_{\mathrm{Bi\text{–}Te}}$ and t_{Cu} were measured as a function of *t* in the range from *t* = 1 up to 11 min, where *t* is the lapse time after imposing a constant voltage of 1.70 V on two Peltier modules connected in series. Two probes were then placed on both end coppers of a composite so that the interval *s* between them satisfies the relation $s = t_{\mathrm{T}} + 0.35$ mm. The electrical resistances of copper leads and two Peltier module connected in series were 1.0 and 1.10 Ω, respectively, so that the electrical current flowing through them was approximately 0.8 A when a voltage of 1.70 V was imposed on two Peltier modules connected in series. Indeed, the current is measured using a digital voltmeter and was also explained well by Ohm's law. In the case of the thickest composite giving the largest temperature difference, one end of the composite was then heated up to about 328 K and another was cooled to about 298 K. Both end temperatures of all composites were thus within this

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	
			p-type	n-type
Electrical resistivity	ρ (μΩm)	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	0.456
Specific heat	C (J/cm^{3}K)	3.44	0.153	0.185

[a] Ref. 24

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)	$t_{\mathrm{Bi\text{–}Te}}$ (mm)	
	p-type	n-type
0.3	0.115	0.102
0.5	0.25	0.20
1.0	0.50	0.50
2.0	1.0	1.0
4.0	2.0	2.0

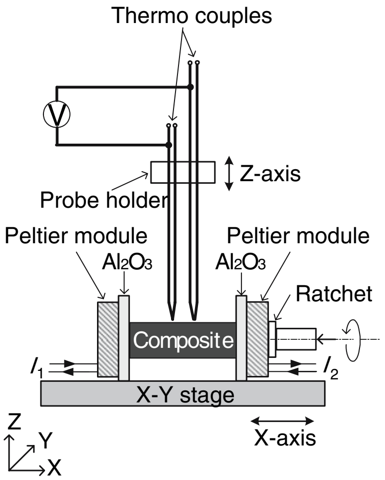

Fig. 2 Schematic configuration for α measurements of composite materials pressed tightly by a ratchet. One end was heated by flowing the electrical current I_1 or I_2 through a Peltier module to produce the temperature differences and another one was then maintained at room temperature. Two alumel–chromel thermocouples of this apparatus were set at the interval *s*

temperature range. The temperature dependences of Seebeck coefficient of the present p- and n-type Bi–Te materials are less than 2.1 and 0.29% in the range from 298 K to 328 K [20], so that the influence of temperature on the thermo-emf ΔV was not taken into account in the later discussion. The resultant α of the touching composites was obtained from the relation $\alpha = \Delta V/\Delta T$. The produced temperature difference ΔT tends to increase with an increase of $t_{\mathrm{Bi-Te}}$ or t_{Cu}. The experimental error arising in measuring temperatures becomes the largest when ΔT between two probes is the smallest, because the experimental error is determined by the ratio of the measurement accuracy of a thermometer to the absolute value of the observed ΔT. The smallest ΔT was 1.2, 4.9, 9.2, 12.7 and 18.4 K for probe intervals of $s = 0.45$, 0.55, 0.85, 1.35 and 2.35 mm. 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%, so that the resultant maximum error of α was 9.3%, 3.1%, 2.1%, 1.8% and 1.6% for probe intervals of $s = 0.45$, 0.55, 0.85, 1.35 and 2.35 mm. The resultant error of the thermoelectric figure of merit ZT was 17.8, 6.0%, 4.2%, 3.5% and 3.2% for probe intervals of $s = 0.45$, 0.55, 0.85, 1.35 and 2.35 mm, at least when the error of ρ is not taken into account.

In addition, the resultant α across the boundary was measured as a function of distance r from the boundary of composites composed of $t_{\mathrm{Bi-Te}}$=2.0 mm and t_{Cu}=0.3 mm, in order to specify the region where the resultant α is enhanced significantly. However, the measurement of ρ was not made on the present touching composites, because the contact resistance is too large to obtain ρ with a high accuracy.

Results and discussion

Dependence of thermo-emf ΔV and generating power ΔV on $t_{\mathrm{Bi-Te}}$ and t_{Cu}

Figures 3 and 4 show the t-dependence of thermo-emf ΔV across two boundaries for the p- and n-type composites. As shown in their figures, the experimental values of ΔV decrease abruptly with an increase of t below $t = 5$ min, while above $t = 7$ min, they tend to saturate to each constant value. The saturation value of ΔV tends to increase with an increase of $t_{\mathrm{Bi-Te}}$ or t_{Cu}. It is found from these experimental results that the copper thicker than Bi–Te material is required to enhance the thermo-emf ΔV. However, the increase in ΔV does not necessarily result in the increase in the available generating power ΔW, as will be shown later. Figure 5 shows the t-dependence of ΔT for $t_{\mathrm{Bi-T}} = 2.0$ mm. Interestingly, the t-dependence of ΔT is found to be very similar to that of ΔV. For this reason, ΔV was plotted as a function of ΔT in Fig. 6. As a result, ΔV tends to increase linearly with an increase of ΔT, so

