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Temperature dependence of the local Seebeck coefficient near the boundary in touching Cu/Bi–Te/Cu composites

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Abstract The thermo-emf ΔV and temperature difference ΔT across the boundary were measured as functions of r and I for the touching p- and n-type Cu/Bi–Te/Cu composites composed of $t_{\mathrm{Bi-Te}} = 2.0$ mm and $t_{\mathrm{Cu}} = 0.3$ mm, where r is the distance from the boundary and I is a direct current producing ΔT which flows through two Peltier modules connected in series. The resultant Seebeck coefficient α across the boundary is obtained from the relation $\alpha = \Delta V/\Delta T$. As a result, the resultant $|\alpha|$ of the touching p- and n-type composites have a great local maximum value at $r \approx 0.03$ mm and decrease rapidly with further increase of r to approach the intrinsic $|\alpha_{\mathrm{Bi-Te}}|$. The maximum resultant α of the p- and n-type composites reached great values of 1,043 and –1,187 μV/K at 303 K corresponding to $I = 0.8$ A and of 1,477 and –725 μV/K at 360 K corresponding to $I = 2.0$ A. Reflecting the temperature dependence of the intrinsic $\alpha_{\mathrm{Bi-Te}}$, the maximum α of the p-type composite increases with an increase of T, while that of the n-type one decrease with an increase of T. Surprisingly, the maximum α of the p- and n-type composites have great gradients of 8.36 and –7.15 μV/K^2 in the range from 303 to 366 K, respectively, which are 21.8 and 134 times larger in absolute value than 0.383 and –0.0535 μV/K^2 of the intrinsic p- and n-type $\alpha_{\mathrm{Bi-Te}}$, so that the maximum resultant α was thus found to be much more sensitive to temperature than the intrinsic $\alpha_{\mathrm{Bi-Te}}$. Moreover, the local Seebeck coefficient α_l(r) derived analytically from the resultant $\alpha(r)$ is enhanced significantly in the narrow region below $r \approx 0.05$ mm and the maximum α_l values of the p- and n-type composites were found to have extremely great values of approximately 1,800 μV/K at 360 K and –1,400 μV/K at 303 K, respectively, which are approximately 7.3 and 6.5 times higher in absolute value than the intrinsic p- and n-type $\alpha_{\mathrm{Bi-Te}}$ at the corresponding temperatures.

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Introduction

The energy conversion efficiency of thermoelectric modules depends on thermoelectric materials properties through the thermoelectric figure of merit $ZT = T\alpha^2/\rho\kappa$, where α is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity and T the absolute temperature [1]. The increase in ZT leads directly to the improvement in the cooling efficiency of Peltier modules and in the electric generation efficiency of generators. Significant advances for increasing ZT have been made based on new ideas to engineer electron and phonon transport [2]. One particularly fruitful approach has been the employment of nanostructures, so that the electron performance can be improved or maintained concurrently with a significant reduction of phonon thermal conductivity [3–6]. Nanostructure-based materials have shown significant increases in ZT compared to their corresponding materials, owing to mainly reduced phonon thermal conductivity of these structures. Indeed, the superlattice structured thin film of Bi_2Te_3/Sb_2Te_3 reached an extremely high *ZT* of 2.4 [7]. Thus, most of the recent studies on the improvement in *ZT* have focused on the nanostructure-based materials.

However, surprisingly high *ZT* values of 1.53 and 1.66 were obtained even in macroscopic p- and n-type Cu/Bi–Te/Cu composites welded with an eutectic solder of Pb–Sn, when the Bi–Te compound was sandwiched between two coppers in which its cleavage planes are aligned partially parallel to the sandwiching direction. Their resultants *ZT* of the p- and n-type composites were then 80% and 66% higher than those of the intrinsic Bi–Te materials, respectively [8]. Such significant increase in *ZT* was attributed to the increase in the resultant α across the boundary, unlike the nanostructure system. 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 [9] 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 [10]. Most recently, similar phenomenon was also observed as an enhancement in the resultant α even in macroscopic thermoelectric composites corresponding to the metal-semiconductor junction, in which a thermoelectric semiconductor is sandwiched between two metals [8, 11]. For example, the resultant maximum α of welded p- and n-type Cu/Bi–Te/Cu composites were 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 [8]. Similarly, the resultant maximum α of the n-type Cu/Bi–Sb/Cu composite welded with $Bi_{0.88}Sb_{0.12}$ alloy was –110 μV/K, which is 29% higher in absolute value than –85 μV/K of Bi–Sb alloy [11]. Such increase in α was owing to the contribution from the additional barrier thermo-emf to the overall thermo-emf. The enhancement in α was also observed even in touching composites [12]. The composite materials with a sandwich structure may thus be considered as useful means of further improvement in *ZT* of macroscopic thermoelectrics. However, such enhancement in α and *ZT* of composites results in an improvement in the energy conversion efficiency for generators, but it may have little effect on the cooling efficiency, because the enhancement in α across the boundary is induced only by imposing the temperature gradient on the composites.

