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Enhancement of the thermoelectric figure of merit in *p*- and *n*-type Cu/Bi-Te/Cu composites

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The resultant thermoelectric properties of welded Cu/Bi-Te/Cu composites were measured at 298 K as a function of relative thickness *x* of Bi-Te compound by changing the interval *s* between two thermocouples and compared with those calculated as a function of *x* by treating it as an electrical and thermal circuit. These composites were prepared by welding with eutectic solder of Pb-Sn, after one end surface of the as-grown *p*- and *n*-type Bi-Te ingots were plated with Ni. It was found that the observed *ZT* of composites has a local maximum at an optimum *x* even when *s* was changed, as in the case of Cu/Bi-Sb/Cu and Ni/Bi-Sb/Ni composites with various relative thicknesses. Appearance of a local maximum in *ZT* is owing to the barrier thermo-emf generated by a sharp temperature drop at the interface between Bi-Te compound and copper. It may be caused by the separation of non-equilibrium carriers at the interface between them. The observed maximum *ZT* values at 298 K of the *p*- and *n*-type composites reached surprisingly great values of 1.53 and 1.66 at $x = 0.98$, which correspond to about twice as large as those of commercially utilized Bi-Te compounds. This enhancement of *ZT* is available for generators, but may be not utilizable as a Peltier module. The composite materials were thus found to be utilizable as useful means of further increase in *ZT* of macroscopic bulk materials. © *2006 Springer Science + Business Media, Inc.*

1. 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 value. 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 effects of the quantum confinement of carriers. Indeed, the dramatic increase in *ZT* has been observed in Si/Ge [8] and Bi_2Te_3/Sb_2Te_3 [9]. superlattice devices, and it was owing to the significant reduction in κ.

Recently, Bergman and Levy [10] proved by using the model based on the classical continuum linear transport theory 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. However, it was demonstrated theoretically [11] and experimentally [12] that when there are a potential barrier and a sharp temperature drop at the interface between a metal and a thermoelectric semiconductor, the barrier thermo-emf appears as a result of the separation of non-equilibrium carriers at the interface, resulting in the increase in α near the interface between them. The mechanism for the generation of the barrier thermo-emf, however, has not yet been established definitively. Most recently, the significant increase in α was indeed 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 [13]. The resultant α of these composites was -110 μV/K at a relative thickness of about 0.7 for Bi-Sb alloy, which is 29% higher in absolute value than -85 μV/K of Bi-Sb alloy. The enhanced *ZT* of M/T/M composites was a low value of 0.44 at 298 K, but the degree of increase in *ZT* reached a large value of 69%. Such a large increase in *ZT* of macroscopic composites

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was attributed to a significant enhancement in α. Similar phenomenon of increase in α was also observed even in the *n*-type Cu/Bi/Cu composite in which the maximum α appears at a relative thickness of about 0.8 for pure Bi and is 21% higher in absolute value than $-70\ \mu$V/K of Bi [14]. However, no enhancement in α occurred in the *p*-and *n*-type Ag/Bi-Te/Ag composites welded with pure Bi [15]. This is because Bi-Te compound and pure Bi of Ag/Bi-Te/Ag composites were melted slightly into each other at the interface during welding so that the definite interface fitted to produce a sharp temperature drop cannot be formed at the boundary. It indicates that it is important to select the welding material not to melt into Bi-Te compounds. When the high-performance Bi-Te compounds were welded well with the optimum welding material, *ZT* of composite materials is expected to be enhanced significantly. If it was realized, the composite materials with a sandwich structure would be considered as useful means of further increase in *ZT* of bulk thermoelectrics.

For this reason, the *p*- and *n*-type high-performance Bi-Te compounds and pure copper were employed to prepare the *p*- and *n*-type Cu/Bi-Te/Cu composites welded with eutectic solder of Pb-Sn, instead of pure Bi. One end surface of Bi-Te compounds was then plated with Ni before welding. Since it is difficult technically to prepare many composites with various thicknesses, the ratio of the thickness of thermoelectric Bi-Te compounds to the total length of composites was controlled by changing the interval between two thermocouples. The resultant thermoelectric properties of Cu/Bi-Te/Cu composites were calculated as a function of relative thickness of a thermoelectric material sandwiched between two pure metals by treating it as an electrical and thermal circuit, and were compared with the experimental values.

The purpose of this paper is to investigate to what degree the resultant *ZT* of Cu/Bi-Te/Cu composites welded with eutectic solder is enhanced at an optimum relative thickness of a Bi-Te compound sandwiched between two coppers, as compared with *ZT* of high-performance Bi-Te compounds used here.

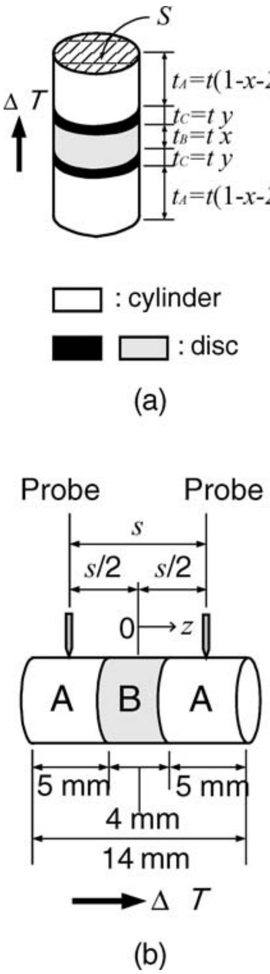

Figure 1 (a) Composite thermoelectric device (CTD) with a sandwich structure (A/C/B/C/A) in which a disc of the thermoelectric material B is sandwiched directly between two thin discs of material C and further it is sandwiched between two cylinders of material A, and (b) a schematic diagram for the Seebeck coefficient and electrical resistivity measurements, where two thin discs of material C are omitted for simplicity.