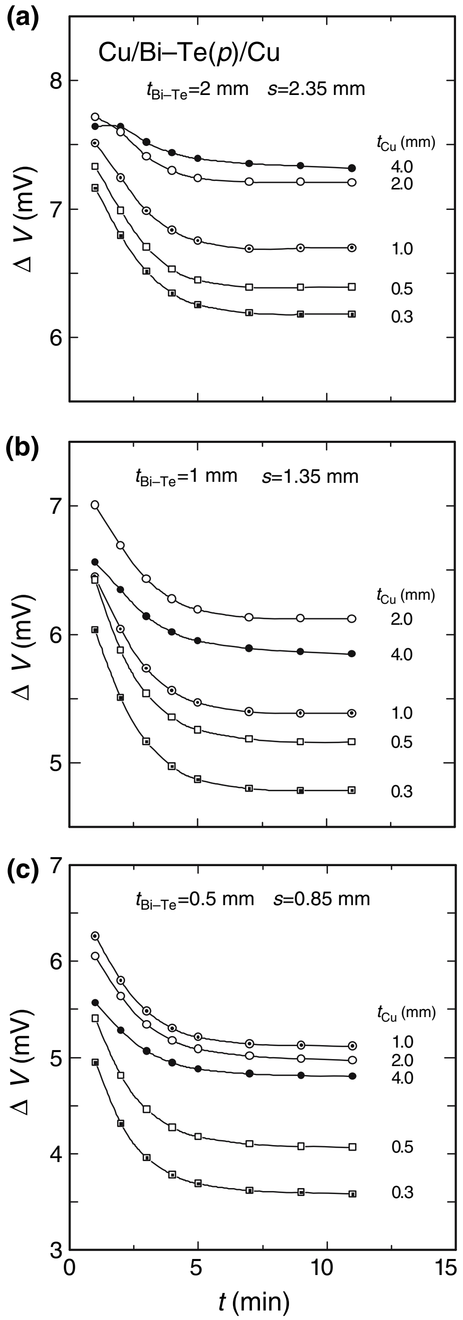

Fig. 3 Thermo-emf ΔV as a function of t for the p-type Cu/Bi–Te/Cu composites composed of the combinations of $t_{\mathrm{Bi-Te}} = 0.5$, 1.0 and 2.0 mm and $t_{\mathrm{Cu}} = 0.3$, 0.5, 1.0, 2.0 and 4.0 mm, where t is the lapse time after a voltage of 1.70 V was imposed on two Peltier modules connected in series

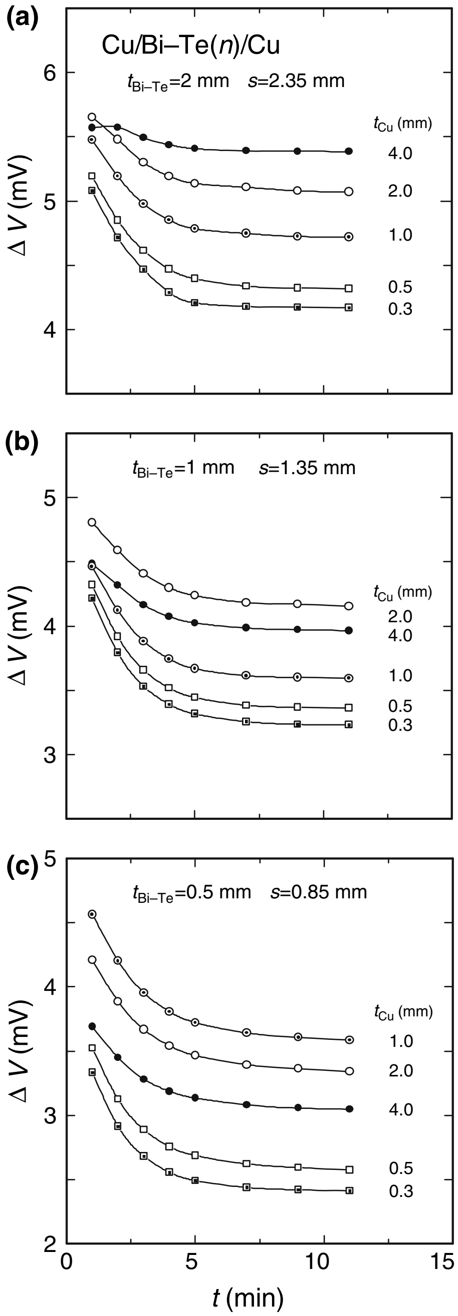

Fig. 4 Thermo-emf ΔV as a function of t for the n-type Cu/Bi–Te/Cu composites composed of the combinations of $t_{\mathrm{Bi-Te}} = 0.5$, 1.0 and 2.0 mm and $t_{\mathrm{Cu}} = 0.3$, 0.5, 1.0, 2.0 and 4.0 mm, where t is the lapse time after a voltage of 1.70 V was imposed on two Peltier modules connected in series