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 [10]. The barrier thermo-emf occurs in the forward-bias direction, at least in the present composites. It has already been clarified in our previous paper (O. Yamashita and H. Odahara submitted) that the resultant α across the boundary of the touching p- and n-type Cu/Bi–Te/Cu composites is enhanced significantly in the narrow region below $r \approx 0.06$ mm and has a great local maximum at $r \approx 0.03$ mm, where r is the distance from the boundary. However, it has not yet clarified whether the temperature dependence of the resultant α across the boundary and local Seebeck coefficient α_l near the boundary has something to do with that of the Seebeck coefficient of the intrinsic thermoelectric materials. For this reason, the resultant α and local Seebeck coefficient α_l of composites were measured as functions of r and T for the touching p- and n-type Cu/Bi–Te/Cu composites, where T is the absolute temperature. However, when the composite is prepared by welding a thermoelectric material with metal, in general, the definite interface is not formed at the boundary, due to the diffusion of constituent atoms at the interface during welding. The reason that the touching composite was employed in the present experiment is to avoid this diffusion and make clearer the effect of the boundary on the resultant α.

The purpose of this paper is to investigate how the resultant α across the boundary and local Seebeck coefficient α_l near the boundary of the touching p- and n-type Cu/Bi–Te/Cu composites vary with changes in temperature and to what extent they reflect the temperature dependence of the Seebeck coefficient of the intrinsic Bi–Te materials, where the local Seebeck coefficient α_l was calculated analytically from the experimental resultant α across the boundary.

Calculations and experiments

Calculation of the local Seebeck coefficient α_l from the resultant α

Let us consider a composite with a sandwich structure (M/T/M) in which a parallelepiped of the thermoelectric material T is sandwiched between two metallic plates M, as shown in Fig. 1. Here, we propose the method to derive analytically the local Seebeck coefficient $\alpha_l(r)$ from the resultant $\alpha(r)$ across the boundary for a composite, where $\alpha(r)$ is the experimental value measured by placing one probe on metal M and another on material T. When one probe is located on the edge of metal adjacent to the boundary and another is placed on material T so that the interval s between two probes just corresponds to the distance r from the boundary,

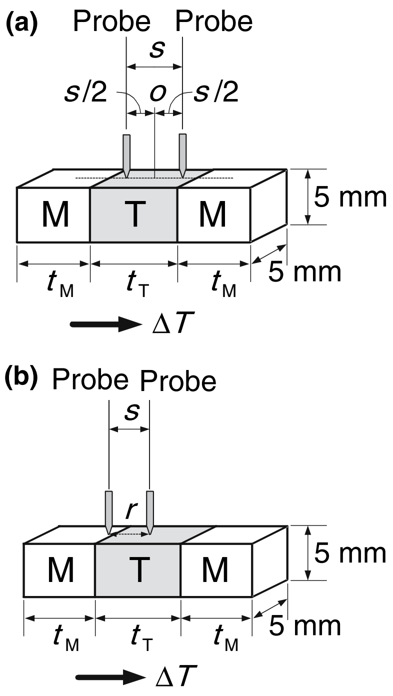

Fig. 1 Touching composite with a sandwich structure (M/T/M) in which a parallelepiped of thermo-electric material T is touched tightly with two metallic plates M at a constant force of 10 N, where t_T is the thickness of Bi–Te compounds, t_M is the thickness of metals and s is the interval between two probes in (**a**) and corresponds to the distance r from the boundary in (**b**)

the resultant $\alpha(r)$ is related to the local Seebeck coefficient $\alpha_l(r)$ by the following expression

$$\alpha(r) = \frac{\int_0^r \alpha_l(r)dr}{\int_0^r dr}. \tag{1}$$

Of course, Eq. 1 is rewritten as

$$\int_0^r \alpha_l(r)dr = r\alpha(r). \tag{2}$$

By differentiating Eq. 2 with respect to r, $\alpha_l(r)$ is related to $\alpha(r)$ as

$$\alpha_l(r) = \alpha(r) + r\frac{d\alpha(r)}{dr}. \tag{3}$$

The local Seebeck coefficient $\alpha_l(r)$ is thus derived analytically from Eq. 3, so that we can know the distribution of the local Seebeck coefficient near the boundary.