2. Calculation and experiments

2.1. Calculations of the resultant ρ, α, κ and *ZT* of a composite material

Let us consider a composite thermoelectric device (CTD) with a sandwich structure (A/C/B/C/A) in which a disc of the thermoelectric material B is sandwiched directly between two discs of material C and further it is sandwiched between two cylinders of material A, as shown in Fig. 1a. Here, we calculate the resultants ρ, κ, α and *ZT* for CTD by treating it as an electrical and thermal circuit, in which the direction of the temperature gradient is along the cylindrical axis. The materials A, B and C have the same cross-sectional area *S* and three different thicknesses t_A, t_B and t_C, respectively, where the thin disc C is dealt and regarded as the interface between two materials A and B. It was assumed here that the scattering of carriers and phonons never occurs at the boundary between two materials A and B. When α, κ and ρ of three materials A, B and C are denoted by α_A, α_B and α_C, κ_A, κ_B and κ_C and ρ_A, ρ_B and ρ_C, respectively, the total electrical resistivity ρ of CTD is expressed as

$$\rho = \frac{1}{t}(2\rho_A t_A + \rho_B t_B + 2\rho_C t_C). \qquad (1)$$

Here if we suppose $t_A = t(1-x-2y)/2$, $t_B = tx$ and $t_C = ty$, where t is the total thickness and x and y are the ratios of t_B of a disc material B and t_C of a disc material C to the total thickness t, respectively, Equation 1 can be rewritten as

$$\rho = \rho_B\{x + b_1(1-x-2y) + 2b_2 y\}, \qquad (2)$$

where $b_1 = \rho_A/\rho_B$ and $b_2 = \rho_C/\rho_B$. Similarly, the total thermal conductivity κ of CTD is expressed as

$$\begin{aligned}\frac{1}{\kappa} &= \frac{(1-x-2y)}{\kappa_A} + \frac{x}{\kappa_B} + \frac{2y}{\kappa_C} \\ &= \frac{1}{\kappa_B}\left\{x + \frac{(1-x-2y)}{c_1} + \frac{2y}{c_2}\right\}, \end{aligned} \tag{3}$$

where $c_1 = \kappa_A/\kappa_B$ and $c_2 = \kappa_C/\kappa_B$. For a given temperature difference ΔT, the temperature difference generated in each thermoelectric should be proportional to thickness but inversely proportional to thermal conductivity, at least for a thin CTD. Taking this into account, the ratios of ΔT_A and ΔT_C to ΔT_B are expressed as

$$\frac{\Delta T_A}{\Delta T_B} = \frac{t_A \kappa_B}{t_B \kappa_A} = \frac{(1-x-2y)}{2c_1 x} \tag{4}$$

and

$$\frac{\Delta T_C}{\Delta T_B} = \frac{t_C \kappa_B}{t_B \kappa_C} = \frac{y}{c_2 x}. \tag{5}$$

The total temperature difference ΔT between both ends of CTD is given by

$$\Delta T = 2\Delta T_A + \Delta T_B + 2\Delta T_C. \tag{6}$$

By substituting Equations. 4 and 5 into Equation 6, the ratios of thermal difference ΔT_B and ΔT_C generated in sandwiched materials B and C to the total thermal difference ΔT are expressed as

$$\frac{\Delta T_B}{\Delta T} = \frac{c_1 c_2 x}{c_2(1-x-2y) + 2c_1 y + c_1 c_2 x} \tag{7}$$

and

$$\frac{\Delta T_C}{\Delta T} = \frac{c_1 y}{c_2(1-x-2y) + 2c_1 y + c_1 c_2 x}, \tag{8}$$

respectively. The total thermal voltage ΔV generated by ΔT_A, ΔT_B and ΔT_C is written as

$$\Delta V = 2\Delta T_A \alpha_A + \Delta T_B \alpha_B + 2\Delta T_C \alpha_C. \tag{9}$$

Therefore, the overall Seebeck coefficient α is expressed as

$$\alpha = \frac{\Delta V}{\Delta T} = \alpha_B \frac{a_1 c_2(1-x-2y) + 2a_2 c_1 y + c_1 c_2 x}{c_2(1-x-2y) + 2c_1 y + c_1 c_2 x} \tag{10}$$

using Equations 4–9, where $a_1 = \alpha_A/\alpha_B$ and $a_2 = \alpha_C/\alpha_B$. When the composite materials satisfy two conditions of $c_1 \gg 1$ and $y \ll 1$, the thermoelectric figure of merit $Z_{\mathrm{comp}}T$ of CTD is expressed rather exactly as a function of x as

$$Z_{\mathrm{comp}}T = \frac{Z_B T\{a_1 c_2(1-x-2y) + 2a_2 c_1 y + c_1 c_2 x\}^2}{c_1 c_2\{c_2(1-x-2y) + 2c_1 y + c_1 c_2 x\}\{x + b_1(1-x-2y) + 2b_2 y\}}. \tag{11}$$