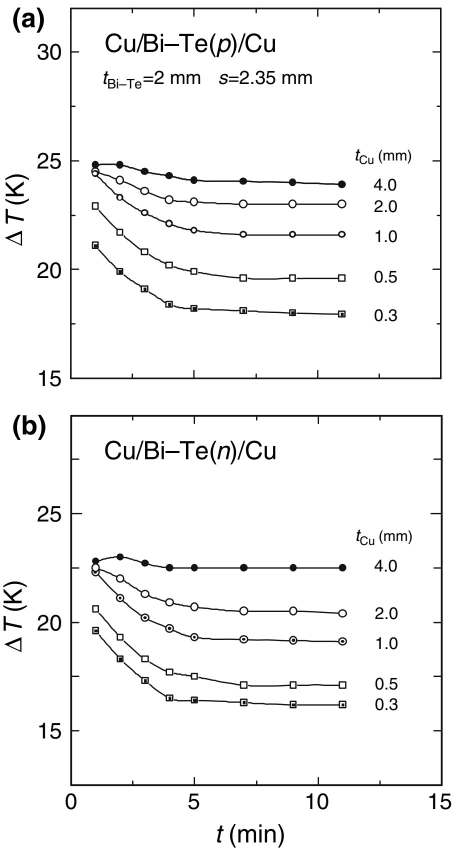

Fig. 5 Temperature difference ΔT as a function of t for the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites composed of the combinations of $t_{\mathrm{Bi-Te}} = 0.5$, 1.0 and 2.0 mm and $t_{\mathrm{Cu}} = 0.3$, 0.5, 1.0, 2.0 and 4.0 mm, where t is the lapse time after a voltage of 1.70 V was imposed on two Peltier modules connected in series

that the t-dependence of ΔV is found to dependent on that of ΔT. Figures 5 and 6 also show that ΔT tends to increase significantly with an increase of t_{Cu}. This increase in ΔT with an increase in t_{Cu} is attributed to the increase in heat capacity of Cu. Probably, this strong dependence of ΔT on t_{Cu} would be caused by a large specific heat of copper, which is approximately 20 times as high as those of Bi-Te compounds, as listed in Table 1.

In order to estimate the generating power ΔW $(=(\Delta V)^2/4R)$ for the p- and n-type composites, the resultant electrical resistance R was calculated from the relation $R = \rho s/S$, where S is the cross-sectional area of a composite and ρ is its resultant electrical resistivity. The resultant ρ of a composite was calculated by substituting x, ρ_{M} and ρ_{T} into Eq. 2, where $x = t_{\mathrm{T}}/s = t_{\mathrm{T}}/(t_{\mathrm{T}}+0.35)$. The generating power ΔW estimated using both the measured ΔV and calculated R was plotted as a function of t_{Cu} in Fig. 7. The dashed curve shown in Fig. 7 is drawn to pass possibly near the local maximum value of ΔW for each $t_{\mathrm{Bi\text{-}Te}}$. As a whole, the local maximum value of ΔW tends to decrease abruptly with an increase of $t_{\mathrm{Bi\text{-}Te}}$, as denoted by the dashed curve in the figure. When a composite has a combination of $t_{\mathrm{Bi\text{-}Te}} = 0.1$ mm and $t_{\mathrm{Cu}} = 1.0$ mm, ΔW has a maximum value of 16.0 mW for the p-type composite and of 8.0 mW for the n-type one, which are

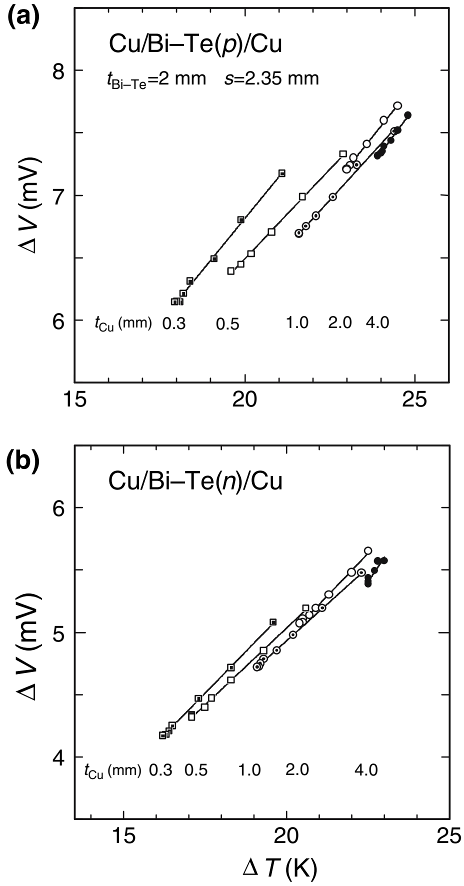

Fig. 6 Thermo-emf ΔV as a function of ΔT for the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites composed of the combinations of $t_{\mathrm{Bi\text{-}Te}}$ = 2.0 mm and t_{Cu} = 0.3, 0.5, 1.0, 2.0 and 4.0 mm