Sample preparations 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 [13, 14]. 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 [13, 14] and is close to one of various growth conditions reported by Yim and Rosi [15]. 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 intrinsic 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 directions of the length of 15 mm and thickness of 3 mm were 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 in which both end coppers are compacted tightly with the Bi–Te material at a constant force of about

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 ($\mu\Omega$ m)	0.0171	30.7	36.1
Seebeck coefficient α (μV/K)	+1.9	223.5	–214.3
Thermal conductivity κ (W/mK)	401[a]	0.559	0.788
Figure of merit ZT	1.57×10^{-4}	0.87	0.48

[a] Ref. 16

10 N using a ratchet, as shown in Fig. 1. The as-grown Bi–Te ingots were cut into a parallelepiped of 5 × 5 × $t_{\text{Bi–Te}}$ mm^3, where $t_{\text{Bi–Te}}$ is 2 mm and is perpendicular to the freezing direction, i.e., perpendicular to the cleavage plane. Coppers were prepared by cutting a long pillar with a square 5 mm on a side into a thickness of t_{Cu} = 0.3 mm, where the purity of copper was 99.99%. Both end surfaces of Bi–Te material 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 2 μm, which is more precise than those used for the previous experiment (O. Yamashita and H. Odahara submitted).

The resultant Seebeck coefficient α across the boundary 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. The measurement of the thermo-emf ΔV 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 ΔV and temperature difference ΔT of the touching composites were measured as functions of r and I, as shown in Figs. 3 and 4, where r is the distance from the boundary, corresponding to the probe interval s, and I is a direct current flowing through two Peltier modules connected in series. The distance r was then varied by a ratchet from 0.01 up to 1 mm and I was

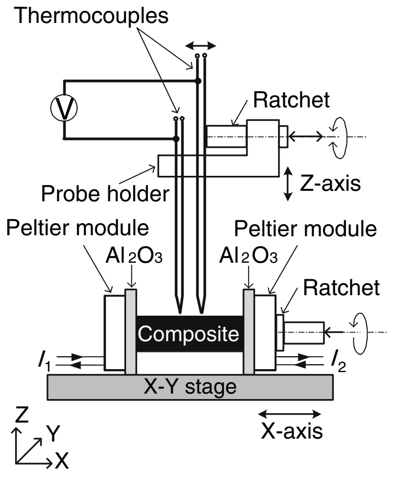

Fig. 2 Schematic configuration for α measurements of composite materials compacted tightly by a ratchet. The left of a composite was heated by flowing the electrical current I_1 or I_2 through a Peltier module to produce the temperature differences and its right was then maintained at room temperature.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

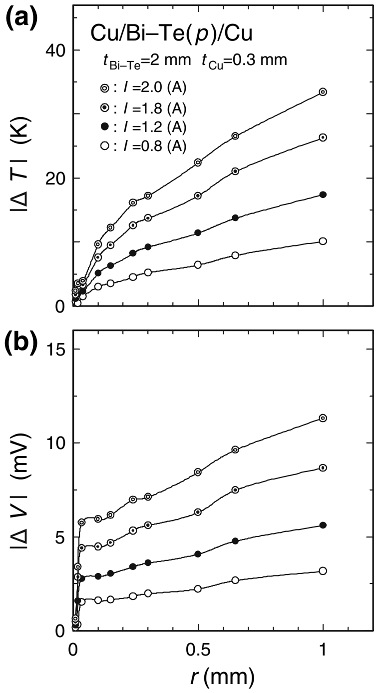

Fig. 3 (**a**) Temperature difference |ΔT| and (**b**) thermo-emf |ΔV| measured as a function of r for the touching p-type composites, where the electric current flowing through two Peltier modules connected in series was varied from 0.8 to 2.0 A

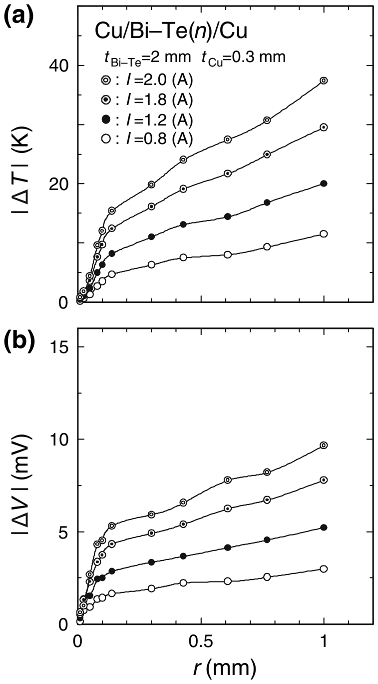

Fig. 4 (**a**) Temperature difference |ΔT| and (**b**) thermo-emf |Δ| measured as a function of r for the touching n-type composites, where the electric current flowing through two Peltier modules connected in series was varied from 0.8 to 2.0 A

varied from 0.8 to 2.0 A. The temperatures (T_h and T_c) of both ends of the composites change with the current I and the hot end was heated to 366 K at most when $I = 2.0$ A. The Seebeck coefficient of the intrinsic Bi–Te material was measured by placing two probes on Bi–Te material at an interval of $s = 1$ mm, as shown in Fig. 1a. In measuring the r-dependence of ΔV and ΔT in the region below $r = 0.30$ mm, the interval of two thermocouples was extended slightly along the y axis so that they do not come in touch with each other. In order to compare the temperature dependence of the resultant α with that of the intrinsic $\alpha_{\text{Bi–Te}}$, they were measured as a function of T by increasing I, where $T = (T_h + T_c)/2$. The resultant α across the boundary was obtained from the relation $\alpha = \Delta V/\Delta T$.