Of course, $Z_{\mathrm{comp}}T$ is also derived by substituting Equations 2, 3 and 10 into the relation $Z = \alpha^2/\rho\kappa$, but it is nothing but approximation, because Equation 11 is derived theoretically only when $c_1 \gg 1$ and $y \ll 1$. These conditions for c_1 and y hold just for the present composites. As proved by Bergman and Levy [10], Z_{comp} has no local maximum at a relative thickness of a thermoelement, as long as the resultant α is not enhanced. Simple formula (11) is rather approximate for a thick CTD, because it holds exactly for a thin CTD alone, in which the thermal loss from the side of CTD is negligibly small.

Next, we consider the method to estimate the magnitude of the Seebeck coefficient of the material C regarded as the interface between two materials A and B. When one probe is placed on Bi-Te compound and another on copper, i.e., $|z| > (s - t_B)/2$, the temperature difference $\Delta T(z)$ between two probes is expressed as functions of s and z as

$$\Delta T(z) = \frac{(s + t_B - 2z)\Delta T_B}{2t_B} + \frac{(s - t_B + 2z)\Delta T_A}{2t_A} + \Delta T_C, \tag{12}$$

where s is the interval between two probes and z is the distance from the center of Bi-Te compound to the middle between two thermocouples, as shown in Fig. 1b. For $c_1 \gg c_2$ and $x > 0.3$, Equation 10 and 12 can be approximated as

$$\alpha = \frac{\alpha_B(2a_2 y + c_2 x)}{(2y + c_2 x)} \tag{13}$$

and

$$\frac{\Delta T(z)}{\Delta T(0)} = \frac{1}{(2y + c_2 x)}\left(\frac{(s + t_B - 2z)c_2 x}{2t_B} + y\right), \tag{14}$$

respectively, where $\Delta T(0)$ is the total temperature difference ΔT at $z = 0$. As will be shown schematically later, the approximation of Equation 13 is supported by the fact that α calculated using Equation 10 remains constant above $x = 0.3$ when the condition of $c_1 \gg c_2$ is satisfied. The gradient m of $\Delta T(z)/\Delta T(0)$ for the z axis is given by

$$|m| = \frac{c_2}{(2t_c + c_2 t_B)}, \tag{15}$$

using the relation $y = x t_C/t_B$, where m is positive for $z < 0$ and is negative for $z > 0$. Substituting $y = x t_C/t_B$ into

Equation 13, the resultant α at $z = 0$ is rewritten as

$$\alpha = \frac{\alpha_B(2a_2t_C + c_2t_B)}{(2t_C + c_2t_B)} \tag{16}$$

It should be noted here that Equations 15 and 16 hold more exactly as x increases. Since t_B is known, the value of t_C/c_2 is obtained from Equation 15 using the measured m. In addition, a_2 is calculated from Equation 16 using this value of t_C/c_2, because α and α_B are known experimentally. In other words, it means that the Seebeck coefficient of the boundary (corresponding to a thin disc material C) is obtained experimentally even when the experimental values of ρ_C, κ_C and t_C are unknown.

2.2. Sample preparations and measurements

The p-type $(Bi_{0.25}Sb_{0.75})_2Te_3$ doped with 12 wt% excess Te alone and n-type $Bi_2(Te_{0.94}Se_{0.06})_3$ codoped with 0.010 wt% CuBr, 0.102 wt% I and 0.026 wt% Te were prepared by the Bridgman method, using purer Bi granules of 99.999% and pure Sb, Te, Se, I and CuBr granules of 99.99% as starting materials [16, 17]. 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 [16, 17] and is close to one of various growth conditions reported by Yim and Rosi [18]. Naturally, the resulting ingots consisted of relatively coarse grains with the cleavage planes aligned partially parallel to the freezing direction.

These as-grown p- and n-type Bi-Te ingots were employed to prepare the p-and n-type Cu/Bi-Te/Cu composites welded with eutectic solder of Pb-Sn. The as-grown Bi-Te ingots were cut into a length of 4 mm after grinding into a cylinder of φ5 mm, where the cylindrical axis is parallel to the freezing direction. Cylindrical copper was prepared by cutting a copper rod with a diameter 5 mm into a length of 5 mm, where the purity of copper was 99.99%. Eutectic solder was melted into a thin disc of φ 5 × t mm, where t is smaller than 0.3 mm. The diameter of these cylinders and thin discs was made slightly smaller than 5 mm, to make it easy to put into a glass tube of an inner diameter φ 5 mm. Both end surfaces of cylindrical Bi-Te compounds and coppers were polished mechanically by the lapping method to make flat the welded surface. After one end of Bi-Te compounds was plated with Ni so that it has a thickness of several μm, a set of cylindrical coppers, eutectic solders and Bi-Te compound was put into a glass tube of an inner diameter φ 5 mm so that eutectic solders are sandwiched between copper and Bi-Te compounds and touched directly with the surface plated with Ni of Bi-Te compounds. Since eutectic solder has the lowest melting point of 456 K among them, eutectic solder is first melted in a glass tube by an electric heater. While eutectic solder is melted, coppers were welded by compacting two cylindrical coppers of both ends at a constant force of 2 N using two nickel rods, as shown in Fig. 2. After a welded cylinder was naturally cooled to room temperature, it was ejected from a glass tube using a nickel rod. In order to investigate whether the composite materials are welded tightly, they were polished along the cylindrical axis of a welded device, so that no crack and no exfoliation were detected at the boundaries of all devices, as shown in Fig. 3. The thickness of solder was nearly equal to or less than 10 μm.