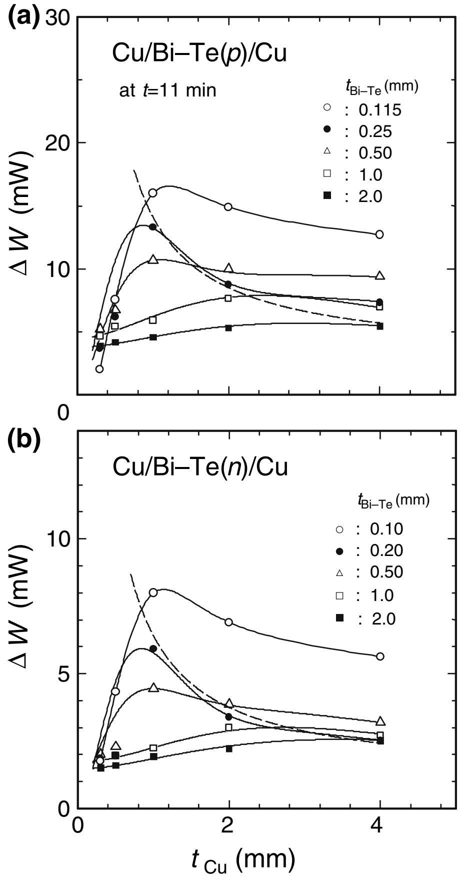

Fig. 7 Generating power ΔW as a function of t_{Cu} for the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites composed of the combinations of various $t_{\mathrm{Bi\text{-}Te}}$ (denoted in the figure) and t_{Cu} = 0.3, 0.5, 1.0, 2.0 and 4.0 mm. The dashed curve is drawn to pass possibly near the local maximum value of ΔW for each $t_{\mathrm{Bi\text{-}Te}}$

4.1 and 5.3 times larger than 3.9 and 1.5 mW obtained for the p- and n-type composites composed of the conventional combination of $t_{\mathrm{Bi\text{-}Te}}$ = 2.0 mm and t_{Cu} = 0.3 mm. Subsequently, the generating power ΔW obtained for t_{Cu} = 0.3 and 1.0 mm was plotted as a function of $t_{\mathrm{Bi\text{-}Te}}$ in Fig. 8. As a result, ΔW for t_{Cu} = 0.3 mm has a local maximum at $t_{\mathrm{Bi\text{-}Te}}$ = 0.5 mm, while for t_{Cu} = 1.0 mm, it tends to decrease monotonically with an increase of $t_{\mathrm{Bi\text{-}Te}}$, so that the dependence of ΔW on $t_{\mathrm{Bi\text{-}Te}}$ changes entirely with the thickness of copper. It is thus found to be necessary to optimize both $t_{\mathrm{Bi\text{-}Te}}$ and t_{Cu}, to make ΔW as high as possible.

Dependence of the resultant α on $t_{\mathrm{Bi\text{-}Te}}$ and t_{Cu}

The resultant α of the touching composites was calculated from the relation $\alpha = \Delta V/\Delta T$ using the saturation values (at t = 11 min) of ΔV and ΔT. Figure 9 shows the t_{Cu}-dependence of the resultant α for various $t_{\mathrm{Bi\text{-}Te}}$. The resultant α has a maximum value at t_{Cu} = 0.3 mm and decreases abruptly with an increase of t_{Cu} below t_{Cu} = 1.0 mm, while above t_{Cu} = 2.0 mm, it decreases slowly with further increase of t_{Cu} to approach the intrinsic Seebeck coefficients of Bi–Te compounds. The maximum resultant α at t_{Cu}=0.3 mm tends to become large as $t_{\mathrm{Bi\text{-}Te}}$ becomes thin. When a composite has a combination of $t_{\mathrm{Bi\text{-}Te}}$ = 0.1 mm and t_{Cu} = 0.3 mm, the maximum resultant α eventually reached extremely great values of 711 and –755 μV/K for the touching p- and n-type composites, respectively, which are 2.9 and 3.7 times larger in absolute value than the Seebeck coefficients of the intrinsic Bi–Te compounds and are much higher in absolute value than approximately 380 and –480 μV/K at 300 K for the p- and n-type $Si_{0.7}Ge_{0.3}$ alloy which have ρ values of 16.0 and 47.5 $\mu\Omega$m [21]. It is surprising that the t_{Cu}-dependence of the resultant α is so strong. The reason for such significant enhancement in α is that the additional barrier thermo-emf generated at both Cu/Bi–Te and Bi–Te/Cu interfaces has the same sign as that of the