In calculating the resultant α using the temperature and voltage appeared on the surface of a material, one must take into account the temperature difference between the surface and central part of a material sandwiched between two coppers. In order to investigate it, the hole processing was performed in copper and bakelite which have the same dimensions (5 × 5 × 2 mm) as Bi–Te materials, where κ of bakelite used here was 0.30 W/mK which is lower than those of Bi–Te materials. A hole was drilled along the z axis at the position corresponding to $r = 0.4$ mm and its diameter and depth are $\phi 0.5$ and 2.5 mm, respectively. The reason that bakelite was employed instead of a Bi–Te material is that bakelite is easy to process a hole than brittle Bi–Te materials. A copper with very high κ was employed to study the effect of the difference in κ on the temperature difference between the surface and central part. When a current of $I = 1.2$ A was flowed through two Peltier modules so that the left of a composite is heated, as shown in Fig. 1b, the temperature of the surface was measured by putting a probe on the surface and that of the central part by putting a thin probe ($\phi 0.25$) into a hole. At $r = 0.4$ mm, the temperature difference between them was approximately 1 K in bakelite with an extremely low κ but was little observed in copper with very high κ. In other words, the temperature difference between the surface and central part tends to decrease with an increase of κ. From this result, the average temperature difference $\Delta T_{\perp}$ along the z axis is estimated approximately as 0.5 K at $r = 0.4$ mm in bakelite. Therefore, $\Delta T_{\perp}$ of Bi–Te materials at the same distance r would probably be somewhat smaller than 0.5 K because Bi–Te materials have κ values higher than bakelite.

Here, let us consider the effect of $\Delta T_{\perp}$ (along the y or z axis) on ΔT (along the x axis) used for estimation of the resultant α. One probe is put on copper near the boundary and another on Bi–Te material. As evident from $\Delta T_{\perp} = 0$ for copper, the surface temperature of copper at the hot side is considered to be almost equal to its central temperature, so that the correction for the temperature at the hot side is thus not necessary at all. However, the temperature measured on Bi–Te material at the cold side must be corrected and elevated by $\Delta T_{\perp}$, resulting in the decrease in ΔT, because the surface temperature measured on Bi–Te material is lowered by $\Delta T_{\perp}$ compared to the average temperature over the cross section. Therefore, the temperature difference ΔT used for the calculation of the resultant α should be replaced by $(\Delta T - \Delta T_{\perp})$, in order to estimate α correctly. When a current of $I = 1.2$ A was flowed through two Peltier modules, this correction increases the resultant α by about 5% at $r = 0.4$ mm. However, the degree to which the correction effects α would probably be reduced with a decrease of r, because $\Delta T_{\perp}$ should decrease as r approaches to 0 mm, owing to copper maintained at an almost constant temperature along the y or z axis. The effect of the correction on the resultant α near the boundary would probably be much less than 5%. Since $\Delta T_{\perp}$ is expected to be negligibly small near the boundary, as compared to $\Delta T_{\perp}$, all of the resultant α were calculated by the relation $\alpha = \Delta V/\Delta T$, as already mentioned.

The temperature difference ΔT was measured with an accuracy of 0.1 K corresponding to the measurement accuracy of a thermometer and the voltage ΔV appeared on two probes was measured within an accuracy of 1%. Therefore, the resultant experimental error changes significantly with ΔT and r, so that the experimental error decreases abruptly with increases of them. In the region below $r = 0.05$ mm, some representative experimental errors of α estimated for each probe interval are denoted by the error bar in Fig. 5, while above $r = 0.08$ mm, the error bars go entirely in the marks of a circle denoting the experimental data.

Results and discussion

Dependences of ΔV and ΔT on r

The thermo-emf ΔV and temperature difference ΔT of the touching p- and n-type Cu/Bi–Te/Cu composites were plotted as a function of r for each current I in Figs. 3 and 4. As shown in their figures, the temperature difference $|\Delta T|$ across the boundary for the p- and n-type composites increases abruptly with an increase of r in the small r region below $r = 0.1$ mm but slowly with further increase of r. As a whole, $|\Delta T|$ at each r tends to increase monotonically with an increase of I. The r-dependence of $|\Delta T|$ for the p-type composite is rather similar to that for the n-type one. However, it should be noted here that $|\Delta T|$ of the present composites tends to approach to 0 K as $r \rightarrow 0$. In other words, it indicates that there is only a little thermal contact resistance at the boundary between copper and Bi–Te material, although there is a significant difference between