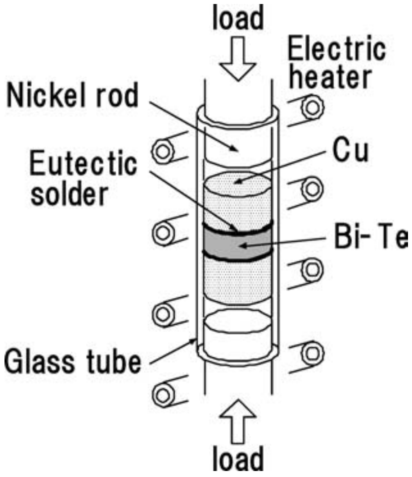

Figure 2 Fabrication method of Cu/Bi-Te/Cu composites welded with eutectic solder of Pb-Sn.

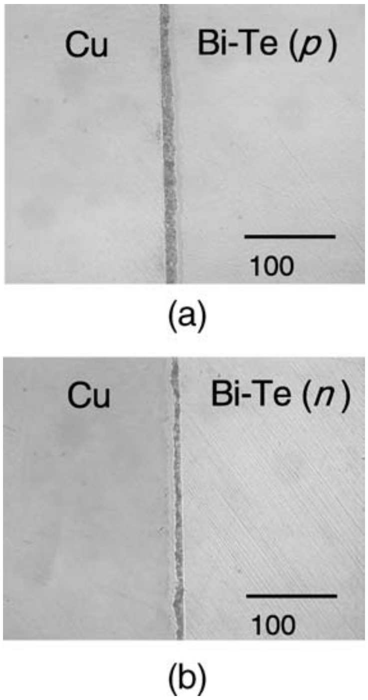

Figure 3 Photographs of boundaries of the p-type (a) and n-type (b) Cu/Bi-Te/Cu composites welded with eutectic solder of Pb-Sn.

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 $10 \times 10 \times 3$ mm^3 were cut from the central part of ingots, where the length of 15 mm and thickness of 3 mm were cut parallel 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. 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. ρ was measured concurrently by the four-probe method. α, ρ and κ were measured at 298 K within an accuracy of 1, 2 and 2%, respectively. The resultant accuracy was about 6% as a thermoelectric figure of merit.

The thermoelectric properties of the composites were measured using an apparatus fabricated by us. Fig. 4 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. The measurement of α was made by producing the temperature difference between both ends of a composite along the freezing direction of Bi-Te ingot. α of composites was measured as a function of z at a scan step of 0.5 mm using thermocouples set at five different intervals of $s = 10.8$, 7.9, 5.8, 4.4 and 4.1 mm, where s is the interval between two probes and z is the distance from the center of Bi-Te compound to the middle between two thermocouples, as shown in Fig. 1b. ρ was measured at 298 K by the four-probe method.

The thermal conductivity of composites was measured as follows. Heat is supplied at one end of a composite of cross-sectional area S at a known rate H and is removed at the other end. Thermocouples are attached at two places along the composite separated by a distance s, and the temperature difference ΔT between them was measured. The thermal conductivity κ was then derived from the relation $\kappa = sH/S\Delta T$, where ΔT was 5–8 K. κ of Bi-Te compounds measured by this method agreed closely with those obtained by the conventional technique.

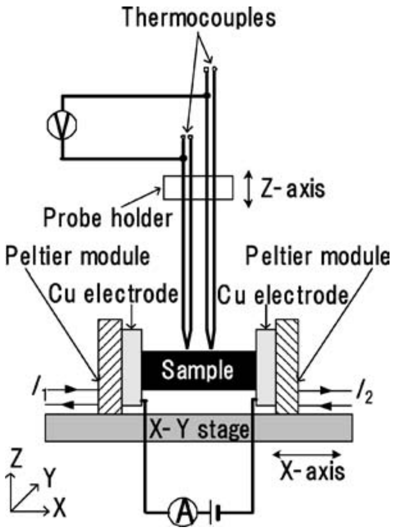

Figure 4 Schematic configuration for measurements of the Seebeck coefficient α and electrical resistivity ρ. One end was heated by flowing the electrical current I_1 or I_2 through a Peltier module to produce the temperature differences and another one was then maintained at room temperature.