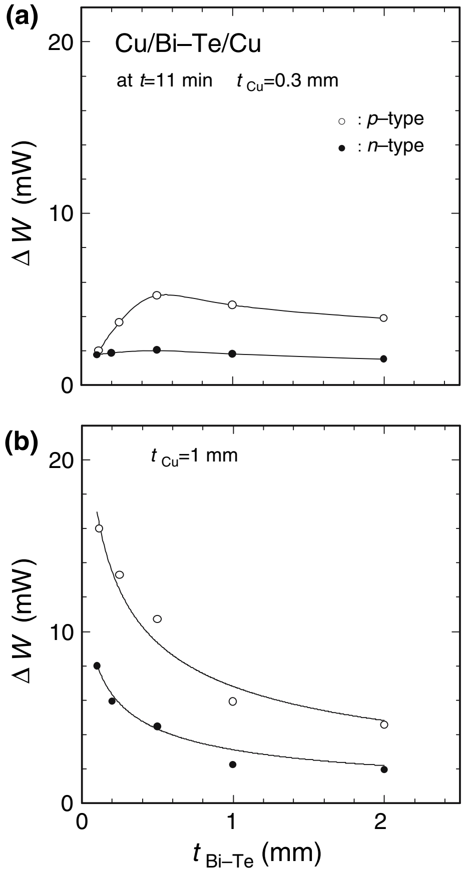

Fig. 8 Generating power ΔW as a function of $t_{\mathrm{Bi-Te}}$ for the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites with t_{Cu} = 0.3 and 1.0 mm

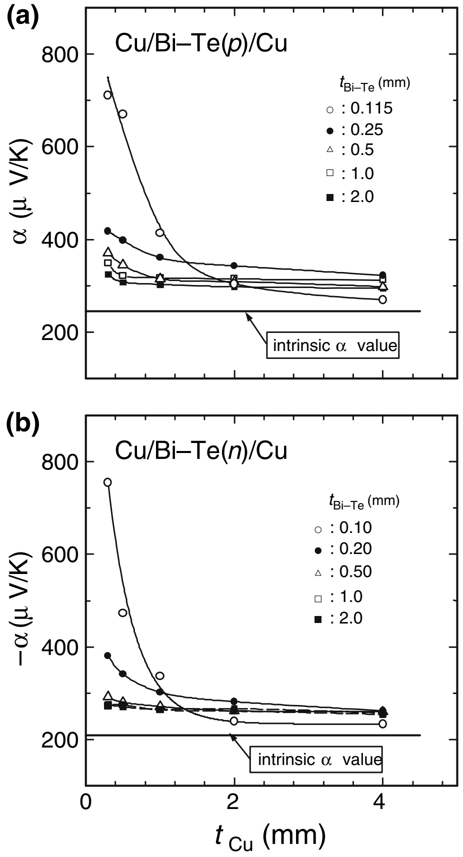

Fig. 9 Resultant α as a function of t_{Cu} for the p-type (**a**) and n-type (**b**) Cu/Bi–Te/Cu composites composed of the combinations of various $t_{\mathrm{Bi-Te}}$ (denoted in the figure) and t_{Cu} = 0.3, 0.5, 1.0, 2.0 and 4.0 mm

intrinsic Bi–Te compounds and is increased remarkably. The significant enhancement in α at $t_{\mathrm{Bi-Te}}$ = 0.1 mm indicates that the barrier thermo-emf may be expected to be generated in the Bi–Te region less than 50 μm from the surface of Bi–Te compounds touched tightly with copper plates, judging from the thickness of Bi–Te compounds.

Figure 10 shows the $t_{\mathrm{Bi-Te}}$-dependence of the resultant $|\alpha|$ for t_{Cu} = 0.3 mm. The resultant $|\alpha|$ has a great value at $t_{\mathrm{Bi-Te}}$ = 0.1 mm but decreases abruptly with an increase of $t_{\mathrm{Bi-Te}}$ to approach the intrinsic α values of Bi–Te compounds. The $t_{\mathrm{Bi-Te}}$-dependence of the resultant $|\alpha|$ was found to be expressed approximately in terms of a hyperbolic curve;$\alpha = 300 + 40/t_{\mathrm{Bi-Te}}$ μV/K for the p-type composite and $|\alpha| = 220 + 48/t_{\mathrm{Bi-Te}}$ μV/K for the n-type one, where $t_{\mathrm{Bi-Te}}$ is expressed in a unit of millimeter. Judging from the fact that the resultant α becomes equal to 1.9 μV/K at $t_{\mathrm{Bi-Te}}$ = 0 mm (see Table 1), therefore, the resultant $|\alpha|$ is expected to have a greater local maximum (>1,000 μV/K in absolute value) in the range from $t_{\mathrm{Bi-Te}}$ = 0 to 0.1 mm.