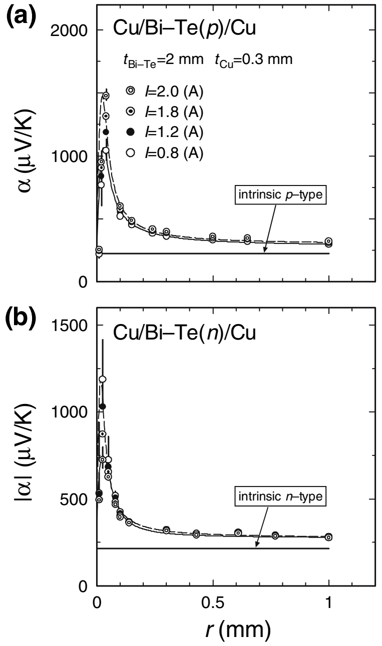

Fig. 5 Resultant Seebeck coefficient |α| measured as a function of *r* for the touching p-type (**a**) and n-type (**b**) composites, where the electric current flowing through two Peltier modules connected in series was varied from 0.8 to 2.0 A. The vertical bars in the small *r* region denote the experimental error. The *dashed* and *solid curves* for the p-type composite (**a**) are expressed as a function of *r* as $\alpha(r) = 295 + 18(1 - \exp(-10^4 r^2/6))r^{-1.25}$ and $\alpha(r) = 275 + 23(1 - \exp(-10^4 r^2/7))r^{-1.10}$, respectively, where *r* is expressed in a unit of millimeter. The *dashed* and *solid curves* for the n-type composite (**b**) are expressed as a function of *r* as $|\alpha(r)| = 275 + 9.1(1 - \exp(-10^4 r^2/3))r^{-1.25}$ and $|\alpha_l(r)| = 275 + 4.3(1 - \exp(-10^3 r^2/1.4))r^{-1.55}$, respectively

the thermal conductivities of their materials, as listed in Table 1. This lowering of the thermal contact resistance would probably be attributed to the fact that the surface roughness of components was made smaller by the lapping and the Bi–Te compound was sandwiched tightly between two coppers by the external force so that their contact surface area is increased substantially.

The thermo-emfs |ΔV| of the p-type composite increase more abruptly with an increase of *r* than that of the n-type one in the small *r* region below *r* = 0.05 mm, while above *r* = 0.1 mm, they tend to increase slowly with an increase of *r*. The thermo-emfs of the p- and n-type composites also increase monotonically with an increase of *I* all over *r*, like the temperature difference. As a whole, in the small *r* region, |ΔV| tends to increase more abruptly with an increase of *r* than |ΔT|, resulting in the increase in the resultant α of composites.

Dependence of the resultant α and local Seebeck coefficient α_l on *r*

The resultant |α| obtained from the relation α = ΔV/ΔT was plotted as a function of *r* in Fig. 5. As a whole, the resultant |α| for the touching p- and n-type composites increase abruptly with an increase of *r*, have a great local maximum value at $r \approx 0.03$ mm and decrease rapidly with further increase of *r* to approach the intrinsic Seebeck coefficient of Bi–Te materials. In order to derive analytically the local Seebeck coefficient $\alpha_l(r)$, a combination of some functions was determined to reproduce well the experimental resultant α(*r*). Consequently, the resultant α of the p-type composite was expressed roughly as a function of *r* as

$$\alpha(r) = 275 + 23\{1 - \exp(-10^4 r^2/7)\}r^{-1.10} \tag{4}$$

for *I* = 0.8 A and

$$\alpha(r) = 295 + 18\{1 - \exp(-10^4 r^2/6)\}r^{-1.25} \tag{5}$$

for *I* = 2.0 A, where *r* is expressed in a unit of millimeter. Similarly, the resultant α of the n-type composite was expressed as a function of *r* as

$$|\alpha(r)| = 275 + 9.1\{1 - \exp(-10^4 r^2/3)\}r^{-1.25} \tag{6}$$

for *I* = 0.8 A and

$$\alpha(r) = 275 + 4.3\{1 - \exp(-10^3 r^2/1.4)\}r^{-1.55} \tag{7}$$

for *I* = 2.0 A. It is surprising that the resultant α at $r \approx 0.03$ mm of the touching p- and n-type composites have great local maxima of 1,043 and –1,187 μV/K at 303 K corresponding to *I* = 0.8 A and of 1,477 and –725 μV/K at 360 K corresponding to *I* = 2.0 A, as shown in Fig. 5. The α values of 1,477 μV/K at 360 K for the p-type composite and –1,187 μV/K at 303 K for the n-type one are approximately 6.0 and 5.5 times higher in absolute value than the intrinsic $\alpha_{\mathrm{Bi-Te}}$ at corresponding temperatures. The maximum resultant α of the p-type composite tends to increase with an increase of *I*, while that of the n-type one decreases with an increase of *I*. In order to investigate here the *I*-dependence of the resultant α, the ratio *R* of the resultant α(*I* = 2.0 A) to α(*I* = 0.8 A) was plotted as a function of *r* in Fig. 6. The ratio *R* for the p-type composite increases abruptly with an increase of *r*, has a local maximum at $r \approx 0.04$ mm and decreases rapidly with further increase of *r* to approach to 1.08 of the intrinsic p-type Bi–Te. In contrast, the ratio *R* for the n-type one decreases abruptly with an increase of *r*, goes through a local minimum at $r \approx 0.03$ mm and increases rapidly with further increase of *r* to approach to 0.98 of the intrinsic n-type Bi–Te. As evident from the *r*-dependence of *R*, the resultant α changes significantly with *I* at the distance *r* giving a local maximum of α. Figure 7 shows the relationship between *I* and the average temperature *T* or the temperature difference Δ*T* at the distance *r* giving the maximum resultant α. Both *T* and Δ*T* tend to increase with monotonically with an increase of *I*. Combining it with the present result, the maximum resultant α of composites is found to be very sensitive to *T*.