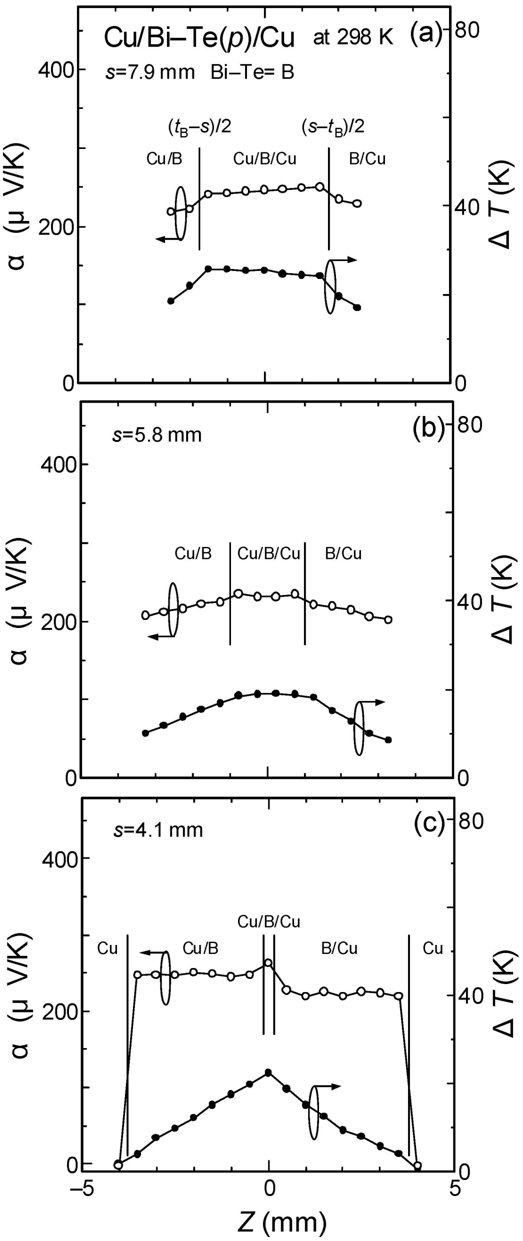

Figure 5 Resultant α and temperature difference ΔT measured as a function of x for the p-type Cu/Bi-Te/Cu composites using thermocouples set at three different intervals of $s = 7.9$ mm (a), 5.8 mm (b) and 4.1 mm (c).

3. Results and discussion

3.1. Dependence of the resultant α of composites on the probe position z and probe interval s

The resultants α and ρ of Cu/Bi-Te/Cu were plotted as a function of z in Figs 5 and 6. It is found from Fig. 1b that when $|z|<(s-t_B)/2$, two probes are placed on two coppers, while when $|z|>(s-t_B)/2$, one probe is placed on Bi-Te compound and another on copper. The measured α exhibits greater values in the region of $|z|<(s-t_B)/2$ than $|z|>(s-t_B)/2$ and has a plateau in the region of $|z|<(s-t_B)/2$. α values of a plateau tend to decrease with an increase of s and was found to vary even with changes in s. α exhibits a tendency to decrease abruptly when $|z|$ exceeded a value of $(s-t_B)/2$. In any case, the z-dependence of α is almost symmetrical with respect to the origin ($z=0$ mm), irrespective of the type of conduction. On the other hand, ρ remained constant in the region of $|z|<(s-t_B)/2$, while when $|z|>(s-t_B)/2$, ρ decreased linearly with an increase of $|z|$. The z-dependence of ρ has a tendency similar to that of α.

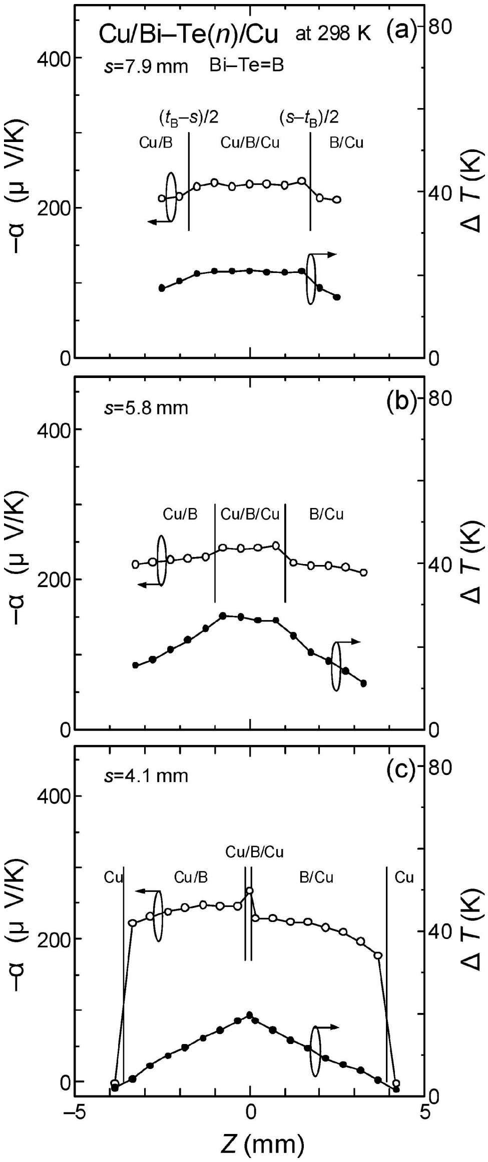

Figure 6 Resultant α and temperature difference ΔT measured as a function of x for the n-type Cu/Bi-Te/Cu composites using thermocouples set at three different intervals of $s=7.9$ mm (a), 5.8 mm (b) and 4.1 mm (c).

3.2. Dependence of the resultant ρ, α and κ on the relative thickness x of Bi-Te compounds

The resultants α, ρ and κ of Cu/Bi-Te/Cu were plotted as a function of x in Fig. 7, where x is the ratio of $t_B(=4$ mm) to the interval s between two probes and α is the averaged value of a plateau at each x.