Next, we consider why such a significant enhancement in α occurs in macroscopic touching composites when the thermal gradient is applied along the sand-

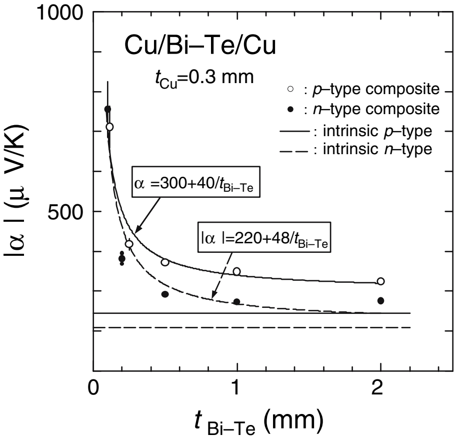

Fig. 10 Resultant $|\alpha|$ as a function of $t_{\mathrm{Bi-Te}}$ for the p- and n-type Cu/Bi–Te/Cu composites sandwiched between two coppers of t_{Cu} = 0.3 mm

wiched direction. It is sure that the resultant α of the composite materials is not enhanced as long as there is no boundary effect. When Bi–Te semiconductor was sandwiched between two coppers, a potential barrier is generally generated at the boundary. When such a barrier was accompanied by a sufficiently great temperature drop, the additional barrier thermo-emf appears at the boundary. If a potential barrier at the interface is too thick for tunneling, the dominating transport mechanism is thermionic emission. According to Mahan and Bartkowiak [22], the boundary Seebeck coefficient α_b and boundary thermal conductivity κ_b due to such a mechanism takes the form

$$\alpha_b = \frac{1}{eT}[U_0 + 2k_B T] \tag{4}$$

and

$$\kappa_b = 2\sigma_b T \frac{k_B^2}{e^2}, \tag{5}$$

where U_0 is the barrier height and σ_b is the electrical conductivity of the boundary. Equation 5 is a boundary form of the Wiedemann–Franz law and is valid only when U_0 is large enough (at least $2k_BT$). For the case of the barrier height optimized for the highest efficiency of a single-barrier thermionic refrigerator, the relation $U_0 \approx 2k_BT$ is obtained by Bartkowiak and Mahan, who get $\alpha_b \approx 340$ μV/K from this relation [23]. This is just a rough estimation, but it indicates that the boundary Seebeck coefficient can be very large. As the present composites have two boundaries at the hot and cold sides, the resultant α is given by

$$\alpha = \alpha_{\mathrm{Bi-Te}} + (\alpha_b - \alpha_{\mathrm{Bi-Te}})\frac{2\delta T}{\Delta T}, \tag{6}$$

where δT is a finite temperature drop across the boundary and assumed to be the same at both sides for simplicity [23]. When α_b has the same sign as $\alpha_{\mathrm{Bi-Te}}$, α is increased in absolute value. The coefficient of $(\alpha_b - \alpha_{\mathrm{Bi-Te}})$ in Eq. 6 should be reversely proportional to $t_{\mathrm{Bi-Te}}$, taking into account the fact that the resultant $|\alpha|$ of composites is expressed as a function $1/t_{\mathrm{Bi-Te}}$, as mentioned above. Therefore, $2\delta T/\Delta T$ can be expressed by

$$\frac{2\delta T}{\Delta T} = \frac{K}{t_{\mathrm{Bi-Te}}}, \tag{7}$$

where K is a constant value in a unit of millimeter. Substituting Eq. 7 into Eq. 6, the resultant α is expressed as

$$\alpha = \alpha_{\mathrm{Bi-Te}} + (\alpha_b - \alpha_{\mathrm{Bi-Te}})\frac{K}{t_{\mathrm{Bi-Te}}}. \tag{8}$$

As a matter of course, K should be smaller than 0.1 mm, as evident from the experimental fact that $2\delta T/\Delta T$ cannot exceed 1 even at $t_{\mathrm{Bi-Te}} = 0.1$ mm. If Equation 8 is equivalent to the experimental expression (denoted in Fig. 10) between α and $t_{\mathrm{Bi\text{-}Te}}$, therefore, $\alpha_{\mathrm{Bi\text{-}Te}}$ is estimated as 300 μV/K for the p-type composite and –220 μV/K for the n-type one and then one gets $|\alpha_b| \geqq 700$ μV/K for both type ones. In addition, the combination of Eq. 4 and the inequality $|\alpha_b| \geqq 700$ μV/K yields the relation $|U_0|/k_BT \geqq 6.12$, whose value is much larger than $\approx$2 which has been derived by Bartkowiak and Mahan [23]. It is thus found that the boundary Seebeck coefficient leading to the great barrier thermo-emf is caused by the significant increase in the barrier height at the boundary. Recently, it was indicated by Bartkowiak and Mahan [23] that the boundary and bulk thermoelectric effects cannot be combined to enhance the resultant Seebeck coefficient in the superlattice systems. However, it does not apply to the present macroscopic composites, because most of phonons and electrons accumulated in thermoelectric materials of composites are almost in thermal equilibrium, unlike in the superlattice systems in which they are out of equilibrium.