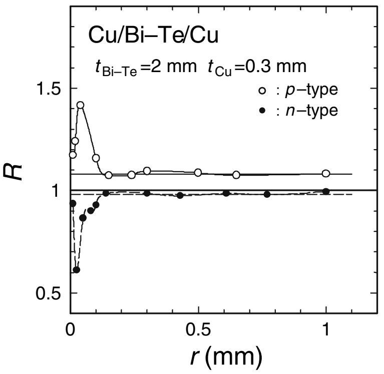

Fig. 6 R as a function of r for the touching p- and n-type composites, where R is the ratio of $\alpha(I = 2.0\ \text{A})$ and $\alpha(I = 0.80\ \text{A})$, which are obtained by flowing electric currents of 2.0 and 0.80 A through two Peltier modules connected in series

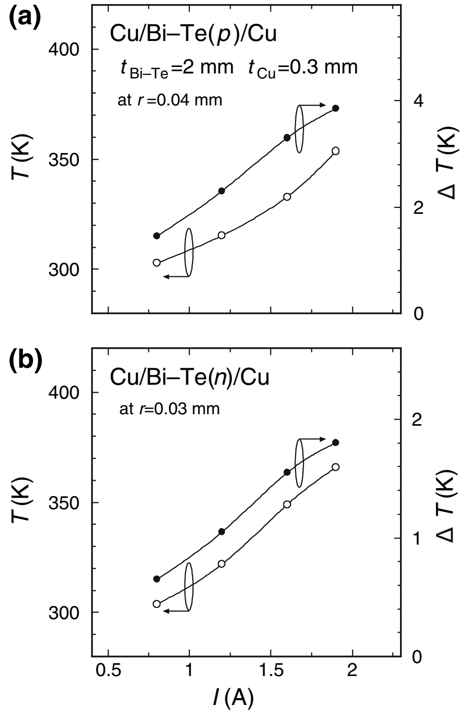

Fig. 7 Average temperature T and temperature difference ΔT as a function of I at $r = 0.04$ mm for the touching p-type composite (**a**) and at $r = 0.03$ mm for the touching n-type one (**b**)

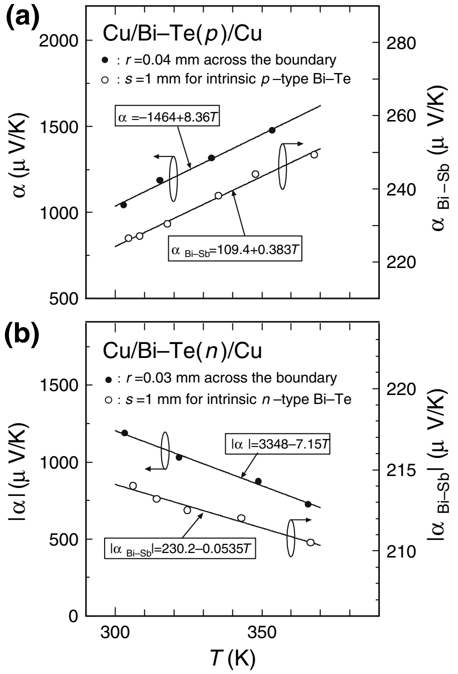

Fig. 8 Temperature dependences of the Seebeck coefficients for the intrinsic p- and n-type Bi–Te materials and the maximum resultant Seebeck coefficients |α| for the touching p- and n-type composites

Next, to investigate how the maximum resultant α and intrinsic $\alpha_{\text{Bi–Te}}$ change with T, they were plotted as a function of T in Fig. 8, where T was the average temperature varied in the region from 303 to 366 K. As shown in the figure, the maximum resultant α and intrinsic $\alpha_{\text{Bi–Te}}$ of the p-type composite increase linearly with an increase of T, while those of the n-type one decrease linearly with an increase of T. Surprisingly, the maximum resultant α of the p- and n-type composites have great gradients of 8.36 and –7.15 μV/K^2, respectively, which are 21.8 and 134 times in absolute value than 0.383 and –0.0535 μV/K^2 of the intrinsic p- and n-type Bi–Te materials. The maximum resultant α was thus found to exhibit the temperature dependence much stronger than the intrinsic $\alpha_{\text{Bi–Te}}$. As shown in Fig. 7, the increase in T also results in the increase of the temperature gradient ΔT. Thus, the reason that the maximum resultant α becomes highly sensitive to temperature is that the additional barrier thermo-emf depends much more strongly on the temperature gradient generated in the Bi–Te material near the boundary, than the bulk thermo-emf resulted from the intrinsic Bi–Te material. In other words, the degree of separation of non-equilibrium carriers (leading directly to the barrier thermo-emf) may vary significantly with only a slight change in the temperature gradient. It is thus strongly desired to clarify theoretically the mechanism for the strong temperature dependence of the barrier thermo-emf.