As shown in Fig. 7a, the observed α of Cu/Bi-Te/Cu tends to increase in absolute value with an increase of x in the region from $x=0.37$ to 0.98 and drops abruptly $x=1.0$. The resultant $|\alpha|$ tends to take a larger value at rather large x, as in the case of Cu/Bi/Cu and Cu/Bi-Sb/Cu. The maximum α values of the p- and n-type composites reached great value of 263 and $=266$ μV/K at $x=0.98$, respectively, which are approximately 32 and 30% higher in absolute value than 202 and -205 μV/K of the intrinsic Bi-Te compounds listed in Table I. These degrees of enhancement in α are more than those (29 and 21%) of the previous n-type Cu/Bi-Sb/Cu [13] and Cu/Bi/Cu [14] composites, and such phenomena of enhancement in α have been observed in the n-type composite materials alone. The reason that α of the present composites was significantly enhanced is that the definite interface was formed at the boundary, as shown in Fig. 3, because no enhancement in α occurred in the previous Ag/Bi-Te/Ag composites welded with Bi in which Bi-Te compound and Bi were melted slightly into each other at the interface during welding, resulting in the formation of the indistinct boundary [15]. In any case, the significant enhancement in α was first realized in both the p- and n-type composite materials and these maximum α values are much higher in absolute value than those of the previous composite materials.

As shown in Fig. 7b, the observed ρ values of the p- and n-type composites increase linearly with an increase

TABLE I Thermoelectric properties measured at 298 K for pure Cu and the p-and n-type Bi-Te compounds

		Cu	Bismuth-telluride	
			p-type	n-type
Electrical resistivity	ρ (μΩm)	0.0171	8.70	7.02
Seebeck coefficient	α (μV/K)	+1.9	202	−205
Thermal conductivity	κ (W/mK)	401[a]	1.64	1.78
Power factor	P (mW/K^{2}m)	0.21	4.60	5.99
Figure of merit	ZT	1.57×10^{-4}	0.85	1.00

[a] Ref. 19.

of x and fall closely on the calculated curves $\rho(x)$ which were obtained from Equation 2 using both $y = 0$ and the experimental values listed in Table I. It indicates that the thin disc material C has little influence on ρ and the carrier scattering hardly occurs at the boundary between Bi-Te compound and copper.

As shown in Fig. 7c, the observed κ values above $x = 0.9$ fall closely on the curves calculated from Equation 3 using both $y = 0$ and the experimental values listed in Table I, while below $x = 0.7$, the experimental values are a little lower than the calculated ones. This disagreement may be considered as follows; since Cu has a thermal conductivity much higher than Bi-Te compounds, a composite with relatively long Cu cylinders (corresponding to small x) suffers some thermal losses through metallic cylinders, so that the temperature difference ΔT is a little increased, resulting in some reduction in the resultant κ.

Here, we try to estimate roughly the magnitude of the boundary Seebeck coefficient to enhance the resultant α of composites. Fig. 8 shows γ $(= \Delta T(z)/\Delta T(0))$ measured with $s = 4.1$ mm as a function of z for the p- and n-type composites, where the experimental ΔT values are plotted as a function of z in Figs 5c and 6c. The solid and dashed straight lines are drawn by the least square fitting to the experimental values. The experimental values of γ fall roughly on their lines, so that the z-dependences of γ are expressed in terms of Equation 14. However, γ of the n-type composite shows a slight deviation from the symmetry with respect to the origin, although the reason is not clear. The value of t_C/c_2 obtained from Equation 15 using both $t_B = 4$ mm and the averaged m is 0.164 mm for the p-type composite and 0.242 mm for the n-type one. From these results, t_C/t_Bc_2 values of the p- and n-type composites are estimated as 0.041 and 0.061, respectively. As evident from the fact that the resultant Seebeck coefficients of both p- and n-type composites are enhanced, the barrier thermo-emf generated at both interfaces is considered to occur in the forward-bias direction (with a plus sign in the p-type specimen and a minus sign in the n-type one). The boundary Seebeck coefficients α_b may result from this barrier thermo-emf. The place producing an extremely large α_b is thus expected to be within the Bi-Te compound adjacent to plated Ni. Therefore, it would be possible to assume $c_2 \approx 1$. If so, the thickness of interface layers giving the large α_b is guessed to be 4–6% of those of bulk Bi-Te compounds at most. By substituting the relation $t_C/t_Bc_2 = 0.061$ or 0.041 into Equation 16 and using the intrinsic α_B and the resultant α at $x = 0.98$, $a_2(= \alpha_C/\alpha_B)$ values of the p- and n-type composites are