Figure 11 shows the dependence of the resultant $|\alpha|$ across the boundary on the distance r from the boundary for the touching p- and n-type composites composed of a combination of $t_{\mathrm{Bi-Te}} = 2.0$ mm and $t_{\mathrm{Cu}} = 0.3$ mm. Here the side of one probe placed on

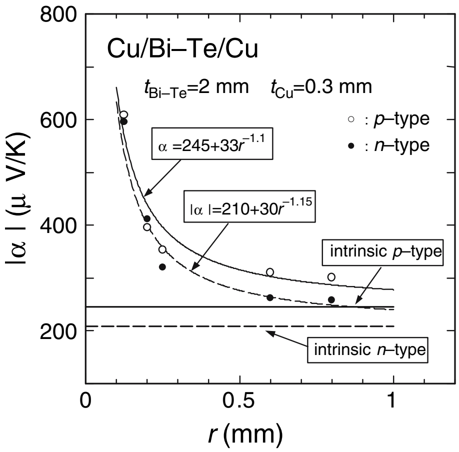

Fig. 11 Resultant $|\alpha|$ as a function of r for the p- and n-type Cu/Bi–Te/Cu composites composed of a combination of $t_{\mathrm{Bi\text{-}Te}} = 2.0$ mm and $t_{\mathrm{Cu}} = 0.3$ mm, where r is the distance from the boundary

copper is right just above the boundary and another put on Bi–Te compound is at the distance r from the boundary, as shown in Fig. 1(b). The resultant $|\alpha|$ across the boundary exhibits a maximum value of approximately 600 μV/K at $r = 0.125$ mm but decreases abruptly with an increase of r below $r = 0.25$ mm, while above $r = 0.6$ mm, it decreases slowly with further increase of r to approach the intrinsic α values of Bi–Te compounds. This is also consistent qualitatively with the above result that the large barrier thermo-emf is generated in the Bi–Te region shallower than 50 μm from the surface. Since the lowest limit of r is determined by the probe diameter (0.25 mm), however, it is impossible to measure directly the resultant $|\alpha|$ in the range below $r = 0.125$ mm.

Thermoelectric figure of merit ZT estimated as a function of $t_{\mathrm{Bi\text{–}Te}}$

For the touching composites sandwiched between two coppers of $t_{\mathrm{Cu}} = 1.0$ mm, the resultant thermoelectric figure of merit ZT was calculated at 298 K as a function of $t_{\mathrm{Bi\text{–}Te}}$ using the relation $ZT = \alpha^2 T/\rho\kappa$, where α is the experimental value and ρ and κ are the resultant electrical resistivity and thermal conductivity which were calculated from Eqs. 2 and 3 using the intrinsic thermoelectric properties listed in Table 1. The resultant ZT estimated here for the touching composites is also applicable to the welded composites. There are two reasons to justify it. One reason is that the rate of increase in the resultant α for the touching composite is nearly equal to that for the welded one, at least when x $(=t_{\mathrm{Bi\text{–}Te}}/s)$ of the touching and welded composites is close to each other. For example, the rates of increase in α for the touching p- and n-type Cu/Bi–Te/Cu are 27% and 17% at $x = 0.75$ [16], respectively, which coincide roughly with 25% and 19% obtained at $x = 0.69$ for the welded p- and n-type ones [15]. Another reason is that the experimental resultants ρ and κ of the welded composites coincided closely with those calculated from Eqs. 2 and 3 using the intrinsic thermoelectric properties [15]. Figure 12 shows the dependences of the resultant ZT on $t_{\mathrm{Bi\text{–}Te}}$ for $t_{\mathrm{Cu}} = 0.3$ mm and on t_{Cu} for $t_{\mathrm{Bi\text{–}Te}} = 0.1$ mm. The resultant ZT of the touching p- and n-type composites composed of a combination of $t_{\mathrm{Bi\text{–}Te}} = 0.1$ mm and $t_{\mathrm{Cu}} = 0.3$ mm have extremely great values of 8.81 and 5.99 at 298 K, respectively, but they decreased rapidly with an increase of $t_{\mathrm{Bi\text{-}Te}}$ or t_{Cu}. These maximum ZT are much greater than 2.4 obtained by Venkatasubramanian et al. for the superlattice structured thin film of Bi_2Te_3/Sb_2Te_3 [8]. The resultant ZT is thus found to be enhanced extremely even in macroscopic composites. When a composite was composed of an optimum combination of $t_{\mathrm{Bi\text{-}Te}}$ and t_{Cu}, moreover, the resultant ZT of Cu/Bi–Te/Cu composites would probably exceed 10 at room temperature. Such enhancement in ZT would be attributed to the fact that non-equilibrium system carriers in the interior of the bismuth–telluride compound near the interface were separated strongly by a sharper temperature drop, resulting in the enhancement of the barrier thermo-emf [11]. However, the present combination of $t_{\mathrm{Bi\text{-}Te}}(=0.1$ mm) and $t_{\mathrm{Cu}}(=0.3$ mm) does not necessarily yield the maximum ΔW, as mentioned earlier. This is because the increase in ZT is owing to the great resultant α produced by the small ΔT, while the increase in ΔW is attributed to the great thermo-emf ΔV produced by the large ΔT.