Subsequently, we derive analytically the local Seebeck coefficient $\alpha_l(r)$ near the interface from the expressions $\alpha(r)$ reproducing the r-dependence of the experimental α. By substituting Eqs. 4 and 5 into Eq. 3, the local Seebeck coefficient $\alpha_l(r)$ for the p-type composite is derived as

$$\alpha_l(r) = 275 + \{-2.30 + (2.30 + 6.57 \times 10^4 r^2) \times \exp(-10^4 r^2/7)\} r^{-1.20} \quad (8)$$

for $I = 0.8$ A and

$$\alpha_l(r) = 295 + \{-4.50 + (4.50 + 6.00 \times 10^4 r^2) \times \exp(-10^4 r^2/6)\} r^{-1.25} \tag{9}$$

for $I = 2.0$ A. Moreover, by substituting Eqs. 6 and 7 into Eq. 3, the local Seebeck coefficient $\alpha_l(r)$ for the n-type composite is obtained as

$$|\alpha_l(r)| = 275 + \{-2.30 + (2.30 + 6.07 \times 10^4 r^2) \times \exp(-10^4 r^2/3)\} r^{-1.25} \tag{10}$$

for $I = 0.8$A and

$$|\alpha_l(r)| = 275 + \{-2.37 + (2.37 + 6.14 \times 10^3 r^2) \times \exp(-10^3 r^2/1.4)\} r^{-1.55} \tag{11}$$

for $I = 2.0$ A. The curves of the local Seebeck coefficient $\alpha_l(r)$ derived for the p- and n-type composites were drawn as a function of r in Fig. 9. Consequently, the curves of $\alpha_l(r)$ tend to increase abruptly with an increase of r, have a great local maximum value at r = 0.02–0.03 mm and tend to approach the intrinsic $\alpha_{\text{Bi–Te}}$ at $r \approx 0.05$ mm. Of course, it is consistent quantitatively with the previous result (O. Yamashita and H. Odahara submitted). The maximum $\alpha_l(r)$ across the boundary for the p- and n-type composites reached extremely great values of approximately 1,800 μV/K at 360 K corresponding to $I = 2.0$ A and –1,400 μV/K at 303 K corresponding to $I = 0.8$ A, respectively, which are 7.3 and 6.5 times higher in absolute value than the intrinsic $\alpha_{\text{Bi–Te}}$ at corresponding temperatures. It is consistent qualitatively with the previous experimental results that α_l was enhanced strongly near the boundary in welded Cu/Bi/Cu, Cu/Bi–Sb/Cu and Ni/Bi–Sb/Ni composites [17].