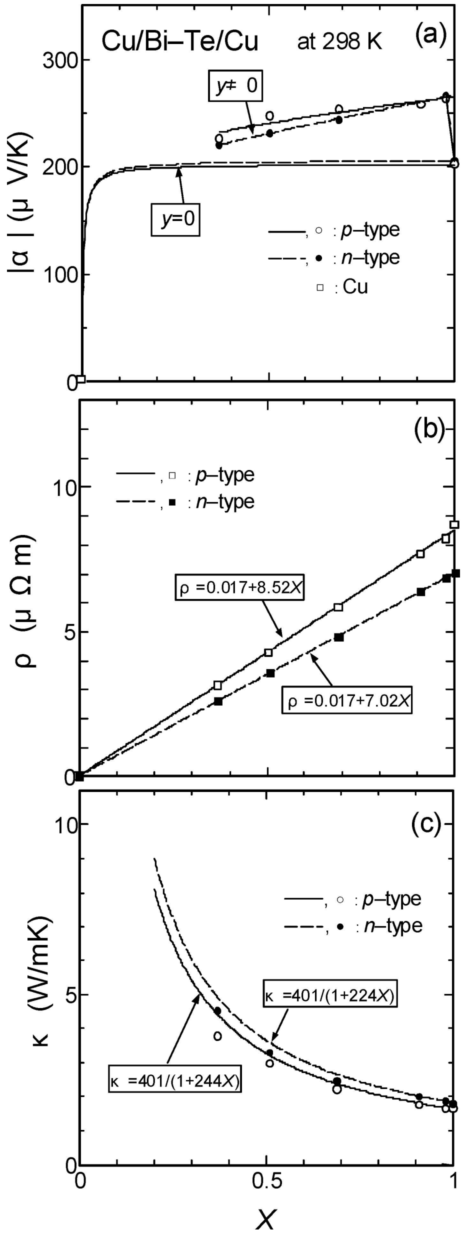

Figure 7 Resultants α(a), ρ(b) and κ(c) measured as a function of relative thickness x of Bi-Te compound for Cu/Bi-Te/Cu composites. The solid and dashed curves indicate the calculated values using both $y = 0$ and the experimental values (listed in Table I) for the p-and n-type composites, respectively. The solid and dashed curves (denoted by $y \neq 0$ in (a)) are drawn by the least square fitting to the experimental α of the p- and n-type composites, respectively.

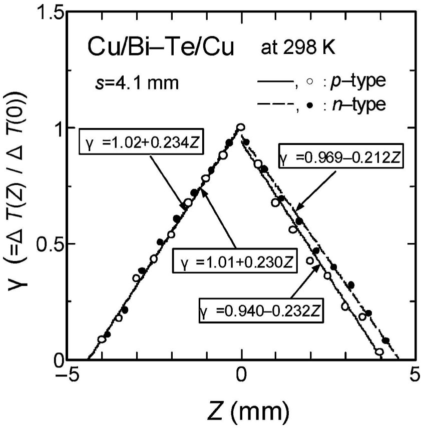

Figure 8 $\gamma(= \Delta T(z)/\Delta T(0))$ measured at a probe interval of $s = 4.1$ mm as a function of z for the p- and n-type composites. The solid and dashed lines indicate straight lines fitted by the least square method to the experimental values of the p- and n-type Cu/Bi-Te/Cu composites, respectively.

estimated as 5.14 and 3.76 at $x = 0.98$, respectively. It indicates that the boundary Seebeck coefficient $\alpha_b (= \alpha_C)$ reaches a surprisingly great value of 800–1000 μV/K in absolute value. The x-dependence of α of the p- and n-type composites can be calculated from Equation 16 using $t_C/t_B c_2 = 0.041$ and $a_2 = 5.14\, x^{0.55}$ for the p-type composite and $t_C/t_B c_2 = 0.061$ and $a_2 = 3.76\, x^{0.80}$ for the n-type one, as well as the intrinsic α_B, where the x-dependence of a_2 was obtained by the least square fitting to the experimental α. The calculation results (denoted by $y \neq 0$) are indicated by the solid and dashed curves for the p- and n-type composites, respectively, as shown in Fig. 7a. The calculated values agree well with the observed ones. The degree of enhancement in α was found to vary significantly with changes in s, although the total length remains constant.

Next, we consider why such a significant enhancement in α occurs in macroscopic Cu/Bi-Te/Cu composites. It was demonstrated theoretically by Dashevsky *et al.* [11] and experimentally by Balmush *et al.* [12] that when there are a potential barrier and a sharp temperature drop at the interface between a metal and a thermoelectric semiconductor, the barrier thermo-emf appears as a result of the separation of non-equilibrium carriers at the interface, resulting in the increase in α near the interface between them. When a Bi-Te compound and a metal were welded with eutectic solder, a metal-semiconductor junction is formed at the interface between Bi-Te compound and plated Ni. When there is a large temperature difference between both ends of the composite, a sharp temperature drop is generated at the interface between Bi-Te compound and copper, due to a significant difference between their thermal conductivities. As well-known, however, no enhancement in α occurs in the commercially utilized Bi-Te modules in which metal electrodes are too thin to behave as a heat sink. Since two cylindrical coppers of both ends of the present composites have a thickness (5 mm) enough to act as a heat sink, however, the phenomenon of enhancement in α may appear definitely. Indeed, this heat sink effect should play a role enhancing a temperature drop at the interface, resulting in an increase in the barrier thermo-emf. In the future, it is thus desired strongly to clarify the mechanism for enhancement in α of the macroscopic composite materials, since it is very useful as means of further increase in ZT of macroscopic bulk materials.