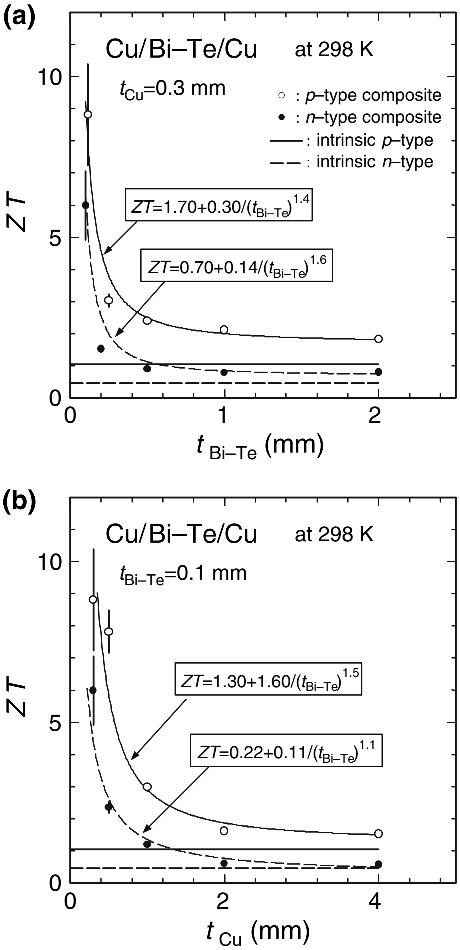

Fig. 12 (**a**) Resultant ZT as a function of $t_{\mathrm{Bi\text{–}Te}}$ for the p- and n-type Cu/Bi–Te/Cu composites with $t_{\mathrm{Cu}} = 0.3$ mm and (**b**) resultant ZT as a function of t_{Cu} for the p- and n-type Cu/Bi–Te/Cu composites with $t_{\mathrm{Bi\text{–}Te}} = 0.1$ mm

Summary and conclusion

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 t, where t is the lapse time after imposing the voltage. Here the temperature difference ΔT was produced by imposing a constant voltage of 1.70 V on two Peltier modules connected in series. Two probes were placed on two coppers of a composite so that the interval s between them satisfies the relation $s = t_T + 0.35$ mm. The experimental values of ΔV decrease abruptly with an increase of t below $t = 5$ min, while above $t = 7$ min, they tend to saturate to each constant value. This t-dependence of ΔV is dependent on that of ΔT. The thermo-emf ΔV saturated at $t = 11$ min tends to increase with an increase of t_{Cu} or $t_{\text{Bi–Te}}$. When a composite has a combination of $t_{\text{Bi–Te}} = 0.1$ mm and $t_{\text{Cu}} = 1.0$ mm, the generating power ΔW estimated using the saturated ΔV and calculated R for the p- and n-type composites reached great values of 16.0 and 8.0 mW, respectively, which are 4.1 and 5.3 times larger than 3.9 and 1.5 mW obtained for the p- and n-type composites composed of the conventional combination of $t_{\text{Bi–Te}} = 2.0$ mm and $t_{\text{Cu}} = 0.3$ mm Judging from the thickness (=0.1 mm) of Bi–Te compounds, it is found that the barrier thermo-emf may be generated in the Bi–Te region less than 50 μm from the surface of Bi–Te compounds. It is surprising that the generating power ΔW is enhanced by sandwiching a very thin Bi–Te material between two thick coppers, unlike the conventional composition of thermoelectric modules.

On the other hand, when the composites are composed of a combination of $t_{\text{Bi–Te}} = 0.1$ mm and $t_{\text{Cu}} = 0.3$ mm, the resultant Seebeck coefficients α of the p- and n-type Cu/Bi–Te/Cu composites exhibited great values of 711 and –755 μV/K, respectively. Subsequently, the resultant α was measured as a function of distance r from the boundary. As a result, the Seebeck coefficients $|\alpha|$ of composites exhibit a maximum value of approximately 600 μV/K at $r = 0.125$ mm and decrease abruptly with an increase of r below $r = 0.25$ mm and slowly with further increase of r to approach the intrinsic α values of Bi–Te compounds. This significant enhancement in α at the small r supports the above result that the barrier thermo-emf is generated in the shallow region from the surface of Bi–Te compounds. The resultant ZT of the p- and n-type Cu/Bi-Te/Cu composed of a combination of $t_{\text{Bi–Te}} = 0.1$ mm and $t_{\text{Cu}} = 0.3$ mm exhibit extremely great values of 8.81 and 5.99 at 298 K, but they decreased hyperbolically rapidly with an increase of $t_{\text{Bi–Te}}$ or t_{Cu}. Such an extreme enhancement in ZT is owing to the generation of the large barrier thermo-emf which results from a great boundary Seebeck coefficient exceeding 700 μV/K in absolute value. The present high-performance composite, however, is available for a generator, not for a Peltier module.

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