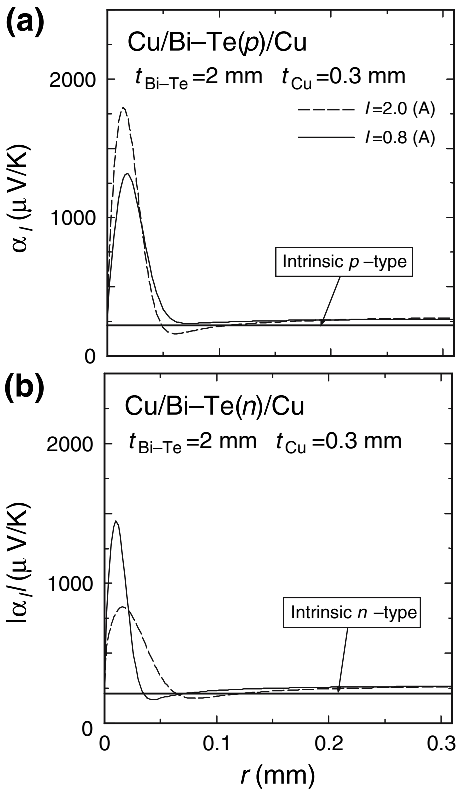

Fig. 9 Local Seebeck coefficient $\alpha_l(r)$ calculated from Eq. 3 using the resultant Seebeck coefficient $\alpha(r)$ measured as a function of r for the touching p- and n-type composites. The *dashed* and *solid curves* for the p-type composite (**a**) are expressed as a function of r as $\alpha_l(r) = 295 + \{-4.50 + (4.50 + 6.00 \times 10^4 r^2)\exp(-10^4 r^2/6)\} r^{-1.25}$ and $\alpha_l(r) = 275 + \{-2.30 + (2.30 + 6.57 \times 10^4 r^2)\exp(-10^4 r^2/7)\} r^{-1.10}$, respectively, where r is expressed in a unit of millimeter. The *dashed* and *solid curves* for the n-type composite (**b**) are expressed as a function of r as $|\alpha_l(r)| = 275 + \{-2.30 + (2.30 + 6.07 \times 10^4 r^2)\exp(-10^4 r^2/3)\} r^{-1.25}$ and $|\alpha_l(r)| = 275 + \{-2.37 + (2.37 + 6.14 \times 10^3 r^2)\exp(-10^3 r^2/1.4)\} r^{-1.55}$, respectively

When one takes the boundary effect due to the barrier thermo-emf in thermoelectric generators, therefore, it is found to be desirable to sandwich a thin thermoelectric material with a thickness of ~0.1 mm between two metals with high electrical and thermal conductivities. Moreover, when a thermoelectric module is designed to operate efficiently at higher temperatures than room temperature, it should be prepared using the thermoelectric materials in which the Seebeck coefficient increases with an increase of temperature, resulting in the significant increase in the barrier thermo-emf. If such modules were fabricated successfully by welding a thin thermoelectric material with metals, it would result in the dramatic improvement in the energy conversion efficiency of thermoelectric generators.

Recently it has been reported by Bartkowiak and Mahan [18] that the boundary and bulk thermoelectric effects cannot be combined to enhance the resultant Seebeck coefficient in the nanostructure systems. As evident from the present experimental result, however, it does not apply to the present macroscopic composites, because most of phonons and electrons accumulated in the present thermoelectric materials are almost in thermal equilibrium, unlike in the nanostructure systems in which they are out of equilibrium.

Summary and conclusion

The thermo-emf ΔV and temperature difference ΔT across the boundary were measured as functions of r and I for the touching p- and n-type Cu/Bi–Te/Cu composites composed of a combination of $t_{\text{Bi–Te}} = 2.0$ mm and $t_{\text{Cu}} = 0.3$ mm, where r is the distance from the boundary and I is a direct current producing ΔT which flows through two Peltier modules connected in series. The distance r was then varied by a ratchet from 0.01 up to 1 mm and I was varied from 0.8 to 2.0 A. The resultant Seebeck coefficient α across the boundary is obtained from the relation

$\alpha = \Delta V/\Delta T$. As a result, the resultant $|\alpha|$ of the touching p- and n-type composites have a great local maximum value at $r \approx 0.03$ mm and decrease rapidly with further increase of r to approach the intrinsic $|\alpha_{\mathrm{Bi-Te}}|$. The maximum resultant α of the p- and n-type composites then have great local maxima of 1,043 and –1,187 μV/K at 303 K corresponding to $I = 0.8$ A and of 1,477 and –725 μV/K at 360 K corresponding to $I = 2.0$ A. The maximum α values at 360 K for the p-type composite and at 303 K for the n-type one are approximately 6.0 and 5.5 times higher in absolute value than the intrinsic $\alpha_{\mathrm{Bi-Te}}$ at corresponding temperatures. The maximum resultant α and intrinsic $\alpha_{\mathrm{Bi-Te}}$ of the p-type composite increase linearly with an increase of T, while those of the n-type one decrease linearly with an increase of T. The maximum α of the p- and n-type composites have surprisingly great values of 8.36 and –7.15 μV/K^2, respectively, which are 21.8 and 134 times larger in absolute value than 0.383 and –0.0535 μV/K^2 of the intrinsic p- and n-type Bi–Te materials, so that the maximum resultant α of composites was thus found to be much more sensitive to temperature than the intrinsic $\alpha_{\mathrm{Bi-Te}}$. In brief, it indicates that the barrier thermo-emf is highly sensitive to the temperature gradient in the Bi–Te material near the boundary. Moreover, the local Seebeck coefficient $\alpha_l(r)$ derived analytically from the resultant $\alpha(r)$ is enhanced significantly in the narrow region below $r \approx 0.05$ mm and the maxima α_l of the p- and n-type composites were found to reach surprisingly great values of approximately 1,800 μV/K at 360 K and –1,400 μV/K at 303 K, respectively, which are approximately 7.3 and 6.5 times higher in absolute value than the intrinsic p- and n-type $\alpha_{\mathrm{Bi-Te}}$ at the corresponding temperatures.

When a thermoelectric generator is designed to operate efficiently at higher temperatures than room temperature, therefore, it should be prepared by sandwiching a thin thermoelectric material between two thick metals, contrary to the composition of conventional modules. At the same time, it should be fabricated using the thermoelectric materials in which the Seebeck coefficient increases with an increase of temperature, resulting in the significant increase in the barrier thermo-emf. If one succeeds to make such a module, it would result in the dramatic improvement in the energy conversion efficiency of thermoelectric generators.

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