3.3. Dependence of the resultant *ZT* on the relative thickness *x* of Bi-Te compounds

ZT values were calculated from the relation $ZT = T\alpha^2/\rho\kappa$ using the experimental ρ, α and κ. They were plotted as a function of x in Fig. 9. The solid and dashed curves (denoted by $y = 0$) indicate ZT values calculated from Equation 11 as a function of x using both $y = 0$ and the intrinsic experimental values listed in Table I. The observed ZT values of both type composites tend to become larger than the calculated ones with an increase of x, have a local maximum at $x = 0.98$ and drop abruptly at $x = 1$. This disagreement between the observed and calculated ZT is attributed to a significant enhancement in α, as mentioned earlier. The x-dependences of ZT were also calculated as $a_1 = 0$ and $b_2 = c_2 = 1$ from Equation 11 using $t_C/t_B c_2 = 0.041$ and $a_2 = 5.14x^{0.55}$ for the p-type composite and $t_C/t_B c_2 = 0.061$ and $a_2 = 3.76x^{0.80}$ for the n-type one, as well as the intrinsic values listed in Table I. However, the calculated ZT values (denoted by $y \neq 0$) coincided with the observed ones above $x = 0.9$, while below $x = 0.7$, they were somewhat lower than the observed ones, as shown in Fig. 9. The disagreement below $x = 0.7$ results from the fact that the observed κ was somewhat lower than the calculated one, as mentioned earlier. The maximum ZT values measured at 298 K for the p- and n-type Cu/Bi-Te/Cu reached surprisingly great values of 1.53 and 1.66, respectively, which are 80 and 66% higher than those of the as-grown Bi-Te compounds. The enhancement in ZT is thus owing to an increase in α. The degree of enhancement in ZT is nearly equal to or more than 69% of M/T/M (M = Cu or Ni and T = $Bi_{0.88}Sb_{0.12}$) composites welded with Bi-Sb alloy [13]. Probably, such an increase in ZT of macroscopic welded composites would be owing to the appearance of the barrier thermo-emf, that is, the boundary Seebeck coefficient. When a thermoelectric material with a higher ZT was welded with metals possessing a low ρ and a high κ, a sharper temperature drop would occur at the interface, so that the resultant ZT of composites is enhanced significantly. Since the present measuring method of ZT is the same fundamentally as that of the efficiency of generators, the enhancement in ZT leads directly to a significant improvement in the conversion efficiency for generators, but it may have little effect on a Peltier module.

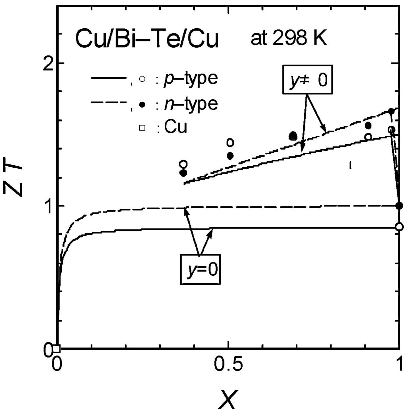

Figure 9 Resultant ZT estimated as a function of relative thickness x of Bi-Te compound for Cu/Bi-Te/Cu composites. The solid and dashed curves (denoted by $y = 0$) indicate the ZT values calculated using both $y = 0$ and the experimental values (listed in Table I) for the p-and n-type composite materials, respectively. The solid and dashed curves (denoted by $y \neq 0$) are drawn by taking some increase in α for the p- and n-type composites into the calculation of ZT.

4. Summary and conclusion

The thermoelectric properties of the *p*- and *n*-type Cu/Bi-Te/Cu composites were measured at 298 K as a function of relative thickness x of Bi-Te compound by changing the interval between two probes and were compared with those calculated as a function of x by treating it as an electrical and thermal circuit. The observed ρ values increase linearly with an increase of x, and their α values also increase with increasing x in the range from $x = 0.37$ to 0.98 and drop abruptly at $x = 1$. The observed ρ values fall on the straight lines calculated using both $y = 0$ and the experimental values, but the observed α disagreed with the calculated ones, particularly at large x. This disagreement is attributed to an enhancement in α at the interface. By taking the enhancement effect of α at the interface into the calculation, however, the calculated α coincided well with the observed values. The observed *ZT* values agreed with the calculated ones above $x = 0.9$, while below $x = 0.7$, they were somewhat lower than the calculated ones. Such an enhancement in α is attributed to the contribution from the barrier thermo-emf appeared as a result of the separation of non-equilibrium carriers due to a sharp temperature drop at the interface. The resultant *ZT* of Cu/Bi-Te/Cu has a large local maximum at $x = 0.98$, owing to a significant increase in α. The maximum *ZT* values at 298 K of the *p*- and *n*-type Cu/Bi-Te/Cu reached surprisingly great values of 1.53 and 1.66, respectively, which are 80 and 66% higher than the *ZT* values of the as-grown Bi-Te compounds and correspond to about twice as large as those of commercially utilized Bi-Te compounds. This degree of enhancement in *ZT* is nearly equal to or more than 69% of M/T/M (M = Cu or Ni and T = $Bi_{0.88}Sb_{0.12}$) composites welded with Bi-Sb alloy. Since the present measuring method of *ZT* is fundamentally the same as that of the efficiency of generators, the enhanced *ZT* is available for generators, but it may be not utilizable as a Peltier module. When a thermoelectric material with a higher *ZT* was welded with a metal possessing a low ρ and a high κ, it would thus result in further improvement in the resultant *ZT* of macroscopic bulk materials.